THE GEOCHEMICAL ATLAS
OF EUROPEAN GROUND WATER
WITH EMPHASIS ON HELLAS

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Abstract

A first impression of the geochemistry and quality of European ground water was obtained by using bottled mineral water as a sampling medium. In total, 1785 bottled waters were purchased from supermarkets of forty European countries, representing 1247 wells/drill holes/springs at 884 locations. All bottled waters were analysed for 72 parameters at the laboratories of the Federal Institute for Geosciences and Natural Resources (BGR) in Germany.

The European geochemical maps give a first impression of the natural variation in ground water at the continental scale. The majority of European bottled waters are classified as of Ca-HCO_3 type, because of the widespread carbonate lithologies, but there is considerable variation from Na-HCO_3 type related to granitic rocks to Na-Cl type associated with deep saline brines. Since, the dominating lithology in Hellas 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.

Chromium, V and U are discussed, because of their importance in Hellenic ground water. In Europe, the former is clearly related to ophiolites, whereas V indicates the presence of recent volcanism and basaltic rocks, and U is associated with granitic intrusions and Bunter (central England) and Keuper (central Europe) sandstone of early and late Triassic, respectively. It can, therefore, be concluded that geology is one of the key factors influencing the observed element concentrations for a significant number of elements.

Keywords: Ground water geochemistry, bottled water, ionic ratios, hydrochemical classification, Europe, Hellas

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Ο ΓΕΩΧΗΜΙΚΟΣ ΑΤΛΑΝΤΑΣ ΤΩΝ ΥΠΟΓΕΙΩΝ ΥΔΑΤΩΝ ΤΗΣ ΕΥΡΩΠΗΣ ΜΕ ΕΜΦΑΣΗ ΣΤΗΝ ΕΛΛΑΔΑ

Δημητριάδης Αλ., Reimann C., Birke M. και η Ομάδα του έργου EGG

Περίληψη

Στην Ευρώπη είναι κατεγραμμένες πάνω από 1.900 μάρκες εμφιαλωμένων «μεταλλικών νερών», η προέλευση των οποίων είναι από υπόγειους υδροφορείς. Η αγορά των εμφιαλωμένων νερών αναπτύσσεται με γοργούς ρυθμούς ως η κύρια παροχή πόσιμου νερού για το γενικό πληθυσμό σε μεγάλα τμήματα της Ευρωπαϊκής ηπείρου. Συνεπώς, θεωρήθηκε ότι η ανάλυσή τους μπορεί να αποτελέσει μιά φθηνή δυνατότητα, πρώτης προσέγγισης, της χημικής σύστασης των υπόγειων υδάτων των Ευρωπαϊκών χωρών. Αναγκαία πληροφόρηση που συμπληρώνει τα αποτελέσματα του Γεωχημικού Άτλαντα της Ευρώπης, ο οποίος περιλαμβάνει ίζημα ρέματος, πλημμυρικό ίζημα, έδαφος (επιφανείας & βάθους) και ποτάμιο νερό [http://www.gtk.fi/publ/foregsatlas/]. Για τη μελέτη αυτή αγοράσθηκαν 1.785 εμφιαλωμένα νερά από όλες τις Ευρωπαϊκές χώρες, τα οποία αντιπροσωπεύουν 1.247 πηγάδια / πηγές / γεωτρήσεις από 884 θέσεις.

Τα δείγματα των εμφιαλωμένων νερών αναλύθηκαν στο εργαστήριο του Ομοσπονδιακού Ινστιτούτου Γεωεπιστημών και Φυσικών Πόρων της Γερμανίας για 72 χημικά στοιχεία και παραμέτρους, ήτοι (i) με ICP-MS για Ag, Al, As, B, Ba, Be, Bi, Cd, Ca, Ce, Co, Cr, Cs, Cu, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr, (ii) με ICP-AES για Ba, Ca, K, Mg, Mn, Na, Sr, P, Si, (iii) με IC για Br-, Cl-, F-, NO_2^-, NO_3^-, SO_4^{2-}, (iv) με AFS για Hg, (v) φωτομετρικά για NH_4^+, (v) ποτενσιομετρικά το pH, (vi) με αγωγιμόμετρο η ηλεκτρική αγωγιμότητα (EC), και (vii) με τιτλοδότηση η ολική αλκαλικότητα (HCO_3-). Ακολουθήθηκε ένα πολύ αυστηρό πρόγραμμα ποιοτικού ελέγχου για να διασφαλισθεί η υψηλών προδιαγραφών αξιοπιστία των αποτελεσμάτων.

Πολλές διεργασίες επηρεάζουν το υδρογεωχημικό αποτύπωμα του υπόγειου νερού. Σημαντικοί παράγοντες είναι η χημική σύσταση του βρόχινου νερού, το κλίμα, τα φυτά και οι διεργασίες που λαμβάνουν χώρα στους εδαφικούς ορίζοντες, οι αλληλεπιδράσεις ορυκτών-νερού, ο χρόνος παραμονής του νερού, η ορυκτολογία και η χημική σύσταση του υδροφορέα (και η ύπαρξη ρύπανσης). Με βάση τα αποτελέσματα που προέκυψαν φαίνεται, ότι η γεωλογία είναι ο βασικός παράγοντας που ελέγχει τη συγκέντρωση και τη γεωγραφική κατανομή των περισσότερων χημικών στοιχείων στα δείγματα του εμφιαλωμένου νερού, για παράδειγμα οι υψηλές τιμές (α) του Cr σχετίζονται σαφώς με οφιόλιθους, (β) του V υποδηλώνουν την παρουσία πρόσφατης ηφαιστειακής δραστηριότητας και βασαλτικά πετρώματα και (γ) του U σχετίζονται με γρανιτικές διεισδύσεις και ψαμμίτες στην κεντρική Αγγλία και την κεντρική Ευρώπη. Ωστόσο, η γνώση της γεωλογίας και μόνο είναι ανεπαρκής για την πρόβλεψη της υδρογεωχημείας του εμφιαλωμένου νερού.

Μια βασική παρατήρηση, είναι ότι η φυσική μεταβολή της χημικής σύσταση των εμφιαλωμένων νερών είναι τεράστια, συνήθως κατά τρεις έως τέσσερεις και για ορισμένα στοιχεία έως και επτά τάξεις μεγέθους. Αυτή η διακύμανση μπορεί να αντανακλά, μεταξύ άλλων παραγόντων, το χρόνο παραμονής του υπόγειου νερού στον υδροφορέα και την ανάμειξή του με βαθειά υφάλμυρα νερά. Οι συγκεντρώσεις ορισμένων στοιχείων στο εμφιαλωμένο νερό δεν είναι αντιπροσωπευτικές των τυπικών, γλυκών υπόγειων νερών μικρού βάθους, αλλά παρουσιάζουν ασυνήθιστα υψηλές τιμές, οι οποίες είναι χαρακτηριστικές των «μεταλλικών νερών» βαθέων υδροφορέων. Παράδειγμα αποτελούν τα στοιχεία B, Be, Br, Cs, F, Ge, Li, Rb, Te

και Zr. Ένα πολύ μικρό ποσοστό των αναλυμένων δειγμάτων των εμφιαλωμένων νερών (σε γενικές γραμμές <1%) παρουσιάζουν συγκεντρώσεις κάποιων χημικών στοιχείων που υπερβαίνουν τις μέγιστες επιτρεπόμενες τιμές για τα «μεταλλικά νερά», όπως καθορίζονται από τις Οδηγίες της Ευρωπαϊκής Επιτροπής. Έχει, επίσης, διαπιστωθεί ότι τα υλικά κατασκευής των φιαλών μπορεί να ασκούν κάποια επίδραση στη χημική σύσταση του εμφιαλωμένου νερού. Για παράδειγμα, η έκπλυση του Sb από το υλικό της πλαστικής φιάλης είναι τόσο μεγάλη, ώστε τα αποτελέσματα των εμφιαλωμένων νερών δεν μπορούν να χρησιμοποιηθούν ως ένδειξη της φυσικής συγκέντρωσής του στα υπόγεια ύδατα.

Τέλος, ένα συμπέρασμα που προκύπτει από την εν λόγω μελέτη είναι ότι τα εμφιαλωμένα νερά μπορεί να χρησιμοποιηθούν για την απόκτηση μιάς πρώτης εικόνας της γεωχημείας των υπόγειων υδάτων της Ευρώπης. *Ο Γεωχημικός Άτλαντας είναι διαθέσιμος από τον ιστότοπο*: http://www.schweizerbart.de/publications/detail/artno/001201002

Λέξεις κλειδιά: Γεωχημεία υπόγειων υδάτων, εμφιαλωμένα νερά, ιοντικοί λόγοι, υδροχημική ταξινόμηση, Ευρώπη, Ελλάδα.

1. Introduction

The EuroGeoSurveys Geochemistry Expert Group is dedicated to provide high quality databases on the geochemistry of earth materials with which humans are in direct contact with to decision makers, geoscientists, researchers and the public alike.

The Geochemical Atlas of Europe provided the first harmonised pan-European multi-determinand databases on residual soil (top- and sub-soil), humus, stream and floodplain sediments, and stream water (Salminen et al., 2005, De Vos et al., 2006). Ground water, although very important was, however, missing from this database. The main reason is that to collect systematically representative ground water samples at the European scale is not an easy task, and may be prohibitively expensive if performed at a high sample density.

It was against this background that the EuroGeoSurveys Geochemistry Expert Group put forward a novel idea that "ground water" samples can be readily bought from supermarkets throughout Europe as bottled mineral water, and used as a first proxy for ground water geochemistry and quality at the European scale. Though the idea was met with some scepticism to begin with, it was finally decided that it was worth testing, because it provided a cost-effective approach. The results of this project are presented in a geochemical atlas (Reimann and Birke, 2010), and in a special issue of the Journal of Geochemical Exploration (Birke et al., 2010a), as well as in other publications (Birke et al., 2010b, Reimann et al., 2010a, b; De Vivo et al., 2010; Lima et al., 2010 – see below).

Hellas is a country with a diverse geology and climate. There are areas blessed with water and others that are not (Kanellopoulou, 2002; Maheras, 2004; Mimikou, 2005; Hatzianastassiou, 2008; Livada, 2008). 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, especially in western part of Hellas, and western and central Crete (>1800 mm; Vassiliades, 2010). Hence, because of the increase 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 6,000 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 litres/person in 1998 and by 2009 it reached over 100 litres/person. The greatest consumption is, of course, during the summer period with the influx of 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 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 (Tab. 1). 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.

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 2003/40/EC (EU 2003) and EU Directive 1998/83/EC (EU 1998), 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. Geotronic 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 Tab. 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 Tab. 1. Tertiary and Recent sediments are not presented on Fig. 1.

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 Pref.
4	Ioli*	Ioli	Moschochori, Fthiotida Prefecture
5	Sariza	Sariza	Apikia, Andros Island, Cycladhes Prefecture
6	Avra*	Avra, Aegion	Dimos Aegiou, 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	Psiloritis, Crete I., Heraklion Prefecture
13	Rouva's	Gergeri, foot of Mt. Psiloritis	Gergeri, Heraklion, Crete I., Heraklion Prefecture
14	Samaria	Stylos	Stylos, Foot of White Mountains, Crete I., Chania Prefecture
15	Lyttos	Chomoprina, Malia Municipality	Cocal 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	Heraklion, Crete I., Heraklion Prefecture
19	Krini	Dikti Mountains, Crete	Kasteli, Pediados, Heraklion Prefecture
20	Dikti	Baboulani, Diktl (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, Korinthias Prefecture
27	Loutraki Hydria	Loutraki	Loutraki (Hydria), Korinthias Prefecture
28	Loutraki Karadanis Provis	Loutraki	Loutraki, Korinthias Prefecture
29	Loutraki ivi	Gerania Mountains	Loutraki, Korinthias Prefecture
30	Iris Loutraki	Loutraki	Loutraki, Korinthias Prefecture
31	Ydor Sourotis*	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 Ypati, Fthiodidhas Prefecture
35	Tzoumerka	Agathi Melissourgon	Melissourgoi, Arta Prefecture
36	Velouhi	Kefalovrisso Aghia Triada	Velouhi, Evritania Prefecture
37	Seli*	Assos, Vermion	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	Kinotita Klinou, Pindos Mountains, Trikalla Prefecture
48	Vitsi	Florina springs	Florina, Florina Prefecture
49	Drossia	Drossia	Mt. Kaimaksalan, Imathia Prefecture

