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General ground water geochemistry of Hellas using bottled water samples

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ABSTRACT

Sixty-one still bottled water samples, representing 41 locations, were collected from Hellas for the purpose of studying the geochemistry of ground water. Since, the dominating lithology comprises limestone, dolomitic limestone, marble, and mafic–ultramafic rocks (ophiolites), the dominant major ions in Hellenic bottled waters are Ca^{2+}, Mg^{2+}, CO_3^{2-} and HCO_3^-, and are, thus, classified in the Ca^{2+}–Mg^{2+}–HCO_3^- hydrochemical facies. The source aquifers of Hellenic bottled water are apparently continuously replenished by fresh water. Comparison of values of Ca, Mg, K, Na, Cl^-, HCO_3^-, NO_3^-, SO_4^{2-}, pH and electrical conductivity, displayed on bottle labels with those of this study, has shown that there is a fairly good correlation between the two data sets, suggesting that the geochemistry of source aquifers is relatively stable over time, at least from 1998 to 2008.

1. Introduction

Hellas is a country with a diverse geology and climate, but also of mythology and ancient rituals with spring and river water. In ancient Hellenic culture, water was not only associated with hygiene and the needs of the human body, but it became an essential part of religious ritual, ensuring the soul's well-being through the metaphorical concept of catharsis (Chrysoulaki, 2010; Håland, 2009). Water was always a part of purification ceremonies, initiation rituals, cures and acts of divination, even conversing with immortality. In myths and fables, heroes searched in vain for the water of life, the 'immortal water', to quench the waterless desert of death. Water makes the earth fertile and the land hospitable. Hence, from prehistoric to the present time, water has guided people's steps, the sites for their settlements, contributed to the management of agricultural activities and survival of their livestock. Rivers and springs became the places near which the first settlements were built, and the benevolence of water allowed cities and their civilizations to flourish. In the imaginative rich world of popular beliefs and symbols, the changeable nature of river courses gave rise to images of powerful and unpredictable daemons capable of continuous change in form, offering in the one hand abundance and in the other threatening with disaster (Chrysoulaki, 2010). Conversely, spouting springs and tranquil lakes were inhabited by youthful girls, the 'naiads' (water nymphs). Holy water is also part of deep Christian traditions, associated with Virgin Mary under her attribute of 'Life-giving Spring' (Zōōdhóchos Pegé), but also with other Saints (Håland, 2009).

In Hellas there are areas blessed with water and others that are not. Climatic change is, in fact, affecting Hellas to a variable degree. This has been observed quite evidently in the bottled water industry, where natural spring water is used for bottling. Up to now two bottling companies have closed down, the first in Thrace in north-east Hellas, and the second in south Peloponnese. The reason in both cases was the reduced capacity of the natural spring. It is here very relevant to quote Benjamin Franklin (1706–1790) "*We will only know the worth of water when the well is dry*". However, ground water resources are still available in areas of Hellas with a comparatively high rainfall. Hence, because of the increased demand for bottled water, new companies have started operations in these areas.

The length of the Hellenic coastline is 13,780 km, and most of it is due to the 6000 islands and islets. Many of the inhabited islands do not have good quality potable water supply, and the islanders rely on bottled water for drinking and cooking, e.g., Aegina, some of the Cyclades and Dodecanese Islands, Zakinthos, an Ionian Sea island, etc. There are also some areas on mainland Hellas that resort to bottled water, because of the poor quality of their ground water resources, e.g., Argholidha (north-east Peloponnese) and Thessaly (eastern central Hellas), because of high nitrates, and some parts of Elia Prefecture (north-west Peloponnese) due to elevated concentrations of iron and manganese.

The consumption of bottled water in Hellas was 380 million litres in 1998, it reached 627 million litres in 2003, and in 2005 was up to 1 billion litres. It appears that the consumption of bottled water increases by about 10–12% per year. On average, the consumption was 45 L/person in 1998 and by 2009 it reached over 100 L/person. The greatest consumption is, of course, during the summer period with the hundreds of thousands of tourists.

To set up a bottled water industry a permit is required from the Health Department of the Prefecture for table water, whereas for

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mineral water from the Ministry of Health. Hence, the difficulty of finding out all bottled water brands available on the Hellenic market, since some of them are very local. The Mineral Water Organisation lists 31 Hellenic brands (http://www.mineralwaters.org/). Whereas, in accordance with Article 1 of Directive 2009/54/EC of the European Parliament and of the Council of 18 June 2009 on "*the exploitation and marketing of natural mineral waters*" (EU, 2009), there are only 38 natural mineral waters recognised officially by Hellas. Nevertheless, there are more brands on the market, and a conservative estimate is about 65 bottled water companies are operating in different parts of the country.

The present paper describes the general geochemistry of ground water sources of Hellenic bottled water, then compares the results of this study with those displayed on bottle labels, and finally discusses concisely the overall geochemical characteristics of ground water using as a 'proxy' Hellenic bottled water samples. It is stressed at the outset that it was never the intention of this project to assess the quality of bottled water, since for such an assessment many more parameters should have been analysed, and specifically organic compounds and microbiological components (refer to Fotiou and Kolovos, 2004). Also, a separation of Natural Mineral Water from Natural Bottled Drinking Water (often called Table Water) should have been made, because each has to comply with a different legislation, i.e., EU Directive 1998/83/EC (EU, 1998) and EU Directive 2003/40/EC (EU, 2003), respectively. However, since readers may be interested in the quality of Hellenic bottled water, it can be safely stated that the concentrations of determined inorganic parameters are below the recommended statutory guideline values. The analytical data of this study are included on the CD-rom accompanying the atlas of the "Geochemistry of European Bottled Water" (Reimann and Birke, 2010).

2. Methodology

2.1. Sampling and analysis

In this project a total of 61 still bottled waters were purchased from supermarkets, representing 41 different locations (Table 1); 57 bottled waters were in soft polyethylene terephthalate (PET) and four in clear glass bottles; eight PET bottles were duplicates, purchased from different supermarkets, and another eight were from the same location, but marketed under a different brand name. Apart from the duplicate bottles that were used for quality control purposes, three different brands of water for injection were

Table 1
Hellenic bottled waters analysed in this study. The star (*) denotes natural bottled mineral water listed in Directive 2009/54/EC (EU, 2009). The others are classified as Table water. In brackets are given bottled waters from the same location, but marketed under a different brand name (see Fig. 1 for their location).

Sample number	Brand name	Name of spring/borehole	Bottling location
1	Vikos*	Vikos	Fteri Perivlepou, Ioannina Prefecture
2	Zagori*	Zagori	Kranoula, Ioannina Prefecture
3	Korpi*	Korpi	Korpi, Monastiraki, Akarnanika Mts., Vonitsa, Aetoloakarnanias Prefecture
4	Ioli*	Ioli	Moschochori, Fthiotida Prefecture
5	Sariza	Sariza	Apikia, Andros Island, Cycladhes Prefecture
6	Avra*	Avra, Aegion	Aegion Municipality, Achaia Prefecture
7	Aqua Vita	Aghia Varvara, Rhodes I.	Aghia Varvara, Rhodes I., Dodekanissos Prefecture
8	Pindos	Ziaka Grevena	Grevena, Grevena Prefecture
9	Samarina*	Goura Samarinas	Samarina, Grevena Prefecture
10	Drosoula	Roditi	Roditi Spring, Kozani, Kozani Prefecture
11	Nera Kritis	Foot of White Mountains	Varipetro Therisso Chania, Crete I., Chania Prefecture
12	Mythical	Psiloritis Mountain	Psiloritis, Crete I., Heraklion Prefecture
13	Rouva's	Gergeri, foot of Psiloritis Mountain	Gergeri, Heraklion, Crete I., Heraklion Prefecture
14	Samaria	Stylos	Stylos, Foot of White Mountains, Crete I., Chania Prefecture
15	Lyttos	Chomoprina, Malia Municipality	Coca Cola 3E, VIPE, Iraklion, Crete I., Chania Prefecture
16	Gortys	Asterousia Mountains, Aghia Marina	Lendas, Crete I., Heraklion Prefecture
17	Zaro's*	Amati, Psiloritis Mt.	Heraklion, Crete I., Heraklion Prefecture
18	Rizitiko	Psiloritis Mountain	Heraklion, Crete I., Heraklion Prefecture
19	Krini	Dikti Mountains, Crete	Kasteli, Pediados, Heraklion Prefecture
20	Dikti	Baboulani, Dikti (Lasithi)	Crete I., Lasithi Prefecture
21	Kimi*	Honeftiko (Kimi)	Honeftiko, Kimi, Euboea I., Euboea Prefecture
22	Eviva (Gargaro, Mitsikeli, Marata, Physiko Nero AB)	Sepeta	Kalpaki, Ioannina Prefecture
26	Loutraki*	Loutraki	Loutraki, Korinthia Prefecture
27	Loutraki Hydria	Loutraki	Loutraki (Hydria), Korinthia Prefecture
28	Loutraki Karadanis Provis	Loutraki	Loutraki, Korinthia Prefecture
29	Loutraki Ivi	Gerania Mountains	Loutraki, Korinthia Prefecture
30	Iris Loutraki	Loutraki	Loutraki, Korinthia Prefecture
31	Hydor Sourotis* (Daily Drink Water)	Anthemia (Anthemounda Basin)	Souroti, Thessaloniki Prefecture
33	Athos (Iro)	S. Platani (Poligiros)	Akonorachi, Poligiros, Chalkidhiki Prefecture
34	Evdoro*	Evdoro	Evdoro, D.D. Mexiatae, Municipality of Ipati, Fthiodidha Prefecture
35	Tzoumerka	Agathi Melissourgon	Melissourgoi, Arta Prefecture
36	Velouhi	Kefalovrisso Aghia Triadha	Velouhi, Evritania Prefecture
37	Seli*	Assos, Vermion Mt.	Spilia, Vermion Mountain, Kozani Prefecture
38	Pigi Paikou	Axioupoulis	Axioupolis, Paiko Mountains, Kilkis Prefecture
39	Krinos*	Anastassopoulou spring	Rododafni Aegio, Achaia Prefecture
40	Zefiros	Zefiros, Achaia Mountains	Chondrolongos, Rio Municipality, Achaia Prefecture
45	Hyas* (Krinea)	Kaliani	Kaliani, Korinthia Prefecture
46	Beles (Aqua)	Angistro	Angistro, Serres Prefecture
47	Klinos*	Palavi	Klinos Community, Pindos Mts., Trikalla Prefecture
48	Vitsi	Florina springs	Florina, Florina Prefecture
49	Drossia	Drossia	Mt. Kaimaksalan, Imathia Prefecture

purchased, and used as blanks. All bottled water samples were analysed at the Federal Institute for Geosciences and Natural Resources (BGR) in Germany, and the analytical methods and quality control results are described by Birke et al. (2010-this volume) and Reimann and Birke (2010). The stable isotope composition of Hellenic bottled waters is discussed in another paper by Dotsika et al. (2010-this volume).

3. Geotectonic zones of Hellas

The lithology of Hellas is comprised from sediments and igneous rocks of Tethys that are grouped into geotectonic zones, consisting of rocks which have a similar development, and representing a unified geomorphological entity (Fig. 1); the Tethyan mafic–ultramafic ophiolitic rocks, and other intrusive–extrusive igneous rocks, as well as the Upper Tertiary intermontane molasse deposits are presented as different entities on the map. The Rhodope Massif is an exception, because it did exist before the opening of the Tethys Sea, and palaeogeographically belongs to the European craton. Almost all geotectonic zones end with flysch, which consists of a rhythmic sequence of sandstone, marl, clay, and more rarely conglomerate or limestone. The general features of the geotectonic zones of Hellas are concisely described in Table 2, together with the bottled water samples falling in each zone, and Fig. 1 shows their geographical distribution and location of bottled water industries of Table 1. The Tertiary and Recent sediments are not presented on Fig. 1.

4. Results and discussion

4.1. General geochemistry of the source aquifers of Hellenic bottled water

The general statistics of parameters determined on the Hellenic bottled water samples ($n = 41$) are tabulated in Table 3. Overall, most parameters vary up to four orders of magnitude, and a few up to five.

The pH of Hellenic bottled water samples varies from 7.08 to 9.2, with a median of 7.9. Hence, bottled water ranges from near-neutral to moderately alkaline.