Tab. 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)*

Πίν. 1. *Ελληνικά εμφιαλωμένα νερά που αναλύθηκαν σε αυτή τη μελέτη. Ο αστερίσκος (*) υποδηλώνει φυσικό εμφιαλωμένο μεταλλικό νερό σύμφωνα με την Οδηγία 2009/54/ΕΚ (ΕΕ, 2009).Τα υπόλοιπα αναφέρονται ως Επιτραπέζια νερά. Σε παρένθεση δίνονται τα εμφιαλωμένα νερά από την ίδια θέση τα οποία διατίθενται στο εμπόριο με διαφορετική εμπορική ονομασία (βλ. Εικ. 1 για τη θέση τους)*
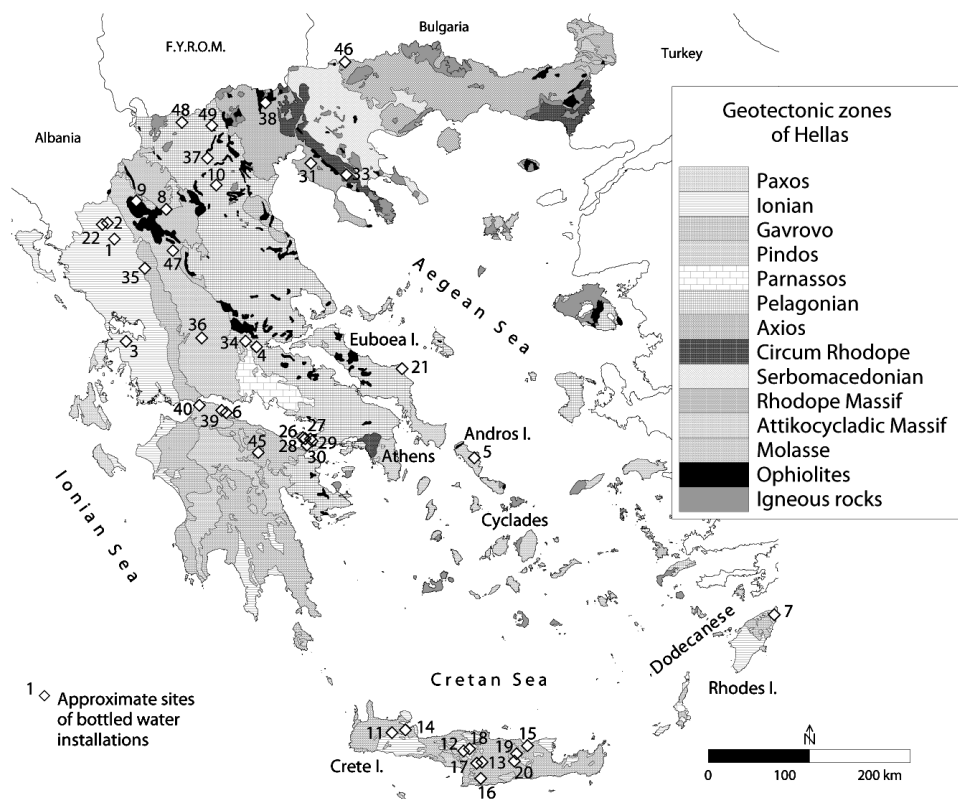
Fig. 1. *Geotectonic zones of Hellas and the approximate sites of bottled water installations (geotectonic zones modified from Bornovas and Rondogianni-Tsiambaou, 1983. Layers digitised by E. Vassiliades, Institute of Geology and Mineral Exploration, Division of Geochemistry and Environment).*

Εικ. 1. *Γεωτεκτονικές ζώνες της Ελλάδας και οι θέσεις, κατά προσέγγιση, των εγκαταστάσεων του εμφιαλωμένου νερού (οι γεωτεκτονικές ζώνες όπως τροποποιήθηκαν από τους Bornovas and Rondogianni-Tsiambaou, 1983. Η ψηφιοποίηση των στρωμάτων έγινε από τον Vassiliades E., 2010, Ινστιτούτο Γεωλογικών και Μεταλλευτικών Ερευνών, Διεύθυνση Γεωχημείας και Περιβάλλοντος).*

3. Materials and Methods
3.1. Sampling

Instructions were sent to all members of the EuroGeoSurveys Geochemistry Expert Group, as well as to friends and colleagues travelling to European countries, to purchase from supermarkets as many different bottled mineral water brands as possible. In case the same bottled water was available with and without gas, both varieties were purchased. If bottled water was marketed in different bottle types (e.g., glass and PET), or in bottles of different colour all varieties were bought whenever possi-

ble. The sampling period started in November 2007 and ended in April 2008.

The total number of bottles purchased in Europe, and subsequently analysed, was 1785 from 884 locations. Whereas, in Hellas a total of 61 still bottled waters were purchased from supermarkets, representing 41 different locations (Tabs 1 and 2, Fig. 1); 57 bottled waters were in soft polyethylene terephthalate (PET) and four in clear glass bottles; eight PET bottles were duplicates, purchased from different Hellenic 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 purchased, and used as blanks.

All bottled water samples were sent to the Federal Institute for Geosciences and Natural Resources (BGR) in Germany, where they were kept refrigerated until their analysis. Before shipping, the analytical results recorded on bottle labels were transferred to an Excel worksheet together with other pertinent information.

3.2. Analysis

The bottled water samples were analysed at the chemical laboratory of the Federal Institute for Geosciences and Natural Resources (BGR) in Berlin. Details of sample preparation and the extensive analytical programme are reported by Reimann and Birke (2010) and Birke et al. (2010b). Thus, only an outline of the analytical methods employed is provided below:

- Inductively coupled plasma atomic quadrupole mass spectrometry (ICP-QMS): Ag, Al, As, B, Ba, Be, Bi, Cd, Ca, Ce, Co, Cr, Cs, Cu, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr;

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); (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 volcanosedimentary massive sulphide deposits; (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; (b) chromite

Bottled water samples	Lithology	Mineralisation
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; (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; (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; (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), (n) magnesite.
Rhodope Massif		
Beles (46)	Marble, gneiss, crystalline schist, amphibolite with marble intercalations, and granite of Palaeozoic to Jurassic age; Lower Tertiary volcanosedimentary 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, Lesvos)
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), (d) Epirus (Upper Miocene) and in the Attico-Cycladic Complex (Upper Miocene)	
Ophiolites		
Samarina (9)	Basalt, diabase, gabbro, pyroxenite,	(a) chromite deposits (e.g., Vourinos,

Bottled water samples	Lithology	Mineralisation
	peridotite, dunite, serpentinite (ophiolite sequence) of Palaeozoic (?), Triassic to Jurassic age	Domokos, Chalkidhiki), (b) Fe-Ni laterites with peridotites (e.g., Larimna, Messapia), (c) magnesite (e.g., Mantoudi, 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)		

Tab. 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)*
Πίν. 2. *Γεωτεκτονικές ζώνες της Ελλάδας με βάση τη λιθολογία και την ορυκτολογική τους σύσταση. Τα δείγματα εμφιαλωμένου νερού τοποθετούνται στις σχετικές γεωτεκτονικές ζώνες. Οι σχηματισμοί ξεκινούν από κάτω προς τα πάνω, και οι γεωτεκτονικές ζώνες περιγράφονται από τα δυτικά προς τα ανατολικά (βλ. Εικ. 1).*

- Inductively coupled plasma atomic emission spectrometry (ICP-AES): Ba, Ca, K, Mg, Mn, Na, Sr, P, Si;
- Ion Chromatography (IC): Br^-, Cl^-, F^-, NO_2^-, NO_3^-, SO_4^{2-};
- Atomic fluorescence spectroscopy (AFS): Hg;
- Titration: total alkalinity - HCO_3^-;
- Photometric: NH_4^+;
- Potentiometric: pH, and
- Conductometric: Electrical Conductivity (EC).

3.2.1. Detection limit
The instrument detection limit (IDL) was estimated at 3 times the standard devi-

ation of sample blank determinations. The reported detection limit (RDL) was calculated at 10 times the standard deviation of sample blanks. The conservative RDL was used as the cut-off value for all statistical graphics and tables, as well as for producing the distribution maps (Tab. 3). The duplicate analyses were also used to estimate the practical detection limit and precision (see Reimann and Birke, 2010; Birke et al., 2010b).

3.2.2. Quality control
A very strict quality control programme was installed and reported by Reimann and Birke (2010) and Birke et al. (2010b).

Parameter	Unit	RDL	Precision %	European results (n=884)			Hellenic results (n=41)		
				Min.	Median	Max.	Min.	Median	Max.
Ag	µg/L	0.002	13	<0.002	<0.002	112	majority of values b.d.l.		
Al	µg/L	0.5	5	<0.5	1.2	966	<0.2	0.77	5.48
As	µg/L	0.03	10	<0.03	0.24	90	0.0194	0.198	2.52
B	µg/L	2	4	<2	39	120000	2.81	14.6	143
Ba	µg/L	0.1	5	0.05	29	26800	<0.005	0.019	7.38
Be	µg/L	0.01	5	<0.01	<0.01	64	majority of values b.d.l.		
Bi	µg/L	0.005	-[b]	<0.005	<0.005	0.69	<0.0005	0.0005	0.0041
Br⁻	µg/L	3	-	<3	35	21700	<0.003	0.032	0.174
Ca	mg/L	0.01	-	0.43	66	611	2.87	55.4	101
Cd	µg/L	0.003	29	<0.003	0.0032	1.1	<0.001	0.00259	0.0231
Ce	µg/L	0.001	13	<0.001	<0.001	6.2	majority of values b.d.l.		

Parameter	Unit	RDL	Precision %	European results (n=884)			Hellenic results (n=41)		
				Min.	Median	Max.	Min.	Median	Max.
Cl⁻	mg/L	0.01	-	0.18	13	3627	1.03	12.8	81.4
Co	µg/L	0.01	5	<0.01	0.023	16	0.004	0.0126	0.0792
Cr	µg/L	0.2	7	<0.2	<0.2	27	0.042	0.627	32.9
Cs	µg/L	0.002	3	<0.002	0.039	415	0.0005	0.0045	4.52
Cu	µg/L	0.1	2	<0.1	0.27	100	0.017	0.398	3.99
Dy	µg/L	0.001	16	<0.001	0.0012	0.39	<0.0002	0.0006	0.0107
EC	µS/cm	-	-	18	588	26500	177	434	891
Er	µg/L	0.001	13	<0.001	<0.001	0.77	<0.0002	0.0005	0.0141
Eu	µg/L	0.001	18	<0.001	<0.001	0.45	<0.0002	0.0006	0.0050
F⁻	mg/L	0.003	-	<0.003	0.19	11	<0.003	0.05475	0.337
Fe	µg/L	0.5	4	<0.5	0.69	13500	<0.01	0.238	0.711
Ga	µg/L	0.005	4	<0.005	<0.005	3.9	<0.0005	0.0036	0.0339
Gd	µg/L	0.002	22	<0.002	<0.002	0.66	<0.0002	0.0008	0.0102
Ge	µg/L	0.03	6	<0.03	<0.03	110	<0.005	0.0107	0.0465
Hf	µg/L	0.002	28	<0.002	<0.002	1.6	majority of values b.d.l.		
Hg	ng/L	-		majority of values b.d.l.					
Ho	µg/L	0.001	19	<0.001	<0.001	0.12	<0.0001	0.0002	0.0046
I	µg/L	0.2	15	<0.2	4.8	4030	0.555	3.28	12.2
K	mg/L	0.1	-	<0.1	2.1	558	<0.05	0.6	7.3
La	µg/L	0.001	9	<0.001	0.0023	10	<0.0001	0.0008	0.0267
Li	µg/L	0.2	5	<0.2	10	9860	<0.01	1.15	14.3
Lu	µg/L	0.001	16	<0.001	<0.001	0.41	<0.00005	0.00009	0.00266
Mg	mg/L	0.01	-	<0.01	16	4010	0.764	11.6	91.2
Mn	µg/L	0.1	2	<0.1	0.54	1870	majority of values b.d.l.		
Mo	µg/L	0.02	4	<0.02	0.28	74	0.0133	0.225	2.55
Na	mg/L	0.1	-	0.4	16	8160	0.7	7.1	77.2
Nb	µg/L	0.01	15	<0.01	<0.01	0.54	majority of values b.d.l.		
Nd	µg/L	0.001	18	<0.001	0.0021	5.1	0.0003	0.0012	0.0152
NH₄⁺	mg/L	0.005	-	0.0025	0.0025	60	majority of values b.d.l.		
Ni	µg/L	0.02	4	<0.02	0.18	95	0.011	0.136	2.4
NO₂⁻		0.01		majority of values b.d.l.					
NO₃⁻	mg/L	0.01 – 1.0[a]	-	<1	1.3	995	0.02	3.76	18.8
P	µg/L	0.01	-	<6.5	33	2863	<0.01	0.0098	0.0489
Pb	µg/L	0.01	6	<0.01	0.016	2.3	0.001	0.0206	0.393
Pr	µg/L	0.001	15	<0.001	<0.001	1.5	<0.00005	0.00017	0.00363
Rb	µg/L	0.01	6	0.015	2.1	631	0.084	0.34	5.82
Sb	µg/L	0.01	6	<0.01	0.27	4.4	0.094	0.201	0.76
Sc	µg/L	0.02	-	majority of values b.d.l.			0.005	0.0483	0.192
Se	µg/L	0.02	19	<0.02	0.054	371	0.038	0.18	0.743
Si	mg/L	0.03	-	0.42	6.5	59	1.36	4.11	20.8
Sm	µg/L	0.001	23	<0.001	0.0013	0.67	0.0001	0.00073	0.00490
Sn	µg/L	0.02	12	<0.02	<0.02	1.8	0.0005	0.00521	0.041
SO₄²⁻	mg/L	0.01	-	0.01	20	20342	1.65	8.38	89.7
Sr	µg/L	0.001	-	2	326	25500	0.006	0.118	0.559
Ta	µg/L	0.005	-[b]	<0.005	<0.005	0.037	majority of values b.d.l.		
Tb	µg/L	0.001	23	<0.001	<0.001	0.077	<0.00005	0.00009	0.00167
Te	µg/L	0.03	-[b]	<0.03	<0.03	0.32	majority of values b.d.l.		
Th	µg/L	0.001	33	0.0005	0.0005	0.15	<0.0001	0.00023	0.00265
Ti	µg/L	0.08	52	0.04	0.04	6.3	0.005	0.0211	0.0899

Parameter	Unit	RDL	Precision %	European results (n=884)			Hellenic results (n=41)		
				Min.	Median	Max.	Min.	Median	Max.
Tl	µg/L	0.002	6	<0.002	0.0041	2.2	0.0015	0.00675	0.02480
Tm	µg/L	0.001	22	<0.001	<0.001	0.19	<0.00005	0.00008	0.00215
U	µg/L	0.001	2	0.0005	0.23	229	<0.00005	0.307	10
V	µg/L	0.1	6	<0.1	0.17	49	0.147	0.676	7.45
W	µg/L	0.05	1	<0.05	<0.05	28	<0.002	0.0204	0.106
Y	µg/L	0.001	7	<0.001	0.012	3.5	0.0006	0.0043	0.267
Yb	µg/L	0.001	17	<0.001	<0.001	1.8	0.0001	0.00050	0.01650
Zn	µg/L	0.2	3	<0.2	0.89	651	0.12	1.11	651
Zr	µg/L	0.001	7	<0.001	0.0075	165	0.001	0.0016	0.2970
pH	-	-	-	4	6.8	9.9	7.08	7.9	9.2
tAlk	mg/L	0.1	-	2	286	16110	112	235.46	472
Total hardness							95.3	234	411
TDS							113	285	570

Tab. 3. *General statistics of European and Hellenic bottled water results, reported detection limit (RDL) and precision at the 95% confidence level (P95%). Superscript notation: (a) depends on total dissolved solids; (b) insufficient values above detection limit to estimate reliably the precision; other notation: EC – electrical conductivity, tAlk – total alkalinity, TDS – total dissolved solids.*

Πίν. 3. Γενικά στατιστικά στοιχεία της των Ευρωπαϊκών και Ελληνικών αποτελεασμάτων εμφιαλωμένου νερού τα οποία ανέφεραν όριο ανίχνευσης (RDL) και ακρίβεια 95% του δείκτη αξιοπιστίας (P95%). Εκθετική σημείωση: (α) εξάρτηση από τα συνολικά διαλυμένα στερεά (β) ανεπαρκή τιμές πάνω από το όριο ανίχνευσης για να εκτιμηθεί αξιόπιστα η ακρίβεια. Άλλη σημείωση: EC – ηλεκτρική αγωγιμότητα, tALK – ολική αλκαλικότητα, TDS – συνολικά διαλυμένα στερεά.

Below a concise outline is given:

(1) Analysis of international reference samples to document the true-ness of analytical results, i.e., the river water reference material SLRS-4 from the National Research Council Canada, and the low level fortified standards for trace elements TM-26.3, TM-27.2, TM-28.2 and TM-28.3 from the National Water Research Institu-te of Canada;

(2) Frequent analysis of an in-house pro-ject standard (MinWas) to check the accuracy of determined parameters;

(3) Frequent analysis of blank samples to detect any contamination issues, and to derive reliable detection limits;

(4) Frequent analysis of sample dupli-cates to determine precision of meas-urements;

(5) Comparison of analytical results of this study with those recorded on bottle la-bels;

(6) Determination of a few parameters by two methods (Ba, Ca, K, Mg, Mn, Na, Sr) by ICP-QMS and ICP-AES, and Hg by ICP-QMS and AFS, and

(7) Buying a new bottle and re-analys-ing the bottled water with unusually high results for important parameters whenever possible.

A general problem of analysing so many elements, as in this study, is that there are no suitable reference materials to cover all elements, e.g., Hg, Ho, I, Lu, Nb, Nd, Pr, Sc, Sm, Ta, Tb, Te, Th, Tm, W, Y, Yb and Zr.

The Canadian standards (SLRS-4, TM-26.3, TM-27.2, TM-28.2 and TM-28.3) have the advantage of covering different concentration ranges for a number of el-ements, and were used to identify ele-ments that presented problems at low concentrations (e.g., Hf, Nb, Sn, Ta and W), but delivered reliable results at high-er values (i.e., over ten times the detec-tion limit).

Overall, certified values, and the gener-

ated project results, are well in agreement for most elements. Since, there exist a number of elements that are not covered by any standards, this drawback was covered by evaluating reliability of results with respect to blank values and coefficient of variation.

3.3. Influence of bottle materials and carbonatisation
3.3.1. Bottle material leaching

Many studies have demonstrated that water samples can be severely contaminated by the material of storage bottles (Lloyd and Heathcote, 1985; Hall, 1998; Reimann et al., 2007), and often extreme cleansing procedures are suggested for sample bottles (Ross, 1984), and/or the use of very expensive special plastic bottles is strongly recommended for water sampling for ultra-trace element analysis. For bottled water, a large variety of different containers are on the market (e.g., glass, hard PET, soft PET, aluminium cans, tetrapacs). Bottle materials have in addition different colours (clear, light and dark green, blue and brown are the most common colours). It must,

thus, be expected that each bottle type will have different properties and leaching characteristics, and will influence the stored water quality in some way. There is considerable documentation that due to the low concentrations of most elements in natural water, water sampling and analysis are required to be performed with great care in order to avoid contamination of water samples during sampling, storage, or analysis (Nriagu et al., 1993).

Glass bottles are known to leach Pb and Zr to the stored water (Misund et al., 1999). More recently, Shotyk et al. (2006), Shotyk and Krachler (2007a, b), Westerhoff et al. (2008), Keresztes et al. (2009) and Krachler and Shotyk (2009) have demonstrated that leaching of elements from bottle materials to stored water does clearly occur. For example, with respect to PET bottles Sb was identified as the main problematic element, whereas for glass leaching Pb (and some additional elements, see below) has been shown to be considerable in relation to natural concentrations of these elements in bottled water (Fig. 2).
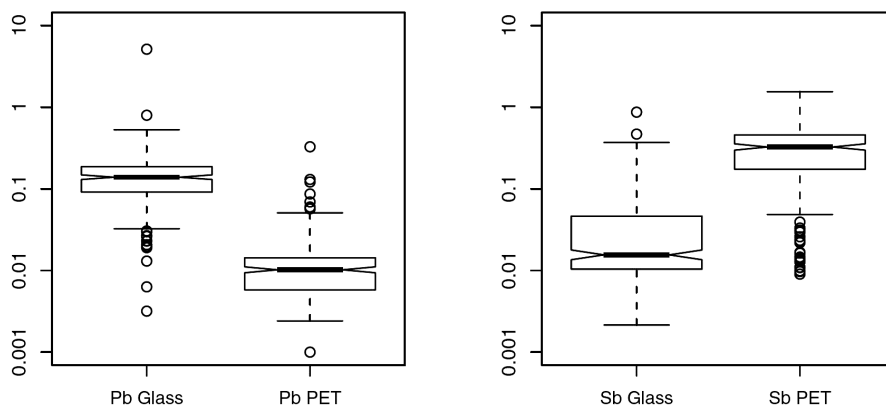
Fig. 2. *Boxplot comparison of the same 131 mineral water brands sold in both glass and PET bottles. Leaching of Pb from glass and of Sb from PET is clearly indicated. Analytical results in μg/L (from Reimann and Birke, 2010, Fig. 22, p.48).*
Εικ. 2. *Διαγράμματα σύγκρισης των ίδιων 131 αντιπροσωπειών μεταλλικών νερών που πωλούνται σε γυάλινα και πλαστικά. Εμφανώς αναφέρεται η έκπλυση του Pb από το γυαλί και του Sb από το πλαστικό. Αναλυτικά αποτελέσματα σε μg/L (Reimann και Birke, 2010, εικ. 22., σ.48).*

Because it was practically impossible to buy only water in a certain bottle material and colour, it was necessary to test the influence of different bottle materials and colours on element concentrations observed in stored water (Reimann and Birke, 2010; Reimann et al., 2010a;2010b). The leaching test was carried out on 126 bottles filled with high purity water (18.2 MegaΩ/cm), and element concentrations were measured after 1, 2, 3, 4, 5, 15, 30, 56, 80 and 150 days. The leaching tests were performed at two different pH values (3.5 and 6.5), and results were directly compared to actual element concentrations in bottled water. The bottle leaching results are summarised below:

- In relation to natural variation observed for the various elements in bottled water, leaching from bottle materials to stored water is a minor problem at a pH of 6.5. At a pH of 3.5 it becomes, however, a serious problem for quite a number of elements (e.g., glass bottles: Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Ga, Hf, I, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, Pb, Rb, Sb, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Zn; soft PET: Ag, Dy, Er, Fe, Gd, Ge, Ho, Lu, Nd, Pr, Sm, Tb, Tm, V, Y, Yb, Zr) (Reimann et al., 2010a)
- PET bottles contaminate the water with Sb to an extent where all measured values cannot any longer be used to investigate natural Sb concentration in the water.
- Glass bottles contaminate stored water with a considerably longer list of elements: Ce, Pb, Al, Zr, Ti, Hf, Th, La, Pr, Fe, Zn, Nd, Sn, Cr, Tb, Ag, Er, Gd, Bi, Sm, Y, Lu, Yb, Tm, Nb and Cu; some glass bottles also leach Sb.
- Green glass bottles leach more Cr (Fe, Zr) to stored water than clear glass bottles and, in general, dark coloured bottles (brown, green, blue, independent of material) leach more than clear bottles.

For the purposes of the published geochemical atlas (Reimann and Birke, 2010), the following conclusions were reached:

(1) Bottled water cannot be used to establish the natural concentration range and variation of Sb, since results from PET bottles were preferentially used for mapping.

(2) Ce, Cr, Pb and Al concentrations observed in bottled water can be seriously influenced by glass bottles.

(3) The majority of elements can be used to produce geochemical maps that are not seriously influenced by contamination from bottle materials.

3.3.2. Carbonatisation effects
Naturally carbonated waters do occur, but carbon dioxide is also added artificially to many still waters to obtain a sparkling "mineral water" variety. The content of most solutes in water should not be affected. However, for geochemical mapping, it was important to check the magnitude of any effects on the observed water chemistry for all parameters determined, because for completeness of coverage results of still and carbonated water were combined at sites where still water samples were not available.