The total dissolved solids (TDS) in bottled water vary from 113 to 570 mg/L, with a median of 285 mg/L. Thus, Hellenic bottled waters belong to the low (50–250 mg/L) to moderate (250–800 mg/L) mineral content waters. Since, TDS < 570 mg/L bottled water is classified as fresh water, according to Hem (1970), and it may be assumed that the residence time of ground water, and distance travelled, are comparatively short.

The Electrical conductivity (EC) varies from 177 to 891 µS/cm, with a median of 434 µS/cm. These values are within the normal range for ground water, and bottled waters are, thus, classified as light (<400 µS/cm) to moderately heavy (<900 µS/cm).

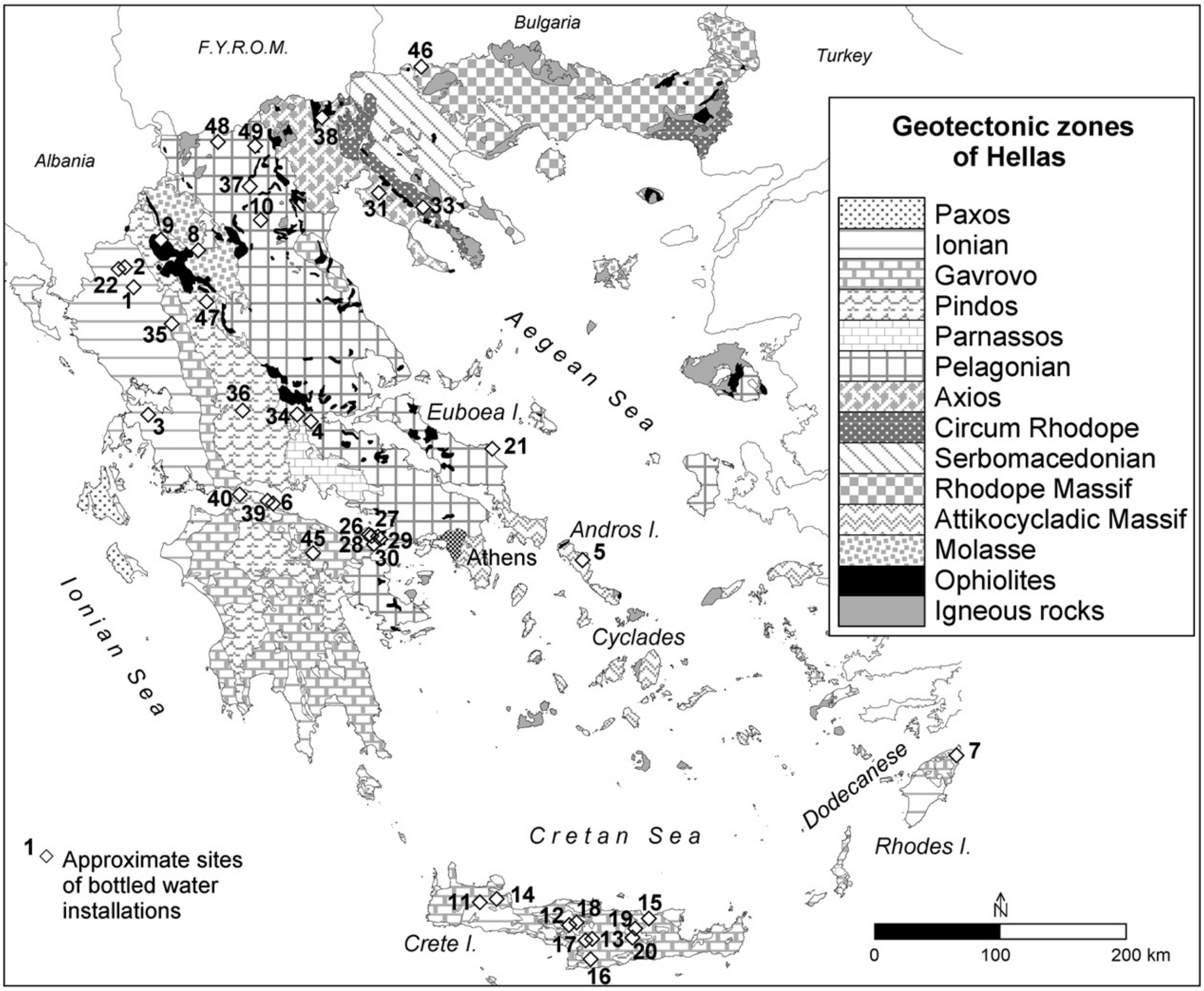

Fig. 1. Geotectonic zones of Hellas and the approximate sites of bottled water installations (geotectonic zones modified from Bornovas and Rondogianni-Tsiambaou, 1983; layers digitised by E. Vassiliades).

Table 2
Geotectonic zones of Hellas, their major lithology and mineralisation. The bottled water samples are placed in the relevant geotectonic zones. The formations begin from bottom to top, and the geotectonic zones are described from west to east (see Fig. 1).

Bottled water samples	Lithology	Mineralisation
Paxos Zone (or Pro-Apulian Zone)		
	Gypsum, limestone and marl of Triassic to Eocene, and flysch of Miocene age	Gypsum
Ionian Zone		
Vikos (1), Zagori (2), Korpi (3), Aqua Vita (7), Mythical (12), Rizitiko (18), Eviva (22)	Evaporites (halite, gypsum, etc.), and red pelagic limestone and shale of Triassic; thin bedded pelagic limestone of Jurassic to Lower Cretaceous age; beige to reddish pelagic limestone of Cretaceous to Eocene age, and flysch of Eocene to Miocene age. In central Peloponnese, and on the islands of Crete and Rhodes the limestone and flysch are metamorphosed into crystalline limestone and phyllite	(a) Jurassic uranium bearing phosphorite; (b) Cretaceous platy limestone with phosphorite; (c) flysch appears to contain Au; (d) Neogene basins host peat–lignite deposits; (e) small oil-fields; (f) salt domes (e.g., at Monolithio); and (g) low enthalpy geothermal fields
Gavrovo–Tripolis Zone		
Nera Kritis (11), Rouva's (13), Samaria (14), Lyttos (15), Gortys (16), Zaro's (17), Krini (19), Dikti (20), Tzoumerka (35)	A sequence of phyllite and quartzite of Permo–Carboniferous to Triassic age occurs as sub-basement to the Gavrovo–Tripolis Zone and is rich in iron mineralisation; Tyros Beds of Upper Palaeozoic to Middle Triassic age consist of low grade metamorphic sequence of shale, tuff, pelite, sandstone, conglomerate, as well as chloritic, quartzitic calc-schist with sulphide mineralisation; neritic to dolomitic limestone sequence of Triassic to Eocene age with flysch of Eocene to Upper Oligocene age	(a) iron mineralisation; (b) Upper Palaeozoic to Middle Triassic volcano sedimentary massive sulphide deposits; and (c) locally bauxitic episodes of Upper Cretaceous to Lower Eocene age (Gavrovo mountain and Pylos area)
Pindos Zone		
Avra (6), Velouhi (36), Krinos (39), Zefiros (40), Hyas (45), Klinos (47)	Triassic volcano–clastic formation; Jurassic radiolarian red-cherts associated with Mn concentrations; flyschoidal and Upper Cretaceous abyssal thin bedded limestone with chert, and flysch of Upper Maastrichtian age. Emplacement of the mafic–ultramafic sequence (ophiolites) during the Upper Jurassic	(a) Manganese concentrations; and (b) chromite
Parnassos Zone		
	Neritic limestone (mainly), dolomite; during the Middle Jurassic, Upper Jurassic and Upper Cretaceous the area was uplifted and was land and during this period it received sediments from the weathering and erosion of ophiolites (oxides of Al, Fe, Mg, etc.), and each time a bauxitic horizon was formed; flysch of mid-Eocene age	(a) three bauxite horizons; (b) thorium–uranium occurrences (e.g., Florina–Prespae)
Pelagonian Zone		
Ioli (4), Drossoula (10), Kimi (21), Loutraki (26), Loutraki Hydria (27), Loutraki Karadani Provis (28), Loutraki Ivi (29), Iris Loutraki (30), Evdoro (34), Seli (37), Vitsi (48), Drossia (49)	Mainly reef and some pelagic limestone and chert of Lower Triassic to Upper Cretaceous age; flysch of Upper Cretaceous to Eocene. The metamorphosed part of the Pelagonian zone covers part of western and central Macedonia, eastern Thessaly, eastern Attiki and the Cyclades Islands, and it comprises of crystalline limestone, marble, foliated hornfels, and schist; it also includes granite and crystalline schist; ophiolite complex, sub-ophiolitic melange	(a) Polymetallic sulphides; (b) Mn; and (c) Fe
Axios (or Vardar) Zone		
Ydor Sourotis (31), Pigi Paikou (38)	Limestone, crystalline schist, marble, granite, ophiolites, and flysch (slightly metamorphosed)	(a) Polymetallic sulphides (Cu–Fe); (b) Fe–Ni; (c) chromite; (d) pyrite; (e) antimony; (f) molybdenite; and(g) geothermal fields.
Circum–Rhodope Zone		
Athos (33)	An alternating sequence of Palaeozoic shale, limestone, and shale; it ends with Jurassic flysch	(a) Polymetallic sulphides; (b) copper; (c) Fe–Mn; and (d) baryte
Serbomacedonian Zone		
	Gneiss, schist, marble, amphibolite, greenschist, and granite	(a) Polymetallic sulphides (Cu–Fe; Pb–Zn; (b) Cu–Fe ± As ± Pb ± Zn; (c) Pb–Zn–Au–Ag; Pb–Zn ± Cu); (d) porphyry copper (Cu–Au ± Mo ± PGE), (e) chromite, (f) magnetite (Fe–Au); (g) epithermal Au; (h) antimonite (Sb ± W), (i) iron–nickel laterite, (j) scheelite (W), (k) molybdenite (Mo), (l) pyrolusite (Mn–Fe ± Pb ± Zn ± Au ± Ag), (m) limonite (Fe–Au ± Mn), and (n) magnesite.
Rhodope Massif		
Beles (46)	Marble, gneiss, crystalline schist, amphibolite with marble intercalations, and granite of Palaeozoic to Jurassic age; Lower Tertiary volcano sedimentary sequences	(a) Massive Cu mineralisation in amphibolites; (b) chromite associated with ophiolites; (c) manganese, (d) iron, and (c) Lower Tertiary polymetallic sulphides, porphyry Cu–Mo, epithermal Au, antimony and uranium occurrences.
Attico–Cycladic Complex		
Sariza (5)	Marble (often dolomitic), mica-amphibole-schist, gneiss, metamafic rocks (greenstone)	(a) Fe–Mn deposits (b) polymetallic sulphides; (c) iron–manganese (d) uranium occurrences (e.g., Samos, Ikaria, and Lesvos)

Table 2 (*continued*)

Bottled water samples	Lithology	Mineralisation
Molasse deposits		
Pindos (8)	Conglomerate, marl, claystone, and sandstone deposited in fault grabens, such as (a) Thrace (Eocene); (b) Thessalia (Eocene to Oligocene); (c) Grevena–Thessalia (Eocene to Miocene), and (d) Epirus (Upper Miocene) and in the Attico–Cycladic Complex (Upper Miocene)	
Ophiolites		
Samarina (9)	Basalt, diabase, gabbro, pyroxenite, peridotite, dunite, serpentinite (ophiolite sequence) of Palaeozoic (?), Triassic to Jurassic age	(a) Chromite deposits (e.g., Vourinos, Domokos, Chalkidhiki), (b) Fe–Ni laterites with peridotites (e.g., Larimna and Messapia), (c) magnesite (e.g., Mantoudi and Chalkidhiki), (d) Cu deposits, (e) Mn deposits with cherts, and (f) talc (e.g., Tinos I.)
Igneous rocks		
Granitoids–granodiorite, monzonite, monzodiorite of (a) Palaeozoic age, such as Rhodope, Serbomacedonian, Pelagonian and Attico–Cycladic sub-basements; (b) Triassic–Jurassic age, such as Vardar and Serbomacedonian Zones (Arnaea, Fanos, Monopigadhon, etc.); (c) Eocene age, such as in the Serbomacedonian Zone and Rhodope Massif, where the Tertiary granitoids are associated with porphyry copper ore deposits; (d) Miocene age, such as in the Rhodope Massif and Attico–Cycladic Complex, and (e) neo-volcanic activity from Eocene to Quaternary age, affecting the whole of the internal Hellenides (from Rhodope to Pelagonian Zones) with intrusions and extrusions of rhyolite, rhyodacite, dacite, andesite, trachyandesite, trachyte, tuff, ignimbrite, basalt, quartz diorite, diorite giving rise to various ore deposits (Thrace area).		

The total hardness varies from 95.3 to 411 mg/L, with a median of 285 mg/L. Hence, the Hellenic bottled waters, according to Hem (1970), belong to the moderately hard (61–120 mg/L) to the very hard (>180 mg/L) varieties. This is understandable because of the widespread occurrence of limestone, marble and dolomite (Table 2).

The alkalinity varies from 112 to 472 mg HCO_3^-/L, with a median of 235 mg HCO_3^-/L. The comparatively low alkalinity probably reflects the hydrochemicallly immature nature of bottled water sources, and also shallow aquifers.

Concentration ratios, expressed in meq/L, of a certain ion in relation to another take values that are related to (a) the aquifer host rocks, or (b) the rocks through which the water passes, or (c) the degree of replenishment of ground water, or (d) its mixing with sea water, etc. (Mandel and Shiftan, 1981). Below are presented various ion relationships; after the bottled water brand name and the separation hyphen, the sample number is given, and in brackets the value of the ratio.

(a) Mg^{2+}/Ca^{2+} ratios denote that the source water of bottled water is derived from Mg-rich rocks or calcium carbonate lithologies:

- ➢ $Mg^{2+}/Ca^{2+} > 0.9$—aquifers with silicate rich rocks rich in Mg; aquifers associated with ophiolite formations usually have Mg/Ca >1.0: Loutraki Karadanis Provis-28 (39.0), Loutraki Hydria-27 (38.7), Samarina-9 (12.9), Loutraki Ivi-29 (12.8), Iris Loutraki-30 (12.1), Loutraki-26 (11.9), Drossia-49 (6.41), Aqua Vita-7 (5.71), and Hydor Sourotis-31 (1.96); all of these bottled waters are associated with mafic–ultramafic rocks, or ophiolitic detritus in sediments.
- ➢ $Mg^{2+}/Ca^{2+} = 0.7–0.9$—aquifers in dolomitic rocks: Drosoula-10 (0.81), Zaro's-17 (0.8), Samaria-14 (0.79), Rizitiko-18 (0.77), Gortys-16 (0.77), and Rouva's-13 (0.73);
- ➢ $Mg^{2+}/Ca^{2+} = 0.5–0.7$—aquifers in limestone or carbonate lithologies: Mythical-12 (0.69), and Ioli-4 (0.59).

The Mg^{2+}/Ca^{2+} ratio distribution map shows that the above relationships do hold (Fig. 2).

(b) Na^+/Cl^- ratios are associated with salinisation and generally sea water intrusion, or with aquifers in which there are remnants of marine salts, or ground water passing through rocks containing evaporitic salts:

- ➢ $Na^+/Cl^- > 1.0$—aquifers in alkaline or metamorphic rocks, exchange of Ca^{2+} and Mg^{2+} by Na^+, and also aquifers in flysch or water percolating through flysch, which is enriched in Na^+: Beles-46 (3.82), Klinos-47 (2.04), Hyas-45 (1.85), Velouhi-36 (1.82), Aqua Vita-7 (1.76), Drosoula-10 (1.74), Vitsi-48 (1.63), Avra-6 (1.61), Zefiros-40 (1.45), Seli-37 (1.42), Tzoumerka-35 (1.41), Ioli-4 (1.36), Pigi Paikou-38 (1.35), Pindos-8 (1.25), Hydor Sourotis-31 (1.22), Krinos-39 (1.11), Evdoro-34 (1.09), Athos-33 (1.08), and Samarina-9 (1.0);
- ➢ $Na^+/Cl^- = 0.876 \pm 10\%$ (i.e., 0.78–0.96)—normal ground water: Kimi-21 (0.9), Gortys-16 (0.88), Drossia-49 (0.86), Mythical-12 (0.84), Dikti-20 (0.82), Rouva's-13 (0.81), Samaria-14 (0.81), Korpi-3 (0.81), Zagori-2 (0.8), Nera Kritis-11 (0.79); Krini-19 (0.79), Zaro's-17 (0.78), and Rizitiko-18 (0.78);
- ➢ $Na^+/Cl^- < 0.78$—denotes probable pollution of the aquifer by sea water intrusion or dissolution of remnant salts within the sedimentary formations; the latter holds in this case, since isotopic studies of bottled water did not indicate any sea water intrusion in the bottled water source aquifers (E. Dotsika, person. commun., 2010): Loutraki Hydria-27 (0.74), Lyttos-15 (0.73), Sariza-5 (0.73), Iris Loutraki-30 (0.73), Loutraki Karadanis Provis-28 (0.7), Loutraki-26 (0.65), Loutraki Ivi-29 (0.65), Vikos-1 (0.63), and Eviva-22 (0.44).

(c) Na^+/K^+ ratios are related to whether the source water is affected by sea or rain water, or is derived from an area of ground water recharge:

- ➢ $Na^+/K^+ = 50–70$—bottled water source at the down dip of the aquifer due to adsorption of Na: Nera Kritis-11 (59.1), Samaria-14 (57), Zaro's-17 (57), and Rizitiko-18 (57);
- ➢ $Na^+/K^+ \approx 47$—sea water: Sariza-5 (47); in this case the source water is associated with mica schist, which is known to have elevated concentrations of Cl, Na and K;
- ➢ $Na^+/K^+ = 15–25$—bottled water source in an area of ground water recharge: Hydor Sourotis-31 (25.8), Gortys-16 (25.8), Samarina-9 (23.8), Evdoro-34 (19.7), Aqua Vita-7 (18), Ioli-4 (17.6), Korpi-3 (16.7), Drossia-49 (16.2), and Velouhi-36 (14.5);
- ➢ $Na^+/K^+ = < 10$—rain water: Seli-37 (9.64), Drosoula-10 (8.84), Beles-46 (8.79), Zagori-2 (8.5), Eviva-22 (7.82), Tzoumerka-35 (5.67), Pigi Paikou-38 (5.1), Klinos-47 (4.54), and Hyas-45 (2.48); these bottled waters are situated in areas with a comparatively high annual rainfall.

Table 3
Instrumental detection limit (IDL), reported detection limit (RDL), practical detection limit (PDL), precision at the 95% confidence level, and statistical parameters of Hellenic bottled waters (n = 41).

Parameter	Unit	IDL	RDL	PDL	Precision%	Minimum	Maximum	Median	Lower quartile	Upper quartile
Ag	μg/L	0.001	0.002	0.002	13	Majority of values below detection limit (b.d.l.)				
Al	μg/L	0.2	0.5	0.2	5	<0.2	5.48	0.77	0.526	1.21
As	μg/L	0.01	0.03	0.001	10	0.0194	2.52	0.198	0.106	0.354
B	μg/L	0.1	2	0.2	4	2.81	143	14.6	9.3	27.9
Ba	μg/L	0.005	0.05	1*	5	<0.005	7.38	0.019	0.006	0.057
Be	μg/L	0.001	0.01	0.005	5	Majority of values b.d.l.				
Bi	μg/L	0.0005	0.005	0.003	–	<0.0005	0.0041	0.0005	0.0003	0.0010
Br^-	μg/L	0.003	0.003	–	–	<0.003	0.174	0.032	0.009	0.075
Ca	mg/L	0.005	0.01	–	–	2.87	101	55.4	27.2	71.3
Cd	μg/L	0.001	0.003	0.002	29	<0.001	0.0231	0.0026	0.0012	0.004
Ce	μg/L	0.0005	0.001	0.0001	13	Majority of values b.d.l.				
Cl^-	mg/L	0.01	0.01	–	–	1.03	81.4	12.8	5.67	27.8
Co	μg/L	0.002	0.01	0.002	5	0.004	0.0792	0.0126	0.0095	0.0217
Cr	μg/L	0.01	0.2	0.014	7	0.042	32.9	0.627	0.425	2.07
Cs	μg/L	0.0005	0.002	0.004*	3	0.0005	4.52	0.0045	0.0024	0.0272
Cu	μg/L	0.01	0.1	0.029	2	0.017	3.99	0.398	0.243	0.551
Dy	μg/L	0.0002	0.001	0.001	16	<0.0002	0.0107	0.0006	0.0003	0.0010
EC	μS/cm	0.1	0.1	–	–	177	891	434	280	594
Er	μg/L	0.0002	0.001	0.0004	13	<0.0002	0.0141	0.0005	0.0002	0.0010
Eu	μg/L	0.0002	0.001	0.001	18	<0.0002	0.0050	0.0006	0.0003	0.0011
F^-	mg/L	0.003	0.003	–	–	<0.003	0.337	0.05475	0.036	0.102
Fe	μg/L	0.01	0.5	0.08	4	<0.01	0.711	0.238	0.173	0.352
Ga	μg/L	0.0005	0.005	0.005	4	<0.0005	0.0339	0.0036	0.0015	0.0068
Gd	μg/L	0.0002	0.002	0.001	22	<0.0002	0.0102	0.0008	0.0004	0.0014
Ge	μg/L	0.005	0.03	0.02	6	<0.005	0.0465	0.0107	0.0058	0.0137
Hf	μg/L	0.0001	0.002	0.001	28	Majority of values b.d.l.				
Hg	ng/L	1	–	–	–	Majority of values b.d.l.				
Ho	μg/L	0.0001	0.001	0.0003	19	<0.0001	0.0046	0.0002	0.0002	0.0004
I	μg/L	0.01	0.2	0.09	15	0.555	12.2	3.28	2.31	4.9
K	mg/L	0.05	0.1	–	–	<0.05	7.3	0.6	0.3	1.0
La	μg/L	0.0001	0.001	0.001	9	<0.0001	0.0267	0.0008	0.0003	0.0016
Li	μg/L	0.01	0.2	0.14	5	<0.01	14.3	1.15	0.486	2.44
Lu	μg/L	0.00005	0.001	0.0002	16	<0.00005	0.00266	0.00009	0.00003	0.00018
Mg	mg/L	0.005	0.01	–	–	0.764	91.2	11.6	6.01	25.5
Mn	μg/L	0.005	0.1	0.111	2	majority of values b.d.l.				
Mo	μg/L	0.001	0.02	0.017	4	0.0133	2.55	0.225	0.0946	0.325
Na	mg/L	0.02	0.1	–	–	0.7	77.2	7.1	3.8	14
Nb	μg/L	0.001	0.01	0.001	15	Majority of values b.d.l.				
Nd	μg/L	0.0001	0.001	0.001	18	0.0003	0.0152	0.0012	0.00061	0.00217
NH_4^+	mg/L	0.005	0.005	–	–	Majority of values b.d.l.				
Ni	μg/L	0.005	0.02	0.01	4	0.011	2.4	0.136	0.0664	0.366
NO_2^-	mg/L	0.005	0.1	–	–	Majority of values b.d.l.				
NO_3^-	mg/L	0.01	1	–	–	0.02	18.8	3.76	2.63	7.05
P	μg/L	0.01	0.01	–	–	<0.01	0.0489	0.0098	0.0065	0.0196
Pb	μg/L	0.001	0.01	0.003	6	0.001	0.393	0.0206	0.0124	0.0414
pH		0.1	0.1	–	–	7.08	9.2	7.9	7.65	8.1
Pr	μg/L	0.00005	0.001	0.0002	15	<0.00005	0.00363	0.00017	0.00009	0.0004
Rb	μg/L	0.001	0.01	0.30*	6	0.084	5.82	0.34	0.192	0.529
Sb	μg/L	0.001	0.01	0.0001	6	0.094	0.76	0.201	0.159	0.252
Sc	μg/L	0.001	0.02	–	–	0.005	0.192	0.048	0.035	0.076
Se	μg/L	0.005	0.02	0.009	19	0.038	0.743	0.18	0.122	0.256
Si	mg/L	0.02	0.05	–	–	1.36	20.8	4.11	2.38	7.85
Sm	μg/L	0.0001	0.001	0.001	23	0.0001	0.0049	0.0007	0.0004	0.0011
Sn	μg/L	0.001	0.02	0.003	12	0.0005	0.041	0.0052	0.0021	0.0077
SO_4^{2-}	mg/L	0.01	0.01	–	–	1.65	89.7	8.38	5.36	22.9
Sr	μg/L	0.001	0.001	–	–	0.006	0.559	0.118	0.065	0.263
Ta	μg/L	0.0005	0.005	0.002	–	Majority of values b.d.l.				
HCO_3^- (alkalinity)	mg/L	2	2	–	–	112	472	235	163	318
Tb	μg/L	0.00005	0.001	0.0002	23	<0.00005	0.00167	0.00009	0.00006	0.00014
Te	μg/L	0.001	0.03	0.01	**	Majority of values b.d.l.				
Th	μg/L	0.0001	0.001	0.0004	33	<0.0001	0.00265	0.00023	0.00017	0.00033
Ti	μg/L	0.005	0.08	0.04	52	0.005	0.0899	0.0211	0.005	0.0298
Tl	μg/L	0.0005	0.002	0.001	6	0.0015	0.02480	0.00675	0.00323	0.00979
Tm	μg/L	0.00005	0.001	0.0002	22	<0.00005	0.00215	0.00008	0.00006	0.00015
U	μg/L	0.00005	0.001	0.006*	2	<0.00005	10	0.307	0.0985	0.445
V	μg/L	0.01	0.1	0.02	6	0.147	7.45	0.676	0.377	1.36
W	μg/L	0.002	0.05	0.009	1	<0.002	0.106	0.0204	0.0125	0.0317
Y	μg/L	0.00005	0.001	0.002	7	0.0006	0.267	0.0043	0.0019	0.0137
Yb	μg/L	0.0001	0.001	0.001	17	0.0001	0.0165	0.0005	0.0003	0.0009
Zn	μg/L	0.01	0.2	0.11	3	0.12	651	1.11	0.467	13.7
Zr	μg/L	0.0001	0.001	0.013	7	0.001	0.297	0.0016	0.0005	0.0026
Total hardness	mg/L	–	–	–	–	95.3	411	214	167	299
TDS	mg/L	–	–	–	–	113	570	285	179	414