The major effects of adding CO_2 to bottled water is on pH and alkalinity. In total, 131 samples were obtained, where the same water was sold in a still and in a sparkling variant (Reimann and Birke, 2010). This subset of samples allowed the direct comparison of analytical results. The pH of carbonated bottled water is considerably lower than its corresponding still water (Fig. 3). The leaching tests have shown that a lower
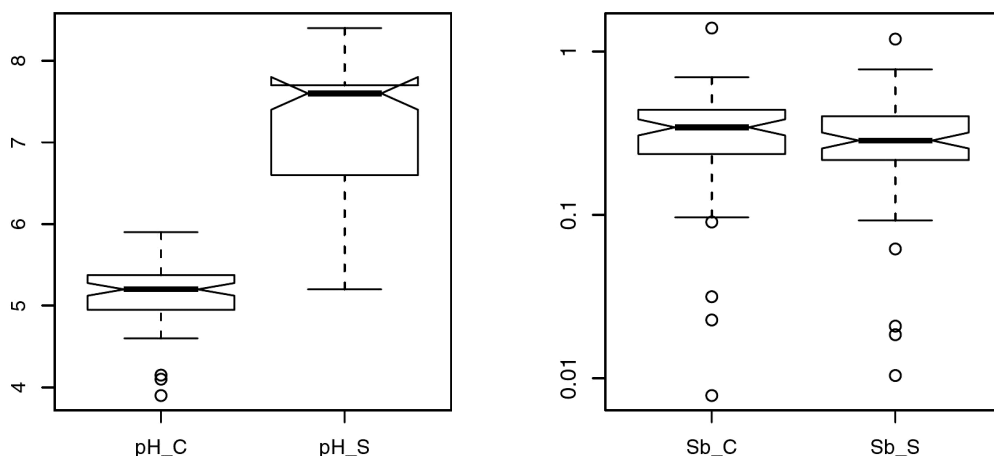
Fig. 3. *Boxplot comparison of pH and Sb concentration in carbonated (C) and still (S) waters, for the same 131 pairs of bottled mineral water that are marketed both in still and carbonated variants. While pH is strongly affected, an effect on the Sb concentration is hardly discernible and statistically insignificant. Analytical results of Sb in μg/L, and pH in units (from Reimann and Birke, 2010, Fig. 24, p.50).*
Εικ. 3. *Διαγράμματα σύγκρισης του pH και της συγκέντρωσης Sb σε ανθρακούχα (C) και φυσικά (S) νερά, για τα ίδια 131 ζεύγη εμφιαλωμένων μεταλλικών νερών που διατίθενται στο εμπόριο σε φυσικές να ανθρακούχες ποικιλίες. Ενώ το pH επηρεάζεται σε μεγάλο βαθμό, μια επίδραση στη συγκέντρωση Sb είναι δυσδιάκριτη και στατιστικά ασήμαντη. Αναλυτικά αποτελέσματα του Sb σε μg/L, και του pH σε μονάδες (Reimann και Birke, 2010, Εικ. 24., σελ.50).*

pH will increase leaching of elements from the bottle material to the stored water (Reimann et al., 2010a).

A difference of 2 pH units in the median of still and carbonated water is indeed substantial.

Phosphorus shows a much lower median in still than carbonated water, which is an unexpected result. The only two elements that otherwise indicate higher concentrations in carbonated water are Pb and Th (Reimann and Birke, 2010; Reimann et al., 2010a).

Both elements had been identified as problematic in relation to leaching from glass bottles, and most carbonated waters are sold in glass bottles. No other element is in fact affected. It was concluded that the pH of carbonated water may not be low enough to substantially increase leaching from the bottle material. However, whenever possible, still water was preferred over carbonated water for plotting geochemical maps.

3.4. Data preparation and treatment

Since, in many cases, several brands of bottled water come from the same locality, it was decided to reduce the data set to "one bottle per site" for presentation in the geochemical atlas (Reimann and Birke, 2010). European Union regulations require that a *bona fi de* mineral water must have a single well dedicated to a given brand. Thus, at many mineral water bottling plants, it is common practice to have several wells, each one dedicated to a specific "brand" name. There will often be some real and significant hydrochemical variation between these different "brand" wells, even at a single site. Hence, by reducing the data set from 1247 to 884 samples, i.e., "one bottle per site", some degree of actual within site hydrochemical variation is discarded.

Due to the results of the bottle leaching test (Reimann and Birke, 2010; Reimann et al., 2010a, b), and the comparison be-

tween carbonated and non-carbonated water, a list of priorities was established for which bottle to choose as being representative for a site:

(1) non-carbonated (still water) was preferred over carbonated water;

(2) clear PET-bottles were preferred against all other bottle materials and colours, and

(3) samples sold in glass bottles were only left in the data set when no other bottle type was available.

The above procedure resulted in a final data set containing 884 samples that was used for the extraction of statistical parameters, and construction of graphs, plots and distribution maps (Reimann and Birke, 2010). Values below detection limit were set to half the detection limit for all graphics, including distribution maps and statistical calculations.

Exploratory data analysis techniques were used for statistical analysis (Tukey, 1977). All graphics and statistical calculations were prepared in R (Reimann et al., 2008; CRAN, 2012). Analytical results expressed in mg/L (or μg/L) are compositional data (Aitchison, 1986; 2003), and the calculation of mean or standard deviation does not make sense for such data (Filzmoser et al., 2009).

Mapping ground water geochemical data is plagued by many problems. The distribution of sample locations is usually very uneven, with large gaps on the maps where no samples could be taken – this is an undesirable situation in terms of obtaining a good impression of the regional distribution of investigated parameters (Reimann, 2005). It is, for example, not possible to produce smoothed colour surface maps from such data sets; even to plot readable point source maps is a challenge. Because the distribution of anomalously "high" values in Europe is probably the most interesting aspect of the published geochemical atlas (Reimann and Birke, 2010), the 'variable-size dot' or 'growing dot' technique, as originally suggested by Bjørklund and Gustavsson (1987), was used for producing all distribution maps. The technique, together with its advantages and disadvantages, is discussed in detail by Reimann et al. (2008). The variable-size dots grow exponentially according to element concentration between the 15th and 99th percentile (Gustavsson et al., 1997; Reimann et al., 2008).

4. Results
4.2. European results

The results of European ground water geochemistry (Tab. 3), using bottled water as a sampling medium, are described in the published geochemical atlas (Reimann and Birke, 2010), in a special issue of the Journal of Exploration Geochemistry (Birke et al., 2010a), and other publications (Birke et al., 2010b, c, d; Bityukova and Petersell, 2010; Bodiš et al., 2010; Brenčič and Vreča, 2010; Brenčič et al., 2010; Cicchella et al., 2010; Demetriades, 2010a, b; 2012, De Vivo et al., 2010; Dinelli et al., 2010; Dotsika et al., 2010; Frengstad et al., 2010; Fugedi et al., 2010; Lourenço et al., 2010; Lima et al., 2010; Peh et al., 2010; Reimann et al., 2010a, b; Petrović et al., 2010, 2011, 2012). Here, only some key results are presented in relation to Hellenic ground water geochemistry (Demetriades, 2010a).

4.3. Hellenic results
4.3.1. General geochemistry of source aquifers of Hellenic bottled water

The general statistics of parameters determined on Hellenic bottled water samples (n=41) are tabulated in Tab. 3 together with the corresponding European

ones. Overall, most parameters vary by 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. 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, bottled water with TDS<570 mg/L 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.

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).

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 (Tab. 2).

Total 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 hydrochemiacally 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, Kallerghis 2000, Soulios 2006). Below are presented various ionic relationships (Notation: 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. 4).

(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
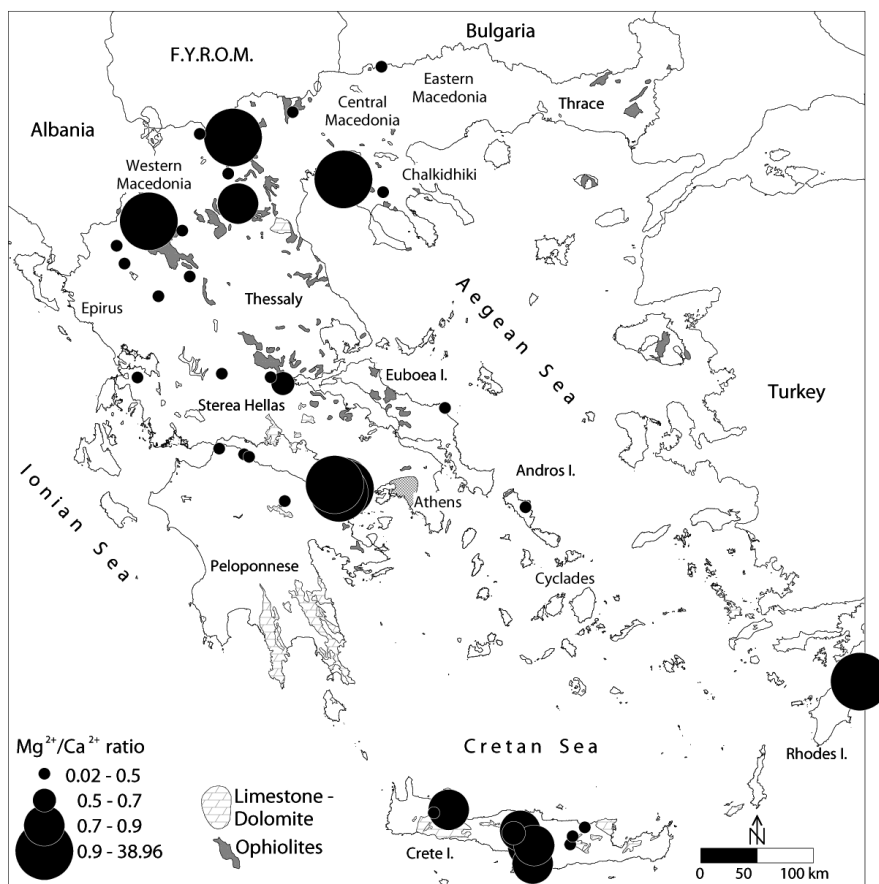
Fig. 4. *Distribution of Mg²⁺/Ca²⁺ ratios in Hellenic bottled water samples (see also Fig. 1 and Tab. 1 for sample location numbers and brand names, respectively).*

Εικ. 4. *Κατανομή των αναλογιών Mg2 +/Ca2 + αναλογίες σε Ελληνικά εμφιαλωμένα δείγματα νερού (βλ. επίσης Εικ. 1 και Πίν. 1 για τη θέση του δείγματος και την επωνυμία, αντίστοιχα).*

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±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 rem-

nant 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^+ ≈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.

(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 – aq-

uifer with a continuous recharge: all bottled waters are in this category with ratio 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 mixing of fresh water with sea water, or with water in evaporitic formations or percolating through sedimentary rocks containing evaporitic salts:-

➢ $Cl^-/Br^- \approx 500\text{-}4000$ – 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, total 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 $Cl^-/\sum$anion ratios varying from 0.01 to 0.43. Since, $Cl^-/\sum$anion ratios are <0.8, 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 Hounslow (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 as-

sumption 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. 5 (Jankowski et al., 1998; Kortasi, 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.
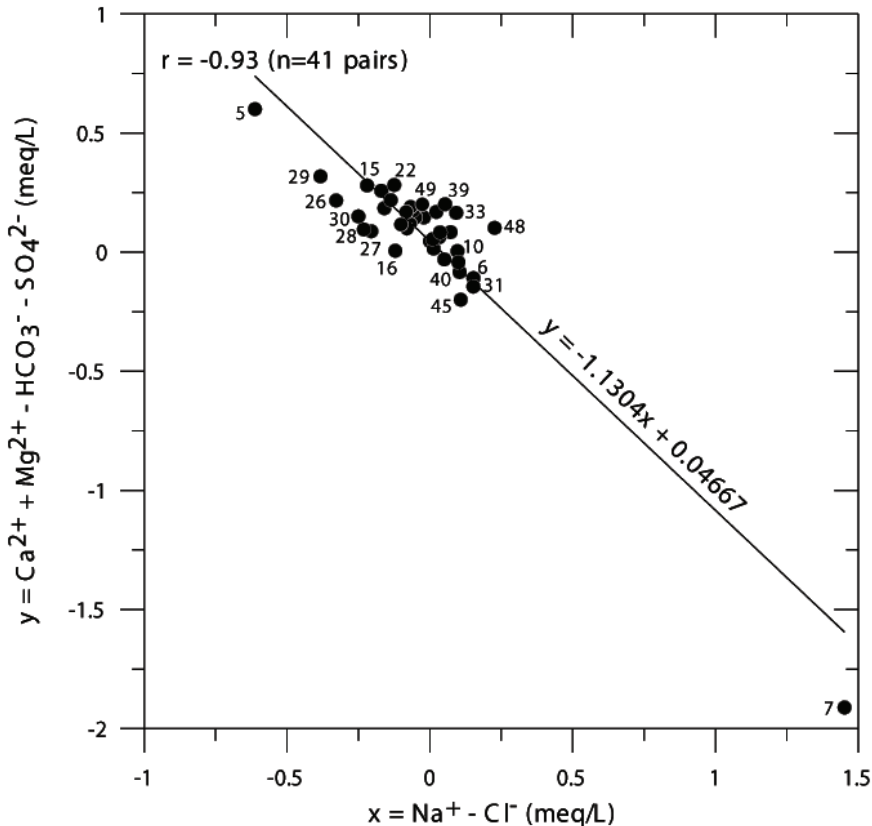
Fig. 5. Bivariate plot of (Na$^+$ - Cl$^-$) versus (Ca^{2+} + Mg^{2+} - HCO$_3$- - SO$_4^{2-}$), Hellenic bottled water samples (for displayed sample numbers refer to Fig. 1 and Tab. 1).
Εικ. 5. Διάγραμμα δύο μεταβλητών (Na$^+$ - Cl$^-$) ως προς (Ca^{2+} + Mg^{2+} - HCO$_3$- - SO$_4^{2-}$), Ελληνικά εμφιαλωμένα δείγματα νερού (οι αριθμοί των δειγμάτων αναφέρονται στην Εικ. 1 και Πίν. 1).