* Too large concentration range and too many high values to reliably calculate PDL.

** Insufficient values above detection limit to estimate precision.

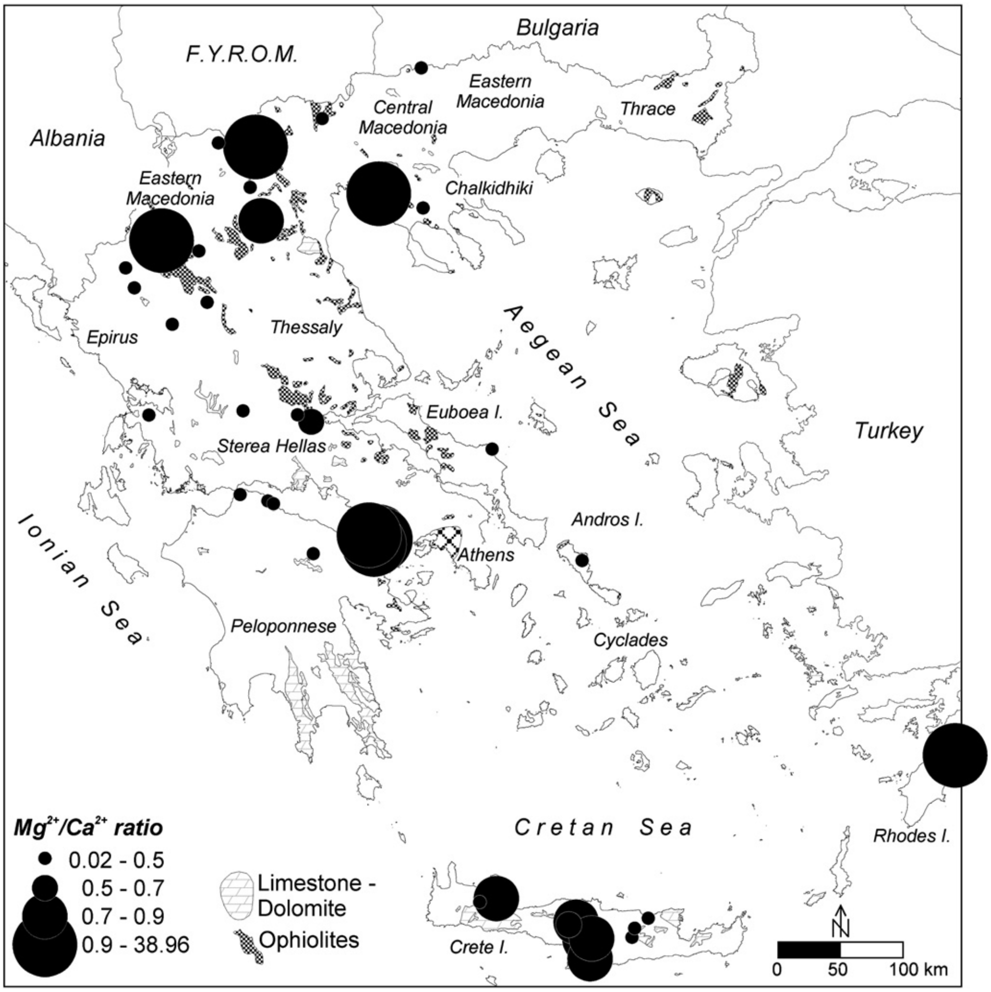

Fig. 2. Map showing the distribution of Mg^{2+}/Ca^{2+} ratios in bottled water samples, Hellas (see also Fig. 1 and Table 1 for sample location numbers and brand names, respectively).

(d) Cl^-/SO_4^{2-} ratios are associated with salinisation and occurrence of residual salts in the aquifers:

- ➢ $Cl^-/SO_4^{2-} = 5$–10—chloride-rich water: Loutraki Ivi-29 (9.89), Loutraki Karadanis Provis-28 (7.03), Loutraki Hydria-27 (7.01), Loutraki-26 (6.97), Iris Loutraki-30 (6.95), and Sariza-5 (5.13);
- ➢ $Cl^-/SO_4^{2-} = 1$–5—water rich in chloride and sulphate: Eviva-22 (4.83), Zaro's-17 (4.29), Rizitiko-18 (4.27), Nera Kritis-11 (4.05), Samaria-14 (4.02), Lyttos-15 (3.83), Aqua Vita-7 (3.05), Rouva's-13 (2.68), Mythical-12 (2.68), Hydor Sourotis-31 (2.59), Evdoro-34 (2.42), Korpi-3 (2.32), Krini-19 (1.48), Dikti-20 (1.33), Athos-33 (1.2), Pindos-8 (1.13), Vikos-1 (1.12), and Gortys-16 (1.06); the sulphate may be derived from the dissolution of gypsum or anhydrite, e.g., Hydor Sourotis is in the Anthemous Basin, where anhydrite occurs (Lambrakis and Kallergis, 2005);
- ➢ $Cl^-/SO_4^{2-} = 0.2$–1.0—water rich in sulphate-chloride: Ioli-4 (0.89), Samarina-9 (0.89);
- ➢ Avra-6 (0.76), Velouhi-36 (0.73), Klinos-47 (0.71), Drossia-49 (0.62), Tzoumerka-35 (0.56), Krinos-39 (0.55), Kimi-21 (0.54), Hyas-45 (0.54), Zagori-2 (0.51), Zefiros-40 (0.48), Beles-46 (0.47), Pigi Paikou-38 (0.29), Vitsi-48 (0.25), and Drosoula-10 (0.22);
- ➢ $Cl^-/SO_4^{2-} < 0.2$—water rich in sulphate: Seli-37 (0.11); the sulphate in this case may be derived from the oxidation of sulphide minerals, since the aquifer is comparatively shallow and dissolved oxygen is most likely available.

(e) $(Ca^{2+} + Mg^{2+})/(K^+ + Na^+)$ ratios:

- ➢ $(Ca^{2+} + Mg^{2+})/(K^+ + Na^+) > 1.0$—aquifer with a continuous recharge: all bottled waters are in this category with ratio

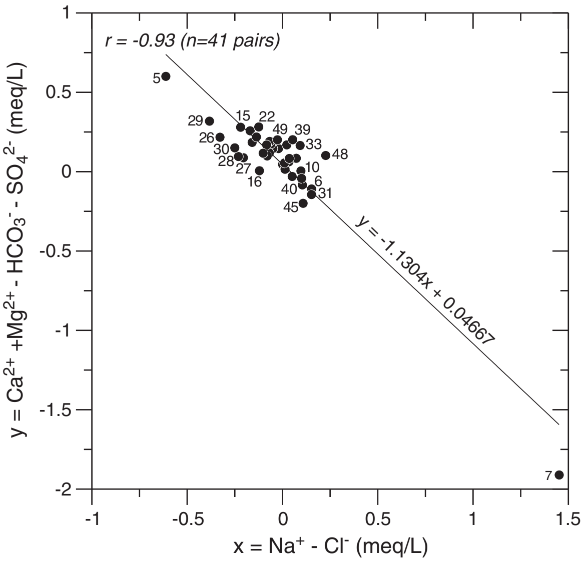

Fig. 3. Bivariate plot of $(Na^+ - Cl^-)$ versus $(Ca^{2+} + Mg^{2+} - HCO_3^- - SO_4^{2-})$, Hellenic bottled water samples (for displayed sample numbers refer to Fig. 1 and Table 1).

Table 4
Comparison of results of this study (shaded) with those displayed on bottle labels.

Parameter	Unit	Number of samples	Min.	Max.	Median	Lower quartile	Upper quartile
Ca	mg/L	41	2.9	101.0	55.4	27.2	71.3
		41	4.8	99.0	50.7	25.2	70.9
Mg	mg/L	41	0.8	91.2	11.6	6.0	25.5
		41	1.0	91.5	12.6	7.6	28.9
K	mg/L	41	0.1	7.3	0.6	0.3	1.0
		41	0.2	6.1	0.8	0.4	1.0
Na	mg/L	41	0.7	77.2	7.1	3.8	14.0
		41	0.8	77.1	8.5	3.4	14.0
Cl^-	mg/L	41	1.0	81.4	12.8	5.7	27.8
		40	1.5	82.2	11.3	5.7	27.0
HCO_3^-	mg/L	41	112.0	472.0	235.5	163.0	318.0
		38	81.7	455.0	242.5	154.8	334.4
NO_3^-	mg/L	41	0.02	18.8	3.8	2.6	7.1
		38	<5.00	15.5	2.7	2.5	6.3
SO_4^{2-}	mg/L	41	1.7	89.7	8.4	5.4	22.9
		41	0.6	65.8	9.4	5.7	22.0
pH		41	7.1	9.2	7.9	7.7	8.1
		37	6.9	8.5	7.7	7.5	8.0
EC	µS/cm	41	177	891	434	280	594
		37	175	864	439	287	590

values varying from 62.87 to 1.69, i.e., Samarina-9 (62.9), Pigi Paikou-38 (60.4), Seli-37 (52.3), Drossia-49 (47), Vikos-1 (45.6), Zagori-2 (42), Eviva-22 (38.8), Tzoumerka-35 (37.3), Klinos-47 (27.2), Velouhi-36 (26), Drosoula-10 (25.6), Korpi-3 (23), Beles-46 (22.2), Ioli-4 (16.4), Hyas-45 (16.3), Pindos-8 (16.1), Loutraki Karadanis Provis-28 (13.6), Loutraki Hydria-27 (13), Evdoro-34 (12.8), Zefiros-40 (11.2), Loutraki-26 (10.2), Iris Loutraki-30 (9.28), Vitsi-48 (8.89), Avra-6 (8.85), Samaria-14 (8.82), Loutraki Ivi-29 (8.75), Krinos-39 (8.69), Rizitiko-18 (8.53), Zaro's-17 (8.24), Kimi-21 (7.64), Rouva's-13 (7.41), Mythical-12 (7.37), Hydor Sourotis-31 (7.31), Nera Kritis-11 (6.35), Lyttos-15 (6.17), Dikti-20 (6.1), Krini-19 (6), Gortys-16 (5.07), Athos-33 (4.96), Sariza-5 (2.11), Aqua Vita-7 (1.69). The order from high to lower (Ca + Mg)/(K + Na) ratios almost follows the trend from areas of higher to lower annual rainfall.

(f) Cl^-/Br^- ratios are associated with the mixing of fresh water with sea water, or with water in evaporitic formations or percolating through sedimentary rocks containing evaporitic salts:

- $Cl^-/Br^- \approx 500–4000$—such ratios denote water in contact with evaporites or water passing through sedimentary rocks containing disseminated evaporitic salts, and halite dissolution. All bottled waters are in this category with values varying from 4620 to 609, i.e., Zefiros-40 (4620), Seli-37 (2765), Pindos-8 (2633), Evdoro-34 (2160), Eviva-22 (1998), Klinos-47 (1818), Vikos-1 (1278), Hyas-45 (1271), Aqua Vita-7 (1219), Ioli-4 (1215), Korpi-3 (1111), Velouhi-36 (1082), Krinos-39 (1060), Sariza-5 (1054), Hydor Sourotis-31 (1043), Avra-6 (1043), Nera Kritis-11 (1035), Lyttos-15 (1019), Zagori-2 (964), Samaria-14 (962), Kimi-21 (943), Beles-46 (939), Athos-33 (933), Vitsi-48 (902), Loutraki Ivi-29 (883), Gortys-16 (878), Rizitiko-18 (856), Zaro's-17 (850), Krini-19 (842), Iris Loutraki-30 (838), Loutraki Karadanis Provis-28 (835), Dikti-20 (835), Loutraki-26 (835), Tzoumerka-35 (819), Pigi Paikou-38 (774), Loutraki Hydria-27 (737), Mythical-12 (687), Rouva's-13 (661), Drossia-49 (640), Drosoula-10 (611), Samarina-9 (609). It is noted that the Cl^-/Br^- ratio for sea and fresh water is approximately 300, and for syngenetic water <300.

TDS, alkalinity and the $(Ca^{2+} + Mg^{2+})/(K^+ + Na^+)$ ratios all suggest that the source aquifers of Hellenic bottled water are shallow, and continuously replenished by fresh water. This observation is verified by the Na^+/K^+ ratios, most of which have values of <50.

Bottled water samples have Cl^-/Σ anion ratios varying from 0.01 to 0.43. Since, Cl^-/Σ anion ratios are <0.8, the bottled water ground water sources are not seriously affected by dissolution of halite or other evaporitic minerals, and sites near the coast are apparently not affected by sea water intrusion. According to Houslow (1995) ground water derived from halite dissolution would have a $Na^+/(Na^+ + Cl^-)$ ratio of approximately equal to 0.5, i.e., $Na^+ \approx Cl^-$. The $Na^+/(Na^+ + Cl^-)$ ratios vary from 0.30 to 0.79, suggesting that some of the bottled water sources do derive their salinity mainly from the dissolution of halite or evaporitic minerals within sedimentary formations, i.e., those with values ≥0.5, e.g., Beles-46 (0.79), Klinos-47 (0.67), Hyas-45 (0.65), Velouhi-36 (0.65), Aqua Vita-7 (0.64), Drosoula-10 (0.63), Vitsi-48 (0.62), Avra-6 (0.62), Zefiros-40 (0.59), Seli-37 (0.59), Tzoumerka-35 (0.59), Ioli-4 (0.58), Pigi Paikou-38 (0.57), Pindos-8 (0.56), Hydor Sourotis-31 (0.55), Krinos-39 (0.53), Evdoro-34 (0.52), Athos-3 (0.52), Samarina-9 (0.5), Kimi-21 (0.47), Gortys-16 (0.47), Drossia-49 (0.46) and Mythical-12 (0.46). The Cl^-/Br^- ratios support the assumption that bottled water sources are not affected by sea water intrusion, and their salinity is derived from the dissolution of halite or evaporitic minerals within the sedimentary sequence.

Evidence of ion exchange is provided by the $(Na^+–Cl^-)$ versus $(Ca^{2+} + Mg^{2+}–SO_4^{2-}–HCO_3^-)$ diagram—Fig. 3 (Jankowski et al., 1998; Kortatsi, 2006). The Hellenic bottled water samples plot approximately along a line with a slope of −1.13, suggesting that some ion exchange is taking place, as it has been already noted in the description of Na^+/Cl^- ratios.

Table 5
Analysis of variance statistics between the analyses displayed on bottle labels and those of this study (notation: df = degrees of freedom).

Parameter	Total sum of squares	Residual sum of squares	Sum of squares	Residual mean square	F-ratio	Estimated p-value
	a	*b*	*c = a–b*	*d = b/df*	*e = c/d*	
Ca	33,640 (df 40)	2809 (df 39)	30,831	72.0	428	<0.00001
Mg	27,691 (df 40)	1328 (df 39)	26,363	34.1	774	<0.00001
K	42.6 (df 40)	3.00 (df 39)	39.6	0.077	515	<0.00001
Na	7654 (df 40)	198 (df 39)	7456	5.08	1469	<0.00001
Cl^-	11,772 (df 39)	689 (df 38)	11,083	18.1	611	<0.00001
HCO_3^-	441,658 (df 37)	21,043 (df 36)	420,615	585	720	<0.00001
NO_3^-	407 (df 37)	122 (df 36)	285	3.39	84.1	<0.00001
SO_4^{2-}	9385 (df 40)	1576 (df 39)	7809	40.4	193	<0.00001
pH	4.58 (df 36)	1.46 (df 35)	3.12	0.042	74.7	<0.00001
EC	1,168,530 (df 36)	80,310 (df 35)	1,088,220	2295	474	<0.00001

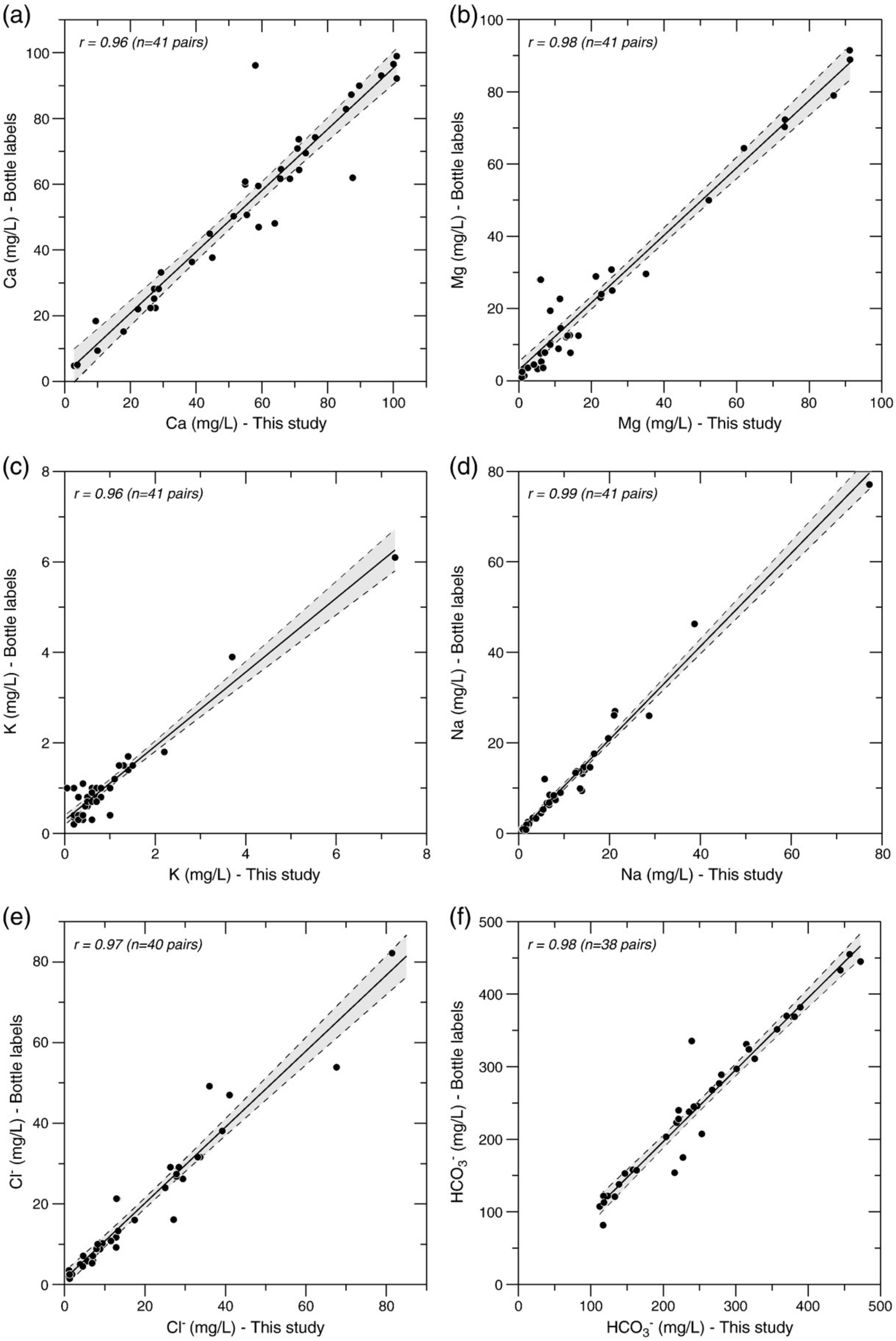

Fig. 4. Bivariate plots of parameters of this study versus the corresponding ones on bottle labels (for displayed sample numbers refer to Fig. 1 and Table 1).

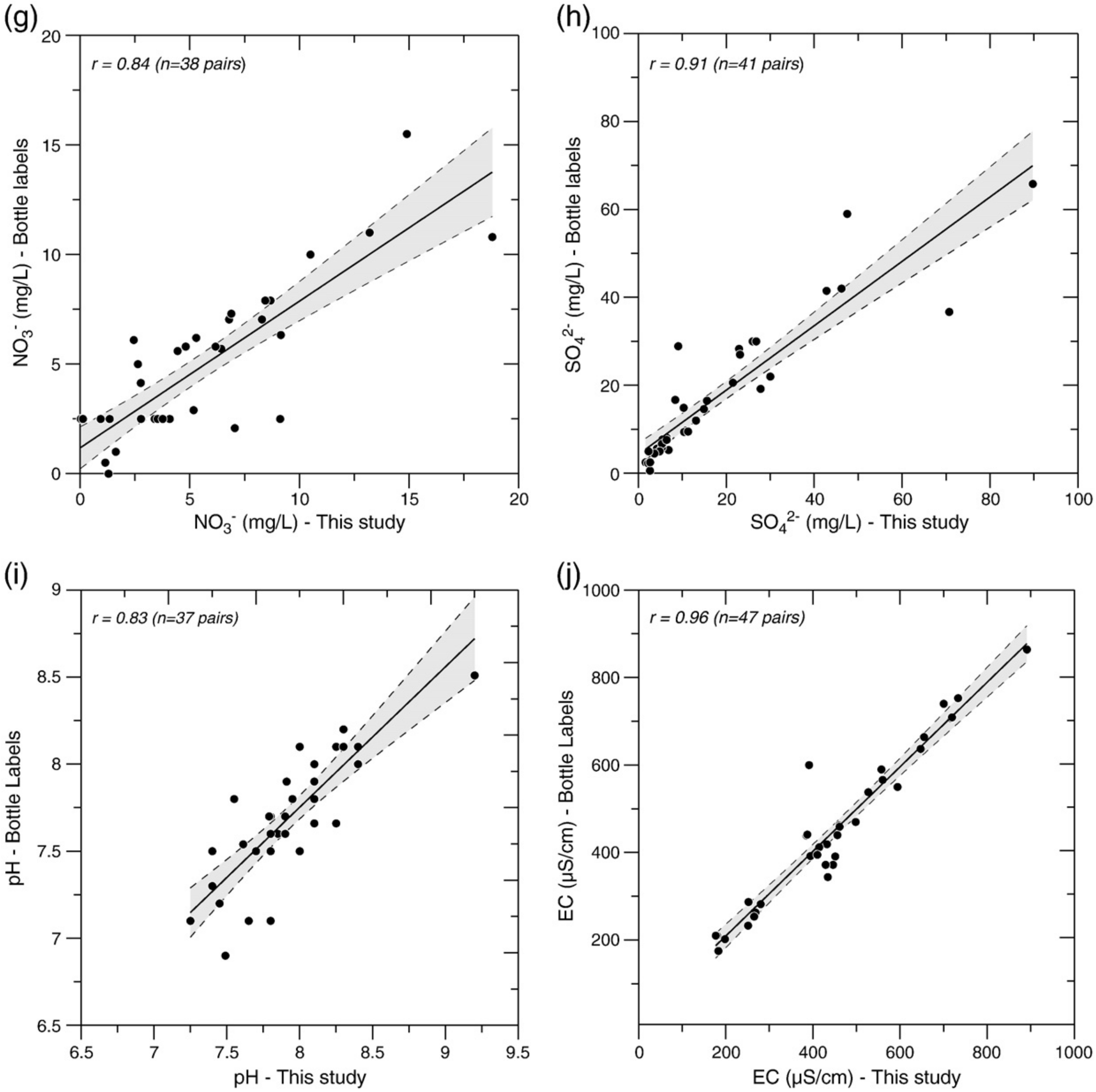

Fig. 4 (*continued*).