4.4. Major ion geochemistry: Europe

Each ground water has a somewhat unique hydrochemical fingerprint that reflects the balance of all the various processes during its evolution, its residence time in the aquifer, the mineralogy of rocks and sediments that it comes into contact with, and so on. It is possible to plot major cations and anions as milliequivalent proportions on a so-called Durov diagram (Fig. 6). The major cations [Na^+(+ K^+), Mg^{2+}, Ca^{2+}] are plotted on the top triangle, while the major anions (Cl^-, SO_4^{2-} and alkalinity or HCO_3^-) are plotted on the left triangle. The points are then projected onto a square central fiel d. On this diagram, dilute, newly recharged waters, which may still possess a weak signature of marine salts in coastal areas, would plot as small dots (i.e., low electrical conductivity) in the lower right field – they would be termed as a "low ionic strength Na–Cl" water type. More "normal" ground waters, albeit still of relatively low mineralisation, of Ca–HCO_3 type, derived from calcite hydrolysis (equation 1), plot in the top left.

$$CO_2 \qquad + H_2O \qquad + CaCO_3 \longrightarrow \quad Ca^{2+} \qquad + 2HCO_3^- \qquad (1)$$

carbon dioxide   + water   + calcite   calcium   +   bicarbonate   (dissolved)
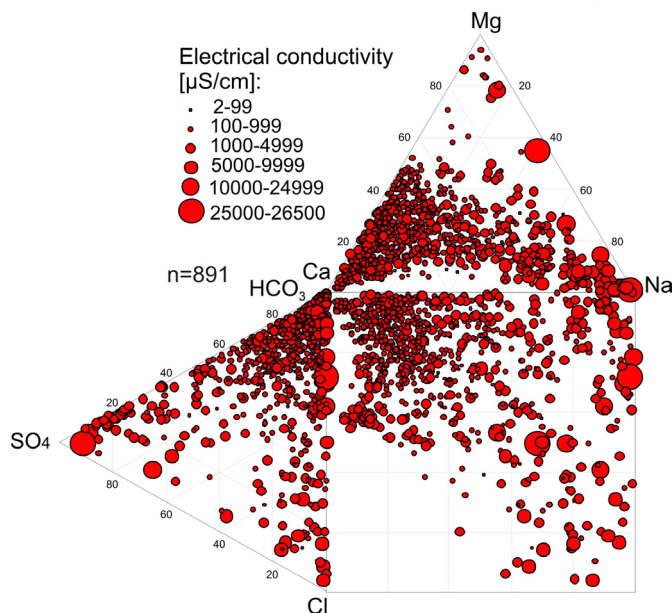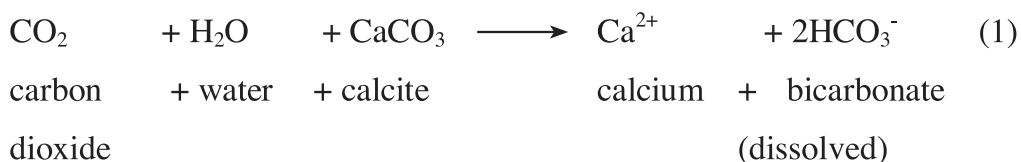
Fig. 6. *Durov diagram for the European bottled water data set (N = 884). The diagram is based on milliequivalent fractions of the major cations and anions. The dot size is related to total dissolved solutes (on the basis of electrical conductivity). Note that for plotting the Durov diagram only Na and not Na+K was used (from Reimann and Birke, 2010, Fig. 7, p.16).*
Εικ. 6. *Διάγραμμα Durov για τα Ευρωπαϊκά αρχεία δεδομένων εμφιαλωμένου νερού (N = 884). Το διάγραμμα βασίζεται στα χιλιοστοϊσοδύναμα κλάσματα των μεγάλων κατιόντων και ανιόντων. Το μέγεθος κουκίδας σχετίζεται με τις συνολικά διαλυμένες ουσίες (με βάση την ηλεκτρική αγωγιμότητα). Σημειώνεται ότι για τη δημιουργία του διαγράμματος Durov χρησιμοποιήθηκε μόνο Na και όχι Na+K (Reimann και Birke, 2010, Εικ. 7, σελ. 16).*

$$2NaCaAl_3Si_5O_{16} \quad +6CO_2 \quad +9H_2O \longrightarrow 2Ca^{2+} \qquad +2Na^+$$

$$+ 6HCO_3^- \qquad +3Al_2Si_2O_5(OH)_4$$

$$+ 4SiO_2 \qquad\qquad (2)$$

feldspar	carbon dioxide	water	+calcium +bicarbonate +silica	+ sodium +clay
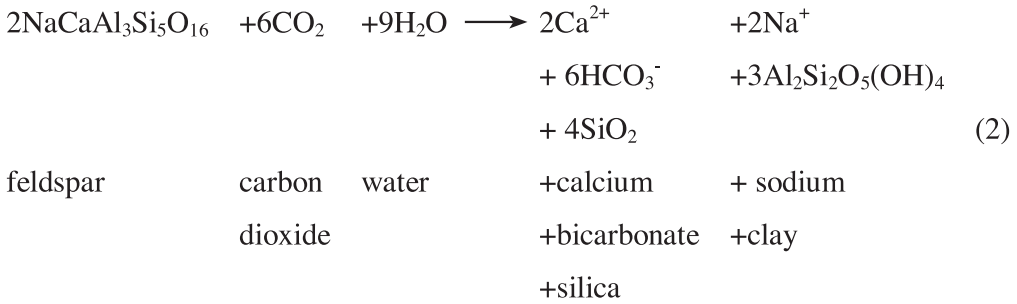
More evolved granitic ground waters, characterised by prolonged aluminosilicate weathering, may be of Na–HCO3 type (equation 2), and plot at the top right. Deep saline brines would most likely be of Na–Cl composition and plot as large-diameter dots (high electrical conductivity) near the bottom right of the diagram.

The Durov diagram shows the large variety of water types that are sold as bottled water in Europe, and describe the major ion geochemistry of ground water. The majority of samples fall, however, into the calcium bicarbonate corner of the diagram (Fig. 6).

4.5. Major ion geochemistry: Hellas

Instead of using the Piper and expanded Durov diagrams (Piper, 1944; Durov, 1948; Lloyd, 1965), the Chadha diagram was utilised (Fig. 7) for the Hellenic data, which is their modified version and it is much simpler to plot (Chadha, 1999; Belkiri et al., 2010). The difference is that the two equilateral triangles are omitted. However, for a more detailed study, one trilinear cations and two anions predominance diagrams, as well as a number of bi-plots have been plotted.

According to Chadha's diagram (Fig. 7), 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.
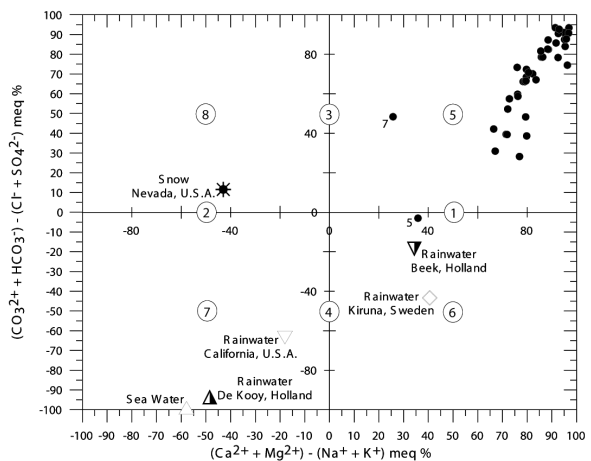
Fig. 7. *Geochemical classification and hydrochemical processes of ground water depicted by bottled water, Hellas (after Chadha, 1999, Fig. 3, p.434; for displayed sample numbers refer to Fig. 1 and Tab. 1).*

Εικ. 7. *Γεωχημική ταξινόμηση και υδροχημικές διαδικασίες των υπόγειων υδάτων όπως απεικονίζονται από εμφιαλωμένα νερά, Ελλάς (σύμφωνα με Chadha, 1999, Εικ. 3, p.434. Οι αριθμοί των δειγμάτων αναφέρονται στην Εικ. 1 και Πίν. 1).*

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. 8). 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; a plausible 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.
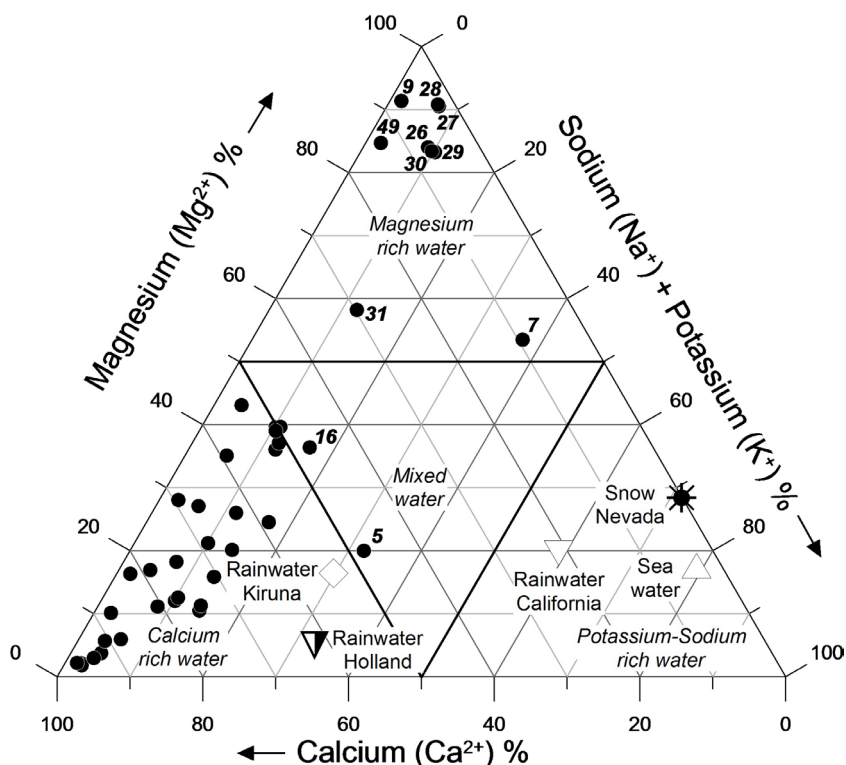
Fig. 8. Trilinear predominance diagram for the cations [Calcium-Magnesium-(Sodium+Potassium)] in Hellenic bottled water (for displayed sample numbers refer to Fig. 1 and Tab. 1).
Εικ. 8. Τρισδιάστατο διάγραμμα επικράτησης κατιόντων [ασβέστιο-Μαγνήσιο-(Νάτριο + Κάλιο)]σε Ελληνικά εμφιαλωμένα νερά (οι αριθμοί των δειγμάτων αναφέρονται στην Εικ. 1 και Πίν. 1).

The two anions predominance diagrams [HCO$_3$- - SO$_4{}^{2-}$ - (Cl$^-$ + NO$_3$-)] (Figure 9a) and [Cl$^-$ - SO$_4{}^{2-}$ - (CO$_3{}^{2-}$ + HCO$_3$-)] (Fig. 9b), 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 (Figs 9a and 9b), suggesting 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 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. 10a) and Na$^+$ versus Cl$^-$ (Fig. 10b).

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. 10b).

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 Kallerghis, 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 (Figs 10a and 10b). 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 mica-schist, which is known to have elevated concentrations of Cl, Na and K, whereas Aqua Vita-7 most likely picks up Na$^+$ and Cl$^-$ ions from remnant salts within the marine sediments.
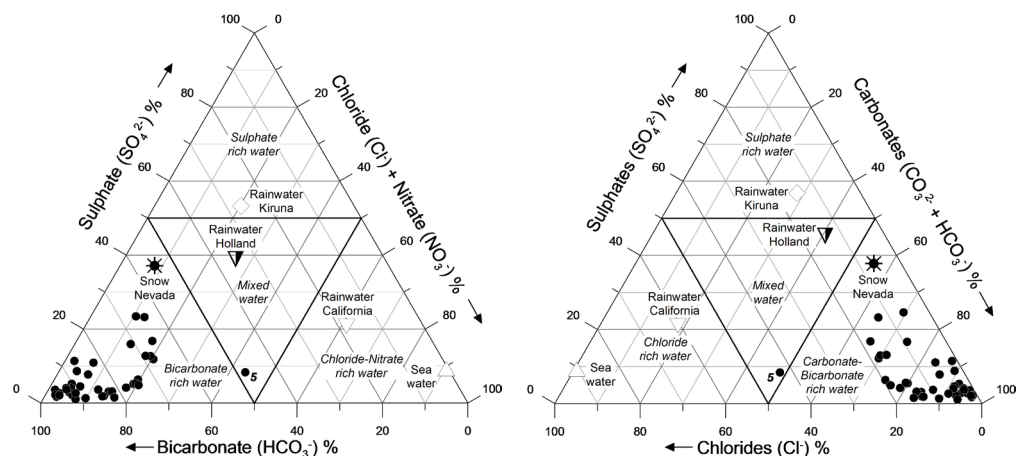
Fig. 9. Trilinear predominance diagram for the anions in Hellenic bottled water: (a) Bicarbonate-Sulphate-(Chloride+Nitrate) and (b) Chlorides-Sulphates-Carbonates (for displayed sample numbers refer to Fig. 1 and Tab. 1).