4.2. Comparison of analytical results of this study with those on bottle labels

Bottled water analyses, displayed on bottle labels, were performed mainly by the Institute of Geology and Mineral Exploration, a few by the General State Laboratory and Aristotelian University of Thessaloniki, and one by the Chemical Institute of Rhodes. Surprisingly, the dates of analysis go back from 1998 to 2007, and only two bottled water companies had analyses performed in 2008. Some bottle labels displayed mean analyses of four seasons from 2004 to 2007.

A comparison of analytical results of Ca, Mg, K, Na, Cl^-, HCO_3^-, NO_3^-, SO_4^{2-}, pH and electrical conductivity (EC) on bottle labels with those of this study was made. The general statistical parameters of the two data sets are tabulated in Table 4, and the similarities are indeed surprising, if one takes into consideration the different laboratories performing the analyses, their instrumentation, detection limits, quality control protocols, time of analysis varying from 1998 to 2008, etc. The analysis of variance has also shown that there is a statistically significant relationship between all parameters of the two data sets, since the estimated p-values are <0.05 at the 95.0% confidence level (Table 5).

In addition, scatter plots were drawn to show visually the relationship between the two data sets, and the linear regression line together with the 95% confidence intervals were superimposed (Fig. 4). Overall, the two data sets show a fairly good correlation, when taking into consideration the aforesaid different laboratory conditions, and periods of sampling. Nitrate (NO_3^-) and pH showed the poorest correlation, since these are two variables that are sensitive to environmental changes (Fig. 4g, i). The high and variable detection limit of nitrate on bottle labels is quite evident (Fig. 4g).

4.3. Hydrogeochemical characteristics of the source aquifers of Hellenic bottled water

A number of diagrams have been plotted, and are used for the classification of Hellenic bottled water to express similarity and dissimilarity in the chemistry of the ground water source, based on major cations and anions. For comparison purposes, on all diagrams are plotted the composition of mean sea water, snow from Nevada U.S.A. at a height of 2344 m that has fallen in the winter of 1958, rain water average between 1978 and 1983 from Beek and De Kooy in The Netherlands (Holland for short), rain water average of the 1957–58 winter from Menlo Park in California, and rain water average between 1955 and 1957 from Kiruna in Sweden (Appelo and Postma, 1994; Freeze and Cherry, 1979; Kallergis, 1970, 2000; Mandel and Shiftan, 1981); Beek is at a distance of 175 km from the coast, whereas De Kooy is a coastal Dutch town.

4.3.1. Major ion hydrogeochemistry

Instead of using the Piper and expanded Durov diagrams (Durov, 1948; Lloyd, 1965; Piper, 1944), the Chadham diagram was utilised (Fig. 5), which is their modified version and it is much simpler to plot (Belkhiri et al., 2010; Chadha, 1999). The difference is that the two equilateral triangles are omitted. However, for a more detailed study, one trilinear cation and two anions predominance diagrams, as well as a number of biplots have been plotted.

According to Chadha's diagram (Fig. 5), the majority of bottled waters belong to Group 5, the Ca–Mg–HCO_3 hydrochemical facies; one sample (no. 5—Sariza) belongs to Group 1, where it means that alkaline earths ($Ca^{2+}+Mg^{2+}$) exceed the alkali metals ($Na^{+}+K^{+}$), and one sample (no. 7—Aqua Vita) is in the transition zone between Group 5 and Group 3, where weak acidic anions ($CO_3^{-}+HCO_3^{-}$) exceed strong acidic cations ($Cl^{-}+SO_4^{2-}$). The Chadha diagram gives, in fact, a summary version of the geochemical characteristics of bottled water sources, described in detail by ionic ratios.

The trilinear cations predominance diagram shows that the majority of bottled water samples are dominated by Ca, and are, thus, classified as 'calcium-rich' water types (Fig. 6). The predominance of Ca is understandable, because of the widespread occurrence of calcium or calcium releasing lithologies in Hellas, e.g., karstic limestone, mafic–ultramafic sequences (ophiolites), but also sedimentary rocks rich in calcium. Some bottled waters fall in the 'magnesium-rich' field, and these are associated with mafic–ultramafic rocks (ophiolites) and dolomitic limestone, i.e., weathering of Mg-rich minerals, such as olivine and pyroxene (Samarina-9), sediments containing a large proportion of ophiolitic detritus (Loutraki-26, Loutraki Hydria-27, Loutraki Karadanis Provis-28, Loutraki Ivi-29, Iris Loutraki-30), and dolomitised marble and ophiolites (Drossia-49), limestone and conglomerate with ophiolitic detritus (Hydor Sourotis-31), and limestone and ophiolitic rocks (Aqua Vita-7). Sample 5 (Sariza) from Andros Island falls in the mixed zone and is enriched in Na, presumably derived from the dissolution of albite ($NaAlSi_3O_8$) occurring in the mica schist; the possible explanation for samples 16 (Gortys) and 17 (Zaro's) from Crete Island is the derivation of Mg from dolomitised limestone, and Na from the dissolution of sodium-rich minerals in the flysch.

The two anions predominance diagrams [HCO_3^{-}–SO_4^{2-}–($Cl^{-}+NO_3^{-}$)] (Fig. 7a) and [Cl^{-}–SO_4^{2-}–($CO_3^{2-}+HCO_3^{-}$)] (Fig. 7b), provide additional information of the controls on ground water geochemistry, and an understanding of water–rock interactions that are dominant in Hellenic aquifers. The majority of Hellenic bottled waters fall in the field of 'bicarbonate-rich' and 'carbonate–bicarbonate-rich' waters (Fig. 7a, b), suggesting the dissolution of carbonate bearing minerals from the weathering of mafic–ultramafic rocks (ophiolites), limestone, marble, and sediments rich in carbonates. On both diagrams sample 5 (Sariza) from Andros Island falls in the mixed zone, possibly suggesting the interaction of ground water with the mica schist, which is known to have elevated concentrations of Cl, Na and K; see also diagrams of Na^{+}/Cl^{-} versus Cl^{-} (Fig. 8a) and Na^{+} versus Cl^{-} (Fig. 8b).

The Na^{+} versus Cl^{-} biplot shows that the bottled water samples plot very close to the 1:1 Na:Cl sea water–rainwater mixing line, with a slight dominance of Na (Fig. 8b). This perhaps suggests an increase of the ground water's weathering capacity due to the probable presence of high CO_2 concentrations that favour the solubility of alkaline elements from siliceous rocks (Ellis and Mahon, 1977; Lambrakis and Kallergis, 2005). In such a case, there may be remobilisation of sodium from Na-bearing silicate rocks, thus causing an increase in the Na^{+}:Cl^{-} ratio above the sea water–rainwater mixing line (Fig. 8a, b). Samples 5 (Sariza) and 7 (Aqua Vita) have elevated Na and Cl concentrations, and because they are situated on islands, and near the coast, they may be ascribed to a marine influence. However, their isotopic composition does not support such an explanation (E. Dotsika, pers. commun., 2010), and are attributed to geogenic sources. In addition, Sariza-5 is associated with the mica schist, which is known to have elevated concentrations of Cl, Na and K,

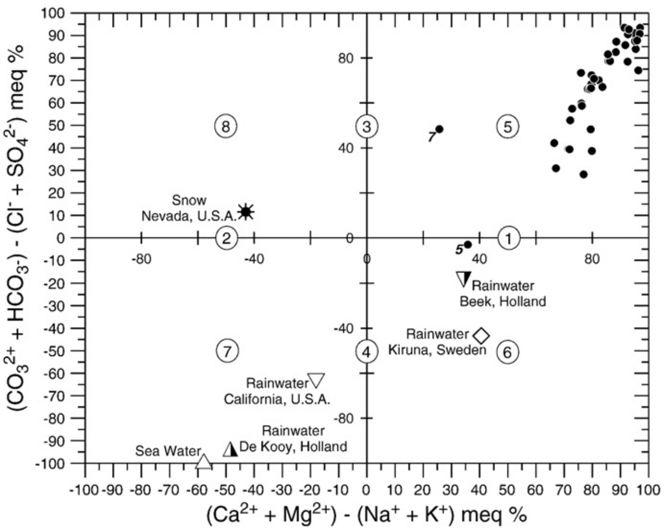

Fig. 5. Geochemical classification and hydrochemical processes of ground water depicted by bottled water, Hellas (after Chadha, 1999, Fig. 3, p. 434; for displayed sample numbers refer to Fig. 1 and Table 1).

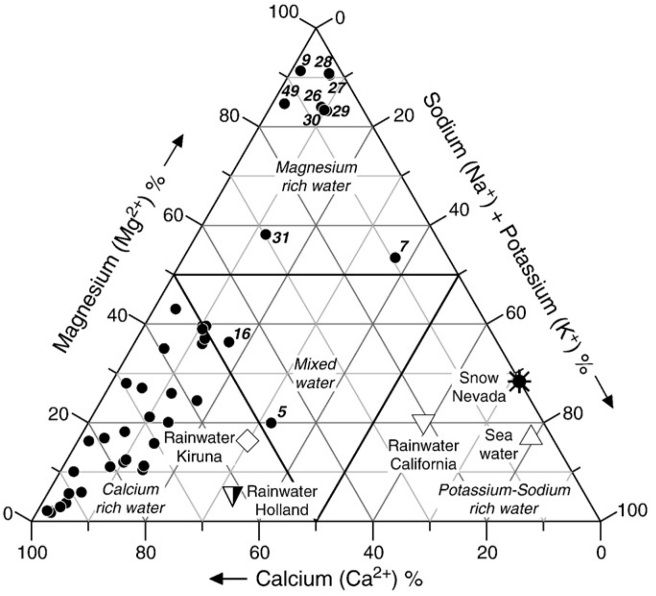

Fig. 6. Trilinear predominance diagram for the cations [Calcium–Magnesium–(Sodium + Potassium)] in Hellenic bottled water (for displayed sample numbers refer to Fig. 1 and Table 1).