Εικ. 9. Τρισδιάστατο διάγραμμα επικράτησης ανιόντων σε Ελληνικά εμφιαλωμένα νερά: (α) Όξινα-Θεικά-(χλωριούχα + νιτρικά) και (β) Χλωριούχα-Θεικά-Ανθρακικά (οι αριθμοί των δειγμάτων αναφέρονται στην Εικ. 1 και Πίν. 1).
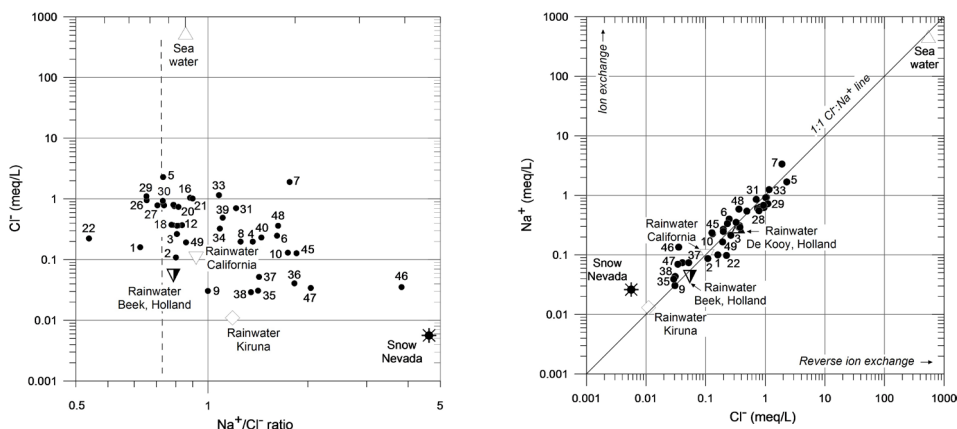
Fig. 10. *Logarithmic plots of relationships between concentration of chemical species: (a) Na$^+$/Cl$^-$ versus Cl$^-$; (b) Cl$^-$ vs. Na$^+$ (for displayed sample numbers refer to Fig. 1 and Tab. 1).*
Εικ. 10. *Λογαριθμικά διαγράμματα των σχέσεων μεταξύ της συγκέντρωσης των χημικών στοιχείων: (α) Na$^+$/Cl$^-$ προς Cl$^-$, (β) Cl$^-$ προς Na$^+$ (οι αριθμοί των δειγμάτων αναφέρονται στο Εικ. 1 και Πίν. 1).*

Other interesting ion biplots are:

(a) Ca^{2+} versus Cl$^-$ (Fig. 11a): 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. 11b): 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. 11c): 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. 11d): 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.

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

(i) Na$^+$ versus K$^+$ (Fig. 12a): 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+}) (Figure 12b): 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.
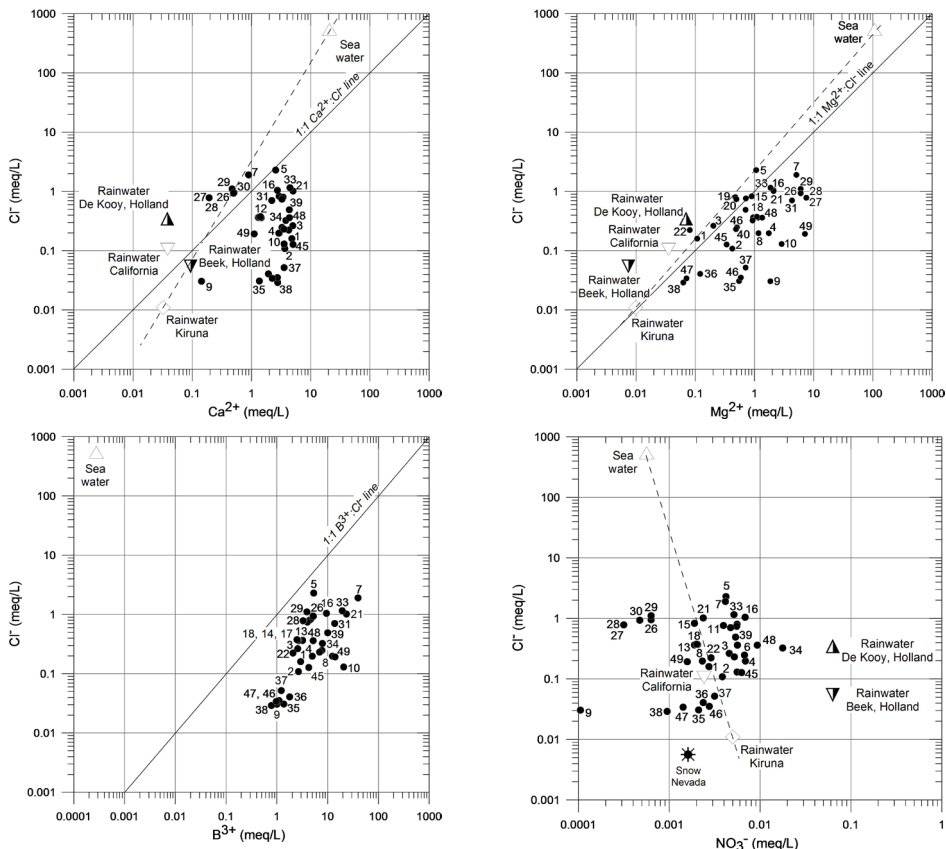
Fig. 11. *Logarithmic plots of relationships between concentration of chemical species: (a) Ca²⁺ vs. Cl⁻; (b) Mg²⁺ vs. Cl⁻; (c) B³⁺ vs. Cl⁻; (d) NO₃⁻ vs. Cl⁻ (for displayed sample numbers refer to Fig. 1 and Tab. 1).*
Εικ. 11. *Λογαριθμικά διαγράμματα των σχέσεων μεταξύ της συγκέντρωσης των χημικών στοιχείων: (α) Ca²⁺ προς Cl⁻ (β) Mg²⁺ προς Cl⁻ (γ) B³⁺ προς Cl⁻ (δ) NO₃⁻ προς Cl⁻ (οι αριθμοί των δειγμάτων αναφέρονται στο εικ. 1 και Πίν. 1).*
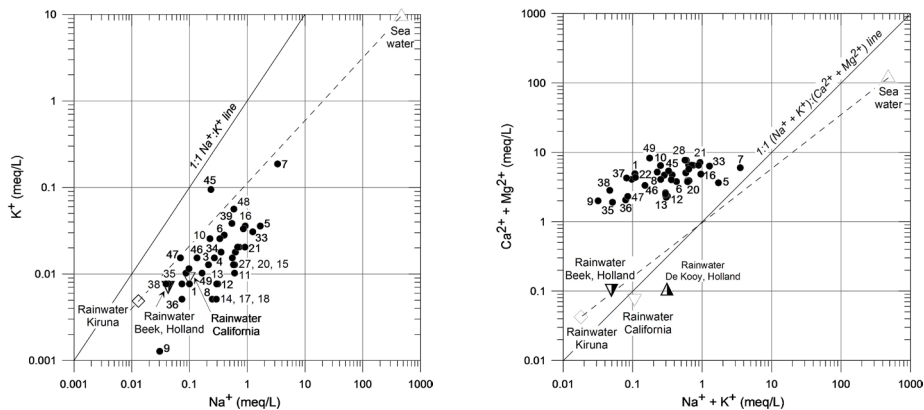
Fig. 12. *Logarithmic plots of relationships between concentration of chemical species: (a) Na⁺ vs. K⁺ and (b) (Na⁺ + K⁺) vs. (Ca²⁺ + Mg²⁺) (for displayed sample numbers refer to Fig. 1 and Tab. 1).*
Λογαριθμικά διαγράμματα των σχέσεων μεταξύ της συγκέντρωσης των χημικών στοιχείων: (α) Na⁺ προς K⁺ και (β) (Na⁺ + K⁺) προς (Ca²⁺ + Mg²⁺)(οι αριθμοί των δειγμάτων αναφέρονται στο εικ. 1 και Πίν. 1).

4.5.1. Gypsum solubility and related plots: Hellas

Gypsum ($CaSO_4.2H_2O$) 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. 13). 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.
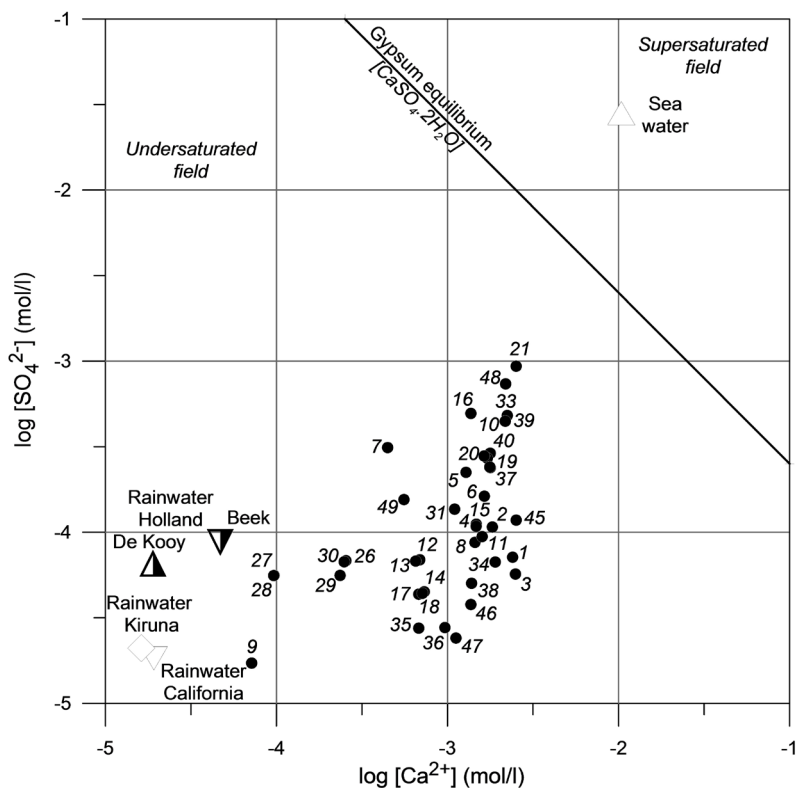
Fig. 13. *Comparison of the Hellenic bottled water data with the gypsum saturation index (for displayed sample numbers refer to Fig. 1 and Tab. 1).*
Εικ. 13. *Σύγκριση των δεδομένων για τα Ελληνικά εμφιαλωμένα νερά με το δείκτη κορεσμού του γύψου (οι αριθμοί των δειγμάτων αναφέρονται στο εικ. 1 και Πίν. 1).*
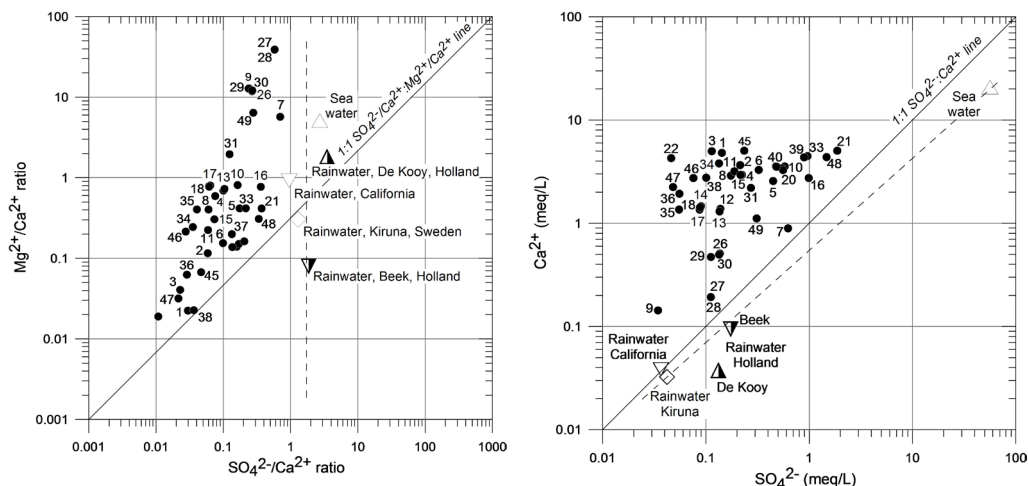
Fig. 14. *Logarithmic plots of relationships between concentration of chemical species: (a) SO$_4^{2-}$/Ca^{2+} vs. Mg^{2+}/Ca^{2+}) and (b) SO$_4^{2-}$ vs. Ca^{2+} (for displayed sample numbers refer to Fig. 1 and Tab. 1).*
Λογαριθμικά διαγράμματα των σχέσεων μεταξύ της συγκέντρωσης των χημικών στοιχείων: (α) SO$_4^{2-}$/Ca^{2+} προς Mg^{2+}/Ca^{2+}) και (β) SO$_4^{2-}$ vs. Ca^{2+} (οι αριθμοί των δειγμάτων αναφέρονται στο Εικ. 1 και Πίν. 1).

This observation is further supported by the ratio plots of SO$_4^{2-}$/Ca^{2+} versus Mg^{2+}/Ca^{2+} (Fig. 14a), and SO$_4^{2-}$ versus Ca^{2+} (Fig. 14b), which show that all Hellenic bottled water samples fall in the Ca^{2+} and Mg^{2+}/Ca^{2+} fields, respectively.

4.6. Trace element geochemistry: Europe and Hellas

Three trace elements were selected for discussion, chromium, vanadium and uranium, because they are significant to the geology of Hellas and are affecting the chemical composition of ground water.

4.6.1. Chromium distribution: Europe

Chromium in European bottled water varies from <0.2 to 27.2 µg/L (n=884), with a median of <0.2 µg/L (Table 3; Reimann and Birke 2010), and in European surface water, Cr has a wider range from <0.01 to 43 µg/L (n=806), and its median is slightly higher at 0.38 µg/L (Salminen et al., 2005). Whereas, Cr in Hellenic bottled water varies from <0.2 to 32.9 µg/L (n=41), with a median 0.627 µg/L, and the Hellenic surface

water has a narrower range from 0.24 to 6.37 µg/L (n=27), and a slightly lower median at 0.57 µg/L (Salminen et al., 2005); the reason for the difference between the maximum value of European and Hellenic bottled water suites is because of the inclusion of samples that were excluded from the European database.

The main pattern on the European Cr distribution map is an extensive anomaly in SE-Europe (Albania, Hellas) (Fig. 15). Northern Europe shows generally slightly lower Cr-levels in bottled water. Geology, and especially the occurrence of mafic and ultramafic rocks (such as ophiolites), is very important for the distribution of Cr in the surface environment. Over 2000 mg/kg Cr occur in rocks and soils associated with the presence of ultramafic rocks. It is, thus, perhaps not surprising that the main anomaly on the distribution map is located in SE-Europe, with its abundance of ophiolites in Albania and Hellas. Note also the high value in Cyprus, with its famous Troodos ophiolite complex.

Many enhanced Cr values are observed in Germany, where the use of glass bottles is widespread. One can speculate whether leaching of Cr from the glass bottles could lead to somewhat enhanced German Cr concentrations.

The six highest Cr values (up to 27.2 μg/L), however, are all reported from Hellas and are related to the occurrence of ultramafic rocks or to ultramafic detritus in sediments, i.e., Drossia-49 (32.9 μg/L), Ydor Sourotis-31 (27.2 μg/L), Iris Loutraki-30 (23.6 μg/L), Loutraki-26 (22.4 μg/L), Loutraki Karadanis Provis-28 (20.1 μg/L), Loutraki Hydria-27 (19.6 μg/L), Loutraki Ivi-29 (17.8 μg/L) (see Fig. 16).

Bottle material leaching test has shown that glass bottles (especially green glass) can leach significant amounts of Cr (up to 0.2 μg/L – 2 μg/L at pH 3.5) to the stored water. The Hellenic samples were all in PET bottles.

The European Union limit for chromium in drinking and mineral water is 50 μg/L (Tab. 2; EC Directive 2003/40/EC).

Even the maximum concentration found in Hellenic bottled water (32.9 μg/L) is well below this limit.

4.6.2. Vanadium distribution

Vanadium in European bottled water varies from <0.1 to 48.9 μg/L (n=884), with a median of 0.17 μg/L (Tab. 3; Rei-
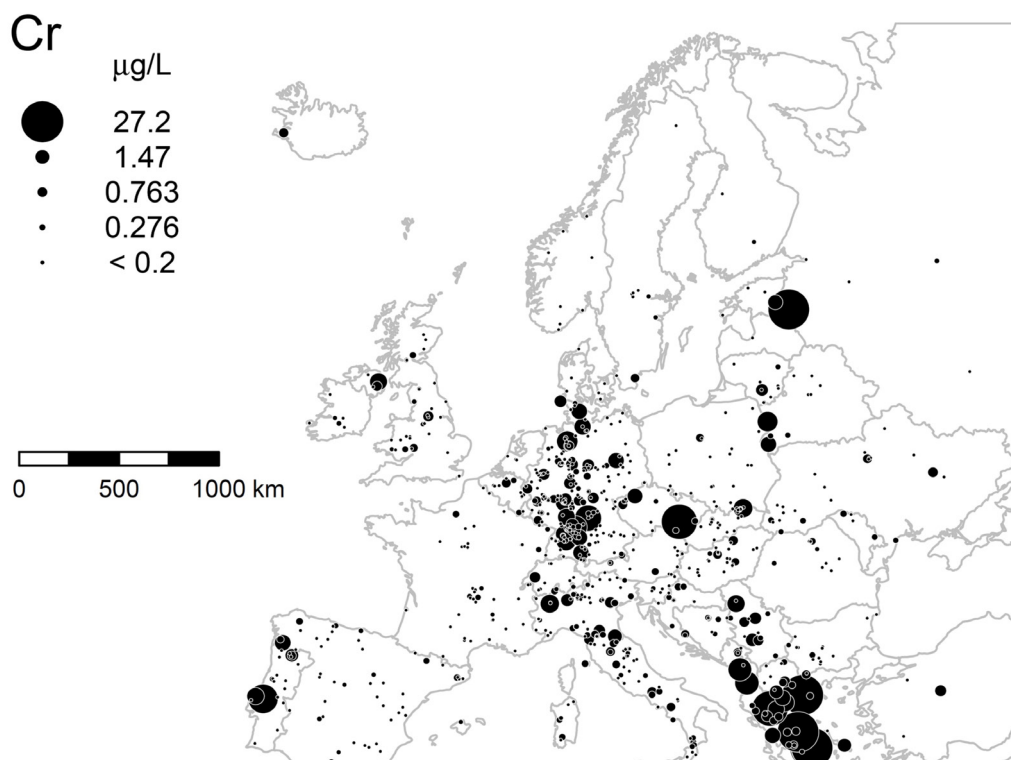
Fig. 15. *Distribution of chromium (Cr) in European bottled water samples (from Reimann and Birke, 2010, p.99).*
Εικ. 15. *Κατανομή του χρωμίου (Cr) σε δείγματα Ευρωπαϊκών εμφιαλωμένων νερών (Reimann and Birke 2010, σελ. 99).*
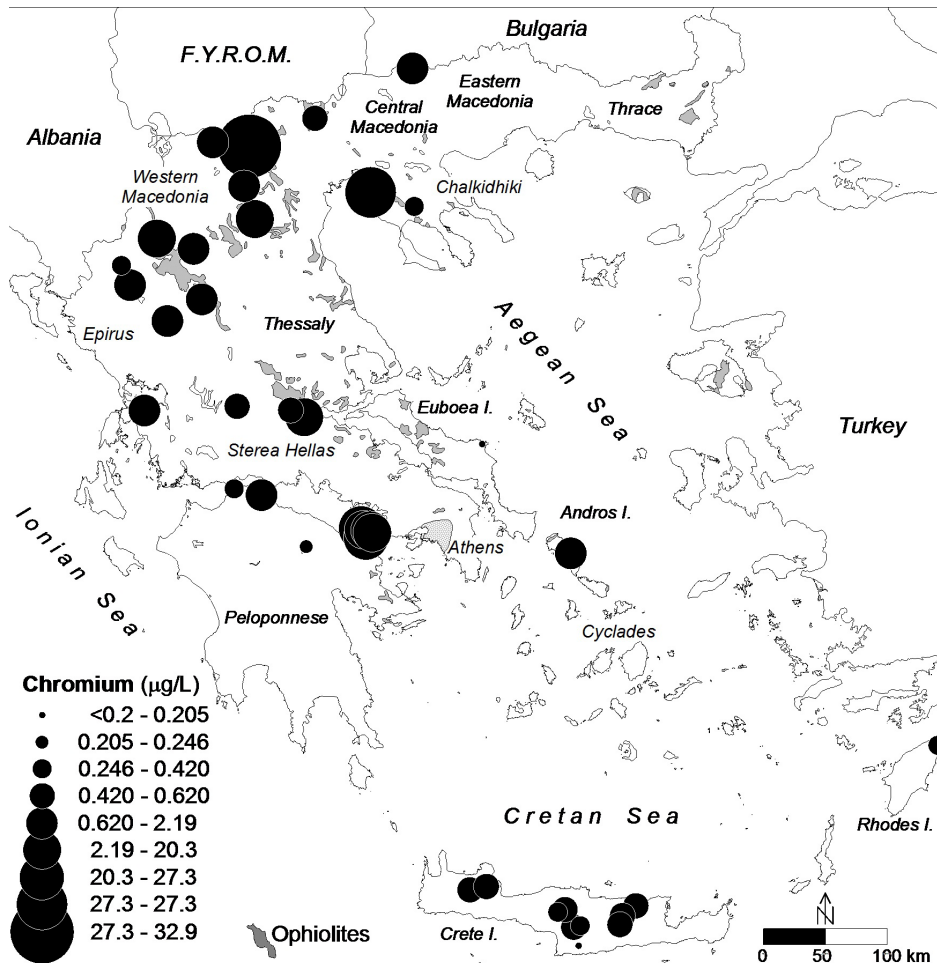
Fig. 16. Distribution of chromium (Cr) in Hellenic bottled water samples (see also Fig. 1 and Tab. 1 for sample location numbers and brand names, respectively).

Εικ. 16. Κατανομή του χρωμίου (Cr) σε δείγματα Ελληνικών εμφιαλωμένων νερών (οι αριθμοί των δειγμάτων αναφέρονται στο εικ. 1 και Πίν. 1).

mann and Birke, 2010), and in European surface water V has a narrower range from <0.05 to 19.5 µg/L (n=807), and its median is slightly higher at 0.46 µg/L (Salminen et al., 2005). Whereas, V in Hellenic bottled water varies from 0.147 to 7.45 µg/L (n=41), with a median 0.676 µg/L, and in Hellenic surface water it has a slightly wider range from 0.17 to 12.40 µg/L (n=27), with an approximately similar median 0.70 µg/L V (Salminen et al., 2005).