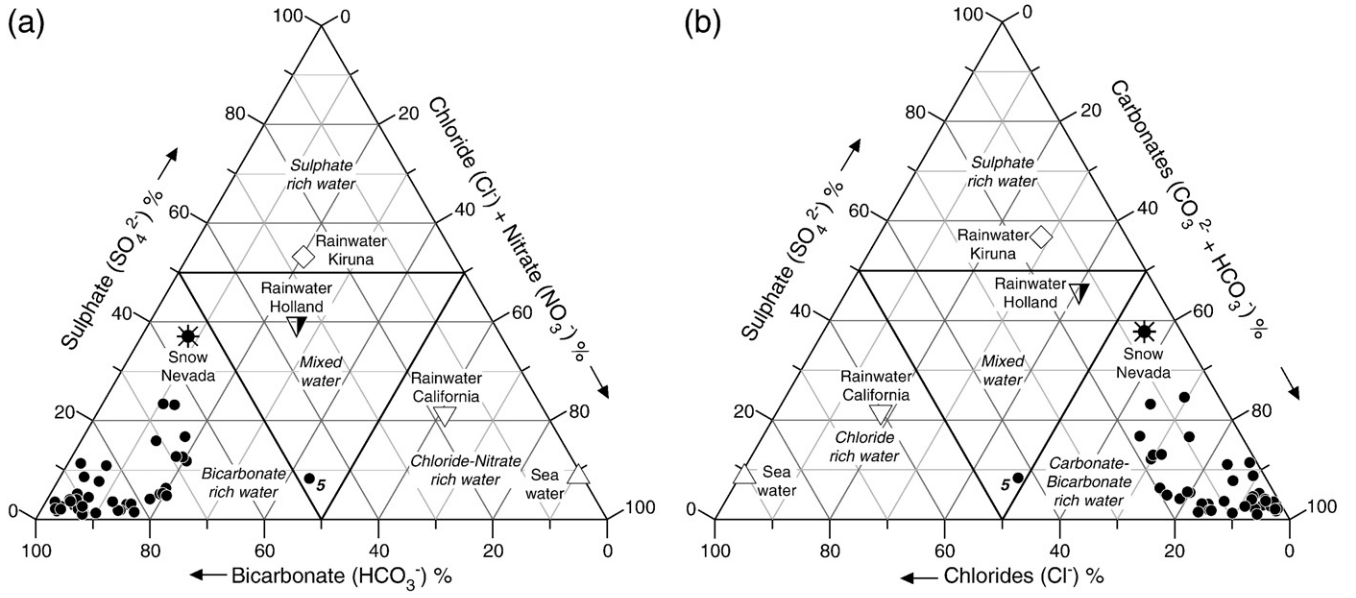

Fig. 7. Trilinear predominance diagram for the anions in Hellenic bottled water: (a) Bicarbonate–Sulphate–(Chloride + Nitrate) and (b) Chlorides–Sulphates–Carbonates (for displayed sample numbers refer to Fig. 1 and Table 1).

whereas Aqua Vita-7 most likely picks up Na$^+$ and Cl$^-$ ions from remnant salts within the marine sediments.

Other interesting ion biplots are:

(a) Ca^{2+} versus Cl$^-$ (Fig. 9a): the majority of bottled water samples fall in the Ca^{2+} field, except Sariza-5 (Andros I.), Aqua Vita-7 (Rhodes I.), Loutraki-26, Loutraki Hydria-27, Loutraki Karadanis Provis-28, Loutraki Ivi-29, Iris Loutraki-30, which have elevated Cl$^-$ concentrations that may be due to meteoric input, but also geogenic sources;

(b) Mg^{2+} versus Cl$^-$ (Fig. 9b): the majority of bottled water samples fall in the Mg^{2+} field, because of water–rock interactions with dolomitic limestone, and ophiolites or ophiolitic detritus in sediments; sample numbers Sariza-5 (Andros I.), Krini-19 and Dikti-20 (Crete I.), Korpi-3, and Vikos-1 fall in the Cl$^-$ field, suggesting dissolution of chloride-rich minerals from mica schist in the case of Sariza-5, and sediments; for the last two samples evaporites may play a role;

(c) B^{3+} versus Cl$^-$ (Fig. 9c): all bottled water samples fall in the boron field, a feature attributed to intensified water–rock interactions (Lambrakis and Kallergis, 2005);

(d) NO$_3^-$ versus Cl$^-$ (Fig. 9d): the majority of bottled water samples fall in the elevated NO$_3^-$ concentrations field, indicating the participation of fresh surface water in the replenishment of aquifers. Gortys-16 (Crete I.) and Kimi-21 (Euboea I.) have the lowest NO$_3^-$ levels. As has already been pointed out in the discussion of the Na$^+$/Cl$^-$ and Na$^+$/(Na$^+$ + Cl$^-$) ratios, elevated Cl$^-$ concentrations may be due to dissolution of halite or evaporitic minerals from marine sediments.

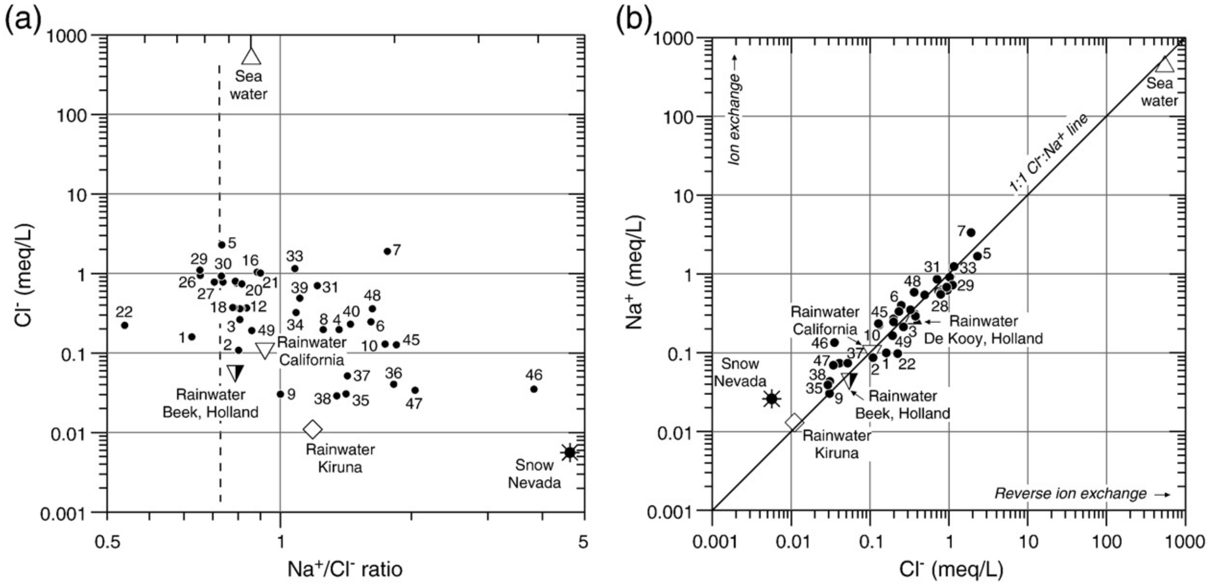

Fig. 8. Logarithmic plots of relationships between concentrations of chemical species: (a) Na$^+$/Cl$^-$ versus Cl$^-$; (b) Cl$^-$ versus Na$^+$ (for displayed sample numbers refer to Fig. 1 and Table 1).

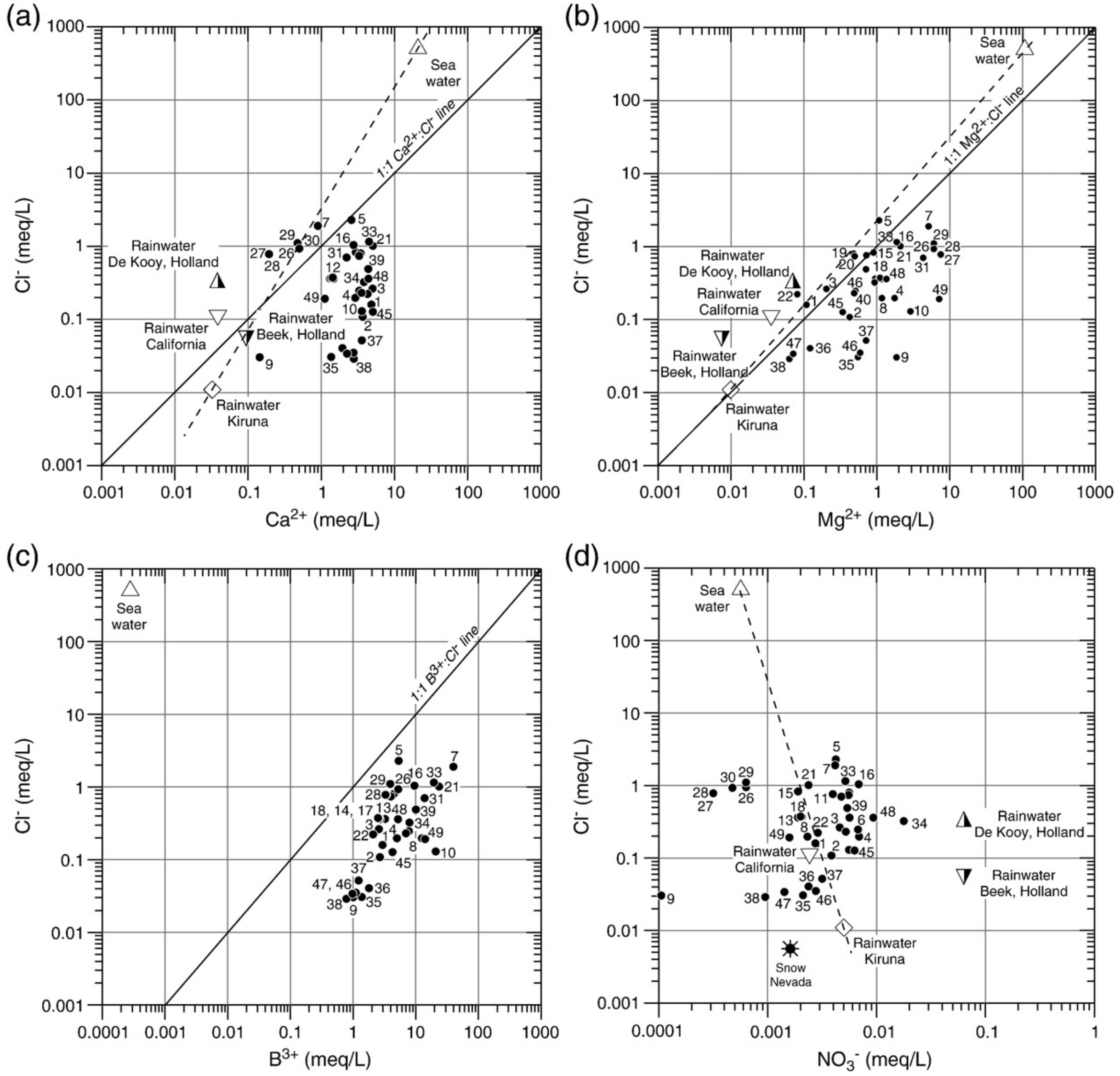

Fig. 9. Logarithmic plots of relationships between concentrations of chemical species: (a) Ca^{2+} versus Cl^-; (b) Mg^{2+} versus Cl^-; (c) B^{3+} versus Cl^-; (d) NO_3^- versus Cl^- (for displayed sample numbers refer to Fig. 1 and Table 1).

Biplots of cations also show interesting features, e.g.,

(i) Na^+ versus K^+ (Fig. 10a): all bottle water samples fall in the Na field, and apart from sample 45 (Hyas), they are below the sea water–rainwater mixing line; this feature indicates that the bottled water's ground water source is richer in Na than K, and
(ii) $(Na^+ + K^+)$ versus $(Ca^{2+} + Mg^{2+})$ (Fig. 10b): all bottled water samples fall in the $(Ca^{2+} + Mg^{2+})$ field, suggesting that these two cations are the most important in Hellenic ground waters, since the dominant rock types are Ca and Mg rich, as has already been mentioned.

4.3.2. Gypsum solubility and related plots

Gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrite ($CaSO_4$) occur as primary minerals in evaporite formations, and as secondary minerals in other sedimentary sequences, especially in the Paxos and Axios geotectonic zones (Fig. 1), but also in the Tertiary sedimentary formations. Since, gypsum could be an important control on the solubility of Ca^{2+} and SO_4^{2-}, and may limit concentrations of these ions in solution, the gypsum saturation index diagram was plotted (Fig. 11). All bottled water samples fall in the undersaturated field with respect to the gypsum equilibrium line. This condition may be explained by other controls on the concentration of Ca^{2+} and SO_4^{2-} in solution, which include insufficient sources of these elements from aquifer lithologies, or the occurrence of lower solubility minerals, which limit the concentration of either ion in solution, such as calcite (Ander et al., 2006) that occurs in the Hellenic lithologies. Since, the bottled water samples are undersaturated with respect to gypsum, it appears that this mineral phase is not expected to be an important control on concentrations of Ca^{2+} and SO_4^{2-} in the source rocks of these waters, or the formations through which ground water passes.

This observation is further supported by the ratio plot of SO_4^{2-}/Ca^{2+} versus Mg^{2+}/Ca^{2+} (Fig. 12b), and SO_4^{2-} versus Ca^{2+} diagram (Fig. 12a), which show that all bottled water samples fall in the Ca^{2+} and Mg^{2+}/Ca^{2+} fields, respectively.