On the V distribution map (Fig. 17), all the active volcanic areas in Europe are clearly marked by anomalies (e.g., Iceland, Canary Islands, Cyprus, Italy). In France, a V anomaly coincides with the Massif Central, possibly linked to volcanic lithologies. In North Ireland, the influence of the Palaeogene basalt is visible. The highest vanadium value (48.9 µg/L) was reported from an Italian bottled water and is linked to the alkaline volcanic province.
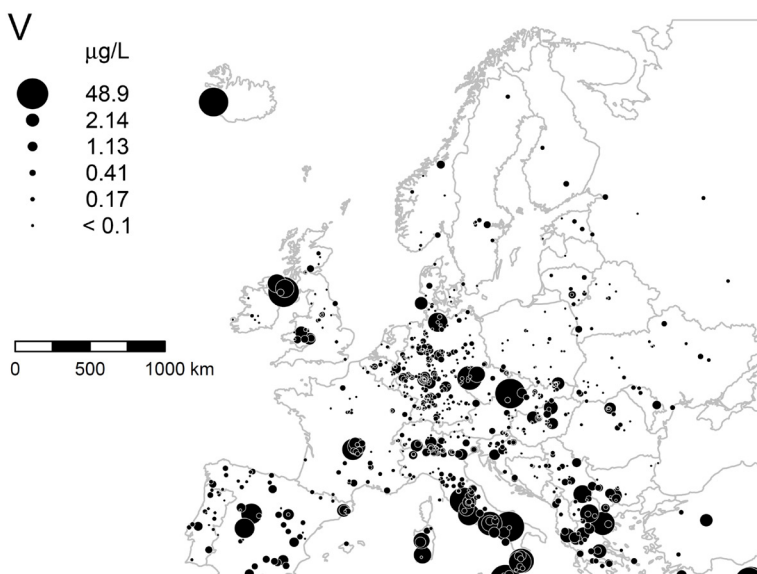
Fig. 17. *Distribution of vanadium (V) in European bottled water samples (from Reimann and Birke 2010, p.189).*
Εικ. 17. *Κατανομή του βανάδιου (V) σε δείγματα Ευρωπαϊκών εμφιαλωμένων νερών (Reimann and Birke 2010, σελ. 189).*
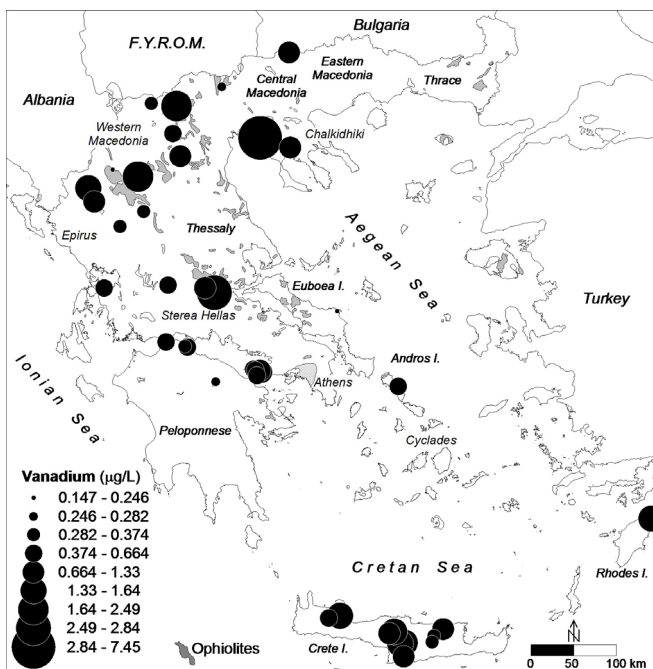
Fig. 18. *Distribution of vanadium (V) in Hellenic bottled water samples (see also Fig. 1 and Tab. 1 for sample location numbers and brand names, respectively).*
Εικ. 18. *Κατανομή του βανάδιου (V) σε δείγματα Ελληνικών εμφιαλωμένων νερών (οι αριθμοί των δειγμάτων αναφέρονται στο εικ. 1 και Πίν. 1).*

In Hellas, the elevated V values in the bottled waters of Ydor Sourotis-31 at 7.45 µg/L (Central Macedonia northern Hellas), Ioli-4 at 2.72 µg/L (Fthiotidha, central Hellas), Pindos-8 at 2.48 µg/L (Grevena, Western Macedonia), and Drossia-49 at 1.94 µg/L (Edessa, Western Macedonia) are all associated directly or indirectly with ophiolites (Fig. 17).

Bottle material leaching can have an impact on the observed V concentrations of water sold in both, glass and PET bottles (up to 0.06 µg/L). At low pH bottle leaching is increased (up to 0.08 µg/L V). No drinking water standard is defined for V by the European Union. Bosnia and Herzegovina, Croatia and F.Y.R.O.M. have set a limit of 5 µg/L V for drinking water, and Serbia 1 µg/L, whereas Ukraine has defined a limit of 100 µg/L V (Reimann and Birke, 2010).

Although vanadium can be biologically active, and is an essential nutrient for several micro-organisms and animals, its role in the human body is unclear and remains controversial.

4.6.3. Uranium distribution

Uranium in European bottled water varies from <0.001 to 229 µg/L (n=884), with a median of 0.228 µg/L (Table 3; Reimann and Birke 2010), and in European surface water, U has a narrower range from <0.002 to 21.4 µg/L (n=807), but a slightly higher median of 0.32 µg/L (Salminen et al., 2005).

According to Hem (1992), a typical concentration of U in surface water has been estimated to be in the range of 0.1 - 10 µg/L. Uranium in Hellenic bottle water varies from <0.001 to 10 µg/L (n=41), with a median of 0.307 µg/L (Salminen et al., 2005), and the Hellenic surface water has a wider range from 0.08 to 20.50 (n=27), with a slightly higher median at 0.41 µg/L. The U distribution map in bottled water is rather noisy (Fig. 19). The median levels in southern Europe are enhanced when compared to northern Europe.

A similar trend exists in European surface water (Salminen et al., 2005). High values can often be traced to wells in granitic bedrock (e.g., Sardinia, Sweden, Finland) or to wells in sandstone (Bunter and Keuper in central England and central Europe, respectively). The constructed histogram and density trace (see Reimann and Birke, 2010) suggest that many samples at the higher end of the distribution (above 1 µg/L U) were diluted and that the map may, thus, not necessarily represent the natural U distribution in ground water. The highest value (229 µg/L) was observed in a bottled water from the Czech Republic. There are, however, reports on single water wells delivering water with considerably higher U values (2 mg/L from a well in Norway– see Reimann et al., 1996, and 14 mg/L from Finland – see Asikainen and Kahlos, 1979).

The four highest U values in Hellenic bottled water are Vitsi-48 (10 µg/L), Beles-46 (2.8 µg/L), Drosoula-10 (1.5 µg/L) and Athos or Iro-33 (1.47 µg/L) are near to granitic masses (Fig. 20).

Bottle material leaching can have a minor influence on the U distribution observed in water sold in glass bottles, especially at a low pH, where the maximum value leaching from a glass bottle was 0.1 µg/L. However, even from soft PET bottles up to 0.06 µg/L U was observed leaching.

A drinking water standard for U is under discussion in the European Union: currently, a limit of 15 µg/L U appears probable. The U.S. Environmental Protection Agency has defined a drinking water limit of 30 µg/L. In Germany, an upper limit of 2 µg/L U has been defined for bottled water used to prepare baby food and 10 µg/L for drinking water.
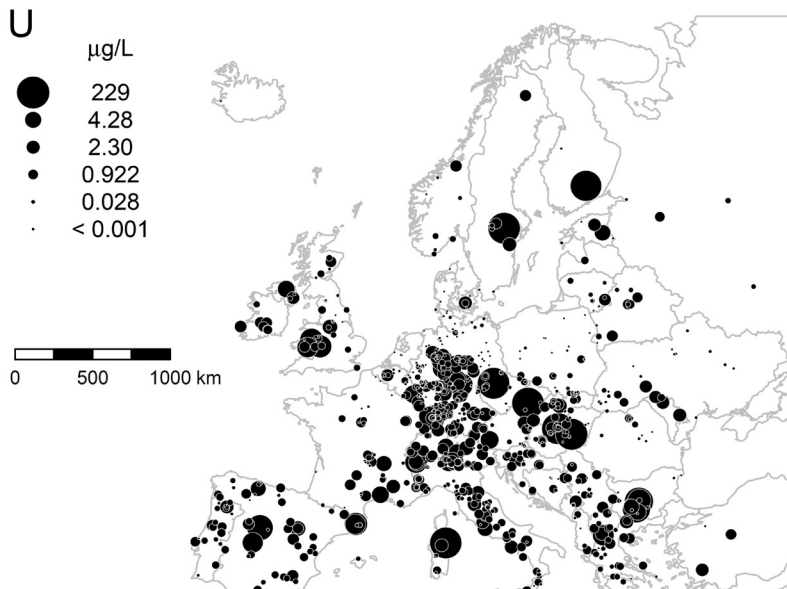
Fig. 19. *Distribution of uranium (U) in European bottled water samples (from Reimann and Birke, 2010, p.187).*
Εικ. 19. *Κατανομή του ουρανίου (U) σε δείγματα Ευρωπαϊκών εμφιαλωμένων νερών (Reimann and Birke 2010, σελ. 189).*
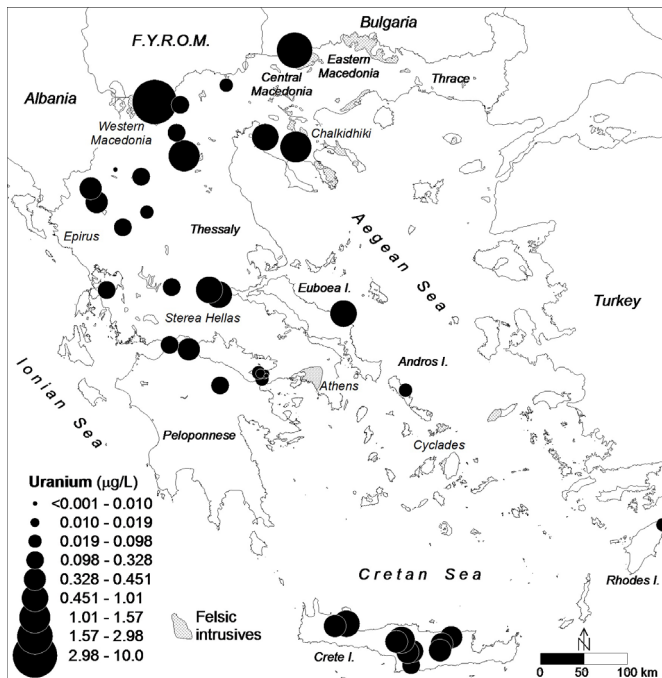

Fig. 20. *Distribution of uranium (U) in Hellenic bottled water samples 962 (see also Fig. 1 and Tab. 1 for sample location numbers and brand names, respectively).*
Εικ. 20. *Κατανομή του ουρανίου (U) σε 962 δείγματα Ελληνικών εμφιαλωμένων νερών (οι αριθμοί των δειγμάτων αναφέρονται στο εικ. 1 και Πίν. 1).*

Russia has defined a limit of 1.8 µg/L U for mineral water (see Appendix A in Reimann and Birke, 2010). Seven samples of the European bottled water data set returned values above 30 µg/L, twelve samples exceed 15 µg/L and 107 samples are above 2 µg/L.

5. Discussion and Conclusions

Geology is one of the key factors influencing the observed European and, of course, Hellenic, element concentrations in bottled water samples for a significant number of elements. Examples include the high values of Cr, clearly related to mafic-ultramafic rocks (ophiolites), V indicates the presence of recent and active volcanism in Europe and ophiolites in Hellas, U is associated with granitic intrusions and Keuper and Bunter sandstone, and Mg/Ca ratios are associated with ophiolites, dolomite and dolomitic limestone in Hellas.

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 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^-/$\sum$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.

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 (Demetriades, 2010a; Reimann and Birke, 2010). 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*".

The data presented in the published geochemical atlas (Reimann and Birke 2010) can, therefore, be used to gain a first impression of the natural variation

of analysed elements in ground water at a European scale. Natural variation is enormous, usually spanning three to four and, occasionally, up to seven orders of magnitude.

Several elements, where no potable water standards are defined in Europe, show surprisingly high concentrations in bottled water. In terms of health effects, more attention at both ends of the concentration range (deficiency as well as toxicity) may be required for quite a number of elements.

For some elements the reported concentrations can be influenced by bottle material. However, only for Sb was bottle leaching, in comparison to its natural concentrations in water, so serious that the results could not be used to plot a distribution map or taken to represent its natural concentration and variation in Europe. In general, glass bottles leach more elements to the stored water than PET bottles. However, all values, observed during the leaching tests, were well below all maximum admissible concentrations (MAC), as defined for drinking water in Europe, and it can, thus, be tentatively concluded that bottle leaching is unlikely to represent a health risk. The bottle leaching test demonstrated that there exist bottles that do not leach any of the indicated elements to the stored water.

In terms of water standards, the majority of samples fulfil the requirements of the European Union legislation for mineral (and drinking) water. For some elements, a few bottled water samples exceed the potable water standards, e.g., the maximum values observed for Al, As, Ba, F^-, Mn, Ni, NO_2^-, NO_3^-, Se and U. It must be noted that the maximum admissible concentration for F^- in bottled mineral water is set very high (5 mg/L instead of the 1.5 mg/L valid for drinking water) in order to avoid too many compliance failures, i.e., about 5% of all mineral water samples report F^- concentrations above 1.5 mg/L. This statutory practice is questionable in view of bottled water increasingly replacing tap water as general drinking water. With very few exceptions (Al, As, B, Ba, Fe, Mn, Ni, and Se – Demetriades 2010a), all values reported in the study of European ground water geochemistry, using bottled water as sampling medium are, however, well below the MAC values as defined by European legislation.

It can be concluded that the idea of using bottled water as a first proxy for ground water geochemistry and quality at the European scale was not as absurd as it might, at first glance, have appeared. Despite all potential problems, it has been shown that natural variation in ground water quality is much larger than the impact of any secondary consideration. Thus, on most element distribution maps, the importance of geology and other natural processes on the chemical composition of ground water is clearly visible.

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