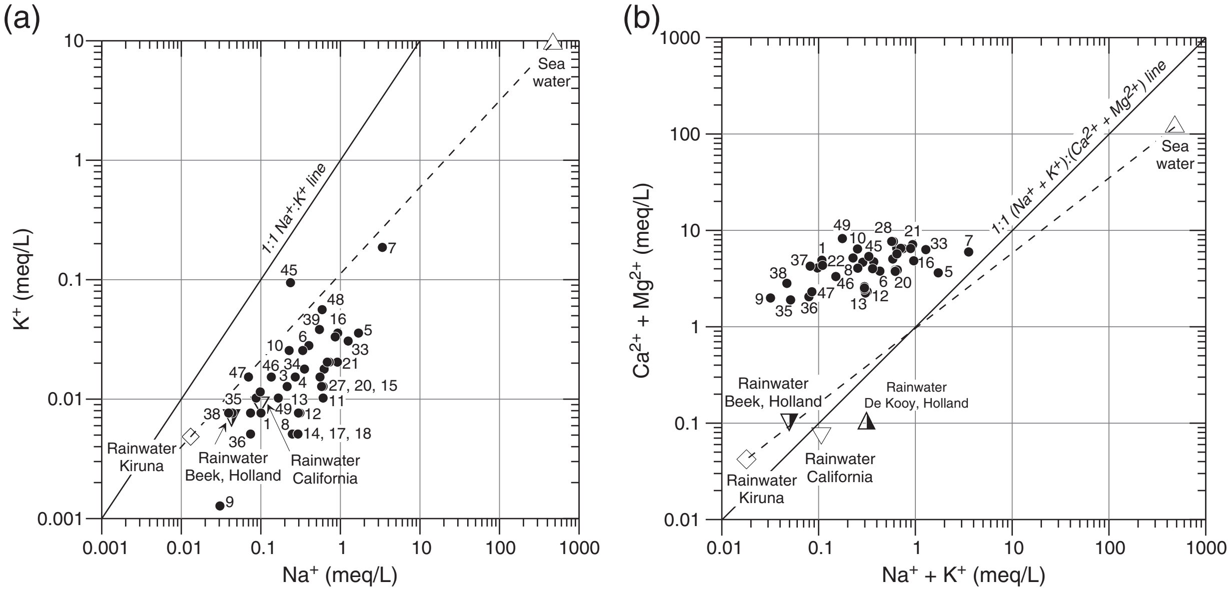

Fig. 10. Logarithmic plots of relationships between concentrations of chemical species: (a) Na^+ versus K^+ and (b) $(Na^+ + K^+)$ versus $(Ca^{2+} + Mg^{2+})$ (for displayed sample numbers refer to Fig. 1 and Table 1).

4.4. Cluster analysis

R-cluster analysis was performed to show the relationships among the parameters determined on the Hellenic bottled water samples. The associations are depicted by the dendrogram (Fig. 13). Since, most of the parameters are not normally distributed, different dendrograms were constructed using the raw data, logarithmically transformed data ($\log_{10}$, $\log_e$), and mixed data files. Finally, it was decided that the raw data file gives the optimum relationships, and this may be due to the method of constructing the dendrogram, which does not use the linear correlation coefficient. For constructing the dendrograms, the Nearest Neighbour and Squared Euclidean distance options of the Multivariate Methods module of Statgraphics were used (Statpoint, 2005); the data of each determinand were standardised by subtracting the sample mean and then dividing by the standard deviation. The Euclidean distance measures the length of a straight line drawn between two determinands; the Squared Euclidean distance is the sum of squared differences between determinands in the n-dimensional space of the samples. The Nearest Neighbour or Single Linkage method finds the two determinands or variables that have the shortest squared Euclidean distance or greatest similarity and places them in the first cluster, and all other determinands are compared with it by recomputing the distance between the groups, and locating the next shortest distance and either joins a third determinand to the first two to form a larger cluster or a new two-determinand cluster is formed. This agglomerative hierarchical process continues by combining the determinands into successively larger clusters until they are all in one cluster.

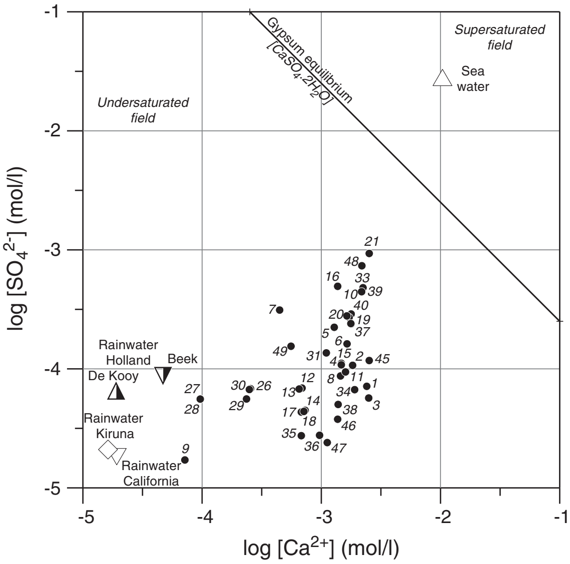

Fig. 11. Comparison of the Hellenic bottled water data with the gypsum saturation index (for displayed sample numbers refer to Fig. 1 and Table 1).

The R-dendrogram depicting the relationships of determined parameters (Fig. 13) shows two large clusters (a) from Al to Mo—the “lithological” cluster, and (b) from As to Sb—the “mineralisation” cluster, since the majority of elements in each cluster are associated with lithology and mineralisation, respectively.

The “lithological” cluster is subdivided into the following sub-clusters:

- Br–Cl–(Na) which is joined to the K–Zr cluster;
- EC–HCO_3^-, which is joined to the Cr–Mg and Sc–Si–(I) clusters;
- the above clusters are joined to the Li–Ni cluster, and all are successively linked to SO_4^{2-}, Al, Ge, Sr, Eu and Mo.

The “mineralisation” cluster is subdivided into the following sub-clusters:

- two interlinked clusters of the REE joined to U and Ba, and subsequently to Th and As;
- a cluster with Cs–Zn–(Rb) and Pb, which is then joined to the above cluster, and the two are interlinked with NO_3^- and Co; at this point the “mineralisation” cluster is linked to the “lithological” cluster; and then both are joined with F and Ti;
- a cluster with Cu–Sn–(Bi) is joined to the above clusters, and
- finally all of the above are linked at a lower correlation to Ca, Se, Tl, Ga, V, P, Cd, Fe, W, Sb and pH.

The above relationships suggest that bottled water is affected by the lithology and mineralisation of the formations through which

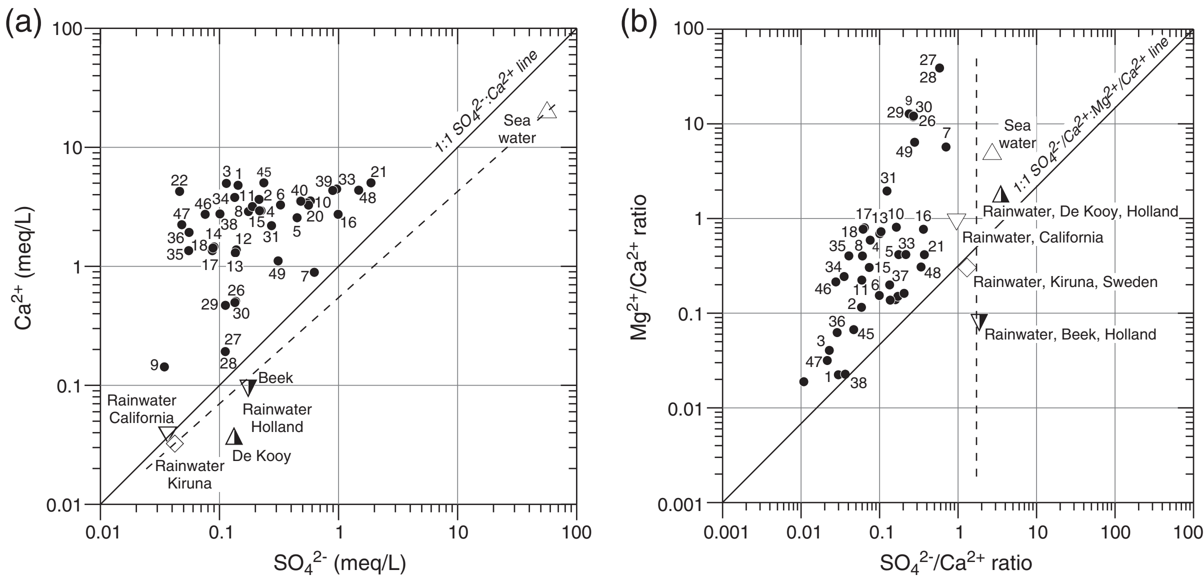

Fig. 12. Logarithmic plots of relationships between concentrations of chemical species: (a) SO_4^{2-} versus Ca^{2+} and (b) SO_4^{2-}/Ca^{2+} versus Mg^{2+}/Ca^{2+} (for displayed sample numbers refer to Fig. 1 and Table 1).

ground water circulates, and its geochemistry depends on the concentrations of the dominant ions that have been leached.

5. Conclusions

The chemical composition of ground water sources of the studied brands of Hellenic bottled water is strongly influenced by lithology, and especially limestone, dolomitic limestone, mafic–ultramafic rocks (ophiolites), and remnant salts within the sedimentary sequences. Hence, geology is the key factor that influences determinand concentrations, not only in Hellas, but also in Europe (Reimann and Birke, 2010).

The processes contributing to the concentration of major ions in ground water depend on carbonate dissolution and precipitation, cation exchange, concentration of evaporitic salts disseminated throughout marine deposited sedimentary rocks, and in some cases to the dissolution of aluminosilicate minerals. Although gypsum and anhydrite occur in many parts of Hellas, the bottled water samples are undersaturated with respect to gypsum and, therefore, it is not considered to be an important control on the concentrations of Ca^{2+} and SO_4^{2-} in the aquifer source rocks of these waters, or the formations through which ground water passes.

The Hellenic bottled water samples are classified in the Ca^{2+}–Mg^{2+}–HCO_3^- hydrochemical facies of the Chadha diagram (Chadha, 1999), and this is due to the lithology, which is dominated by dolomitic limestone, limestone, marble, and mafic–ultramafic rocks (ophiolites). Similarly, the dominant cations and anions are respectively ($Ca^{2+}+Mg^{2+}$) and (HCO_3^- and CO_3^{2-}).

The source aquifers of Hellenic bottled water are apparently continuously replenished by fresh water. A conclusion, which is supported by TDS, alkalinity, ($Ca^{2+}+Mg^{2+}$)/(K^++Na^+) and Na^+/K^+ ratios, and the NO_3^- versus Cl^- biplot.

The Cl^-/Br^- ratios, together with Cl^-/Σ anion ratios, and $Na^+/(Na^++Cl^-)$ ratios support isotopic data (E. Dotsika, person. commun., 2010) that the source aquifers of Hellenic bottled water are not affected by sea water intrusion, even at sites near the coast. The concentrations of Na^+ and Cl^- ions mainly originate from the dissolution of evaporitic salts within the aquifer host rocks, or from the rock formations through which ground water percolates.

Water–rock interactions are supported by the (Na^+-Cl^-) versus ($Ca^{2+}+Mg^{2+}-SO_4^{2-}-HCO_3^-$) and B^{3+} versus Cl^- biplots, and, of

Fig. 13. Dendrogram depicting the relationships among determined parameters on Hellenic bottled water samples (n = 41).

course, the dendrogram that depicts the relationships among the parameters determined on the Hellenic bottled water samples. The latter shows that ions in solution are derived from the dominant lithology and mineralisation through which the ground water passes.

Finally, the chemical composition of source aquifers of the studied bottled water samples appears to be comparatively stable over time, since there is in fact a good correlation between the results of this study and those displayed on bottle labels going back to 1998. Stable chemistry of source aquifers is, in fact, a requirement in the Natural Mineral Waters Directive (EU, 2009; Annex I, I.3, p. 51), i.e., "*The composition, temperature and other essential characteristics of natural mineral water shall remain stable within the limits of natural fluctuation; in particular, they shall not be affected by possible variations in the rate of flow*".

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