STABLE ISOTOPE AND CHLORIDE, BORON STUDY FOR TRACING SOURCES OF BORON CONTAMINATION IN GROUNDWATER: BORON CONTENTS IN FRESH AND THERMAL WATER IN DIFFERENT AREAS IN GREECE

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Abstract. Boron is biologically an essential element but is toxic at high concentrations to plants (above approximately 1 mg/L in irrigation water) and probably to humans: The EU Drinking Water Directive fixes a threshold of 1 mg/L and the World Health Organisation (WHO) set a recommended limit at 0.3 mg/L now increased to 0.5 mg/L. Because of this potential toxicity and the need of implementation of EU regulation on national level, the study of the boron levels in both ground- and surface water is of great significance for water management.

In Greece, a significant number of thermal, mineral and superficial water springs are found especially in Northern Greece, that present high boron values rendering such water unacceptable according to the European standards. Nevertheless, such ground waters or borehole water with high temperature and high boron content are used for irrigation and drinking purposes, and could therefore have an antagonistic effect on crop yield and health.

In order to study the boron contamination and to elucidate the origin of B, we collected a number of hot and fresh water all over Greece. In all the water sampled, the boron concentration exceeds the limit of 0.3 mg/L, which is the former recommended WHO limit. Moreover, in the irrigation water examined, the boron concentration exceeds the value of 0.75 mg/L, which is the limit for sensitive plants (for plants of moderate and plants of high tolerance, these values vary between 0.75–3 and >3 mg/L respectively).

In all cases, elevated boron could be attributed to natural sources, geothermal activity and/or seawater intrusion into the aquifers. This finding has important implications for water management: In a setting of high natural geochemical background values, source control of the pollution is not possible and water managers have to cope with a local to regional geochemical anomaly that implies boron specific water treatment or mixing with unpolluted resources to bring concentrations down.

Keywords: Greece, hydrochemical methods, stable isotopes, origin of boron, pollution

1. Introduction

Boron is not found as a free element in nature. It usually occurs as orthoboric acid in some volcanic spring waters and as borates like borax and colemanite. In the earth's crust, the average boron concentration is 10 ppm, a value that characterises boron as a lithophilic element.

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In order to understand the geochemical cycle of boron, we consider a basaltic magma, from which boron can be obtained by slow cooling and deformation of a range of rocks such as gabbros, diorite, tonalites, granodiorite (Jansen and Bateman, 1979). During its crystallisation, boron is concentrated in magmatic residues and forms boron silicate minerals. The creation of borate and boron silicate raw materials can therefore be regarded as the products of the deformation and crystallisation of basaltic magma. Furthermore, boron is present in volcanic environments where it appears at the surface either in the form of soluble compounds or in liquid or as gas phase (Harder, 1973). If boron is in the form of boron compounds, then they may either dissolve and discharge into the sea or concentrate in closed basins; if boron appears in gaseous form, it either remains in the atmosphere or goes back to the biosphere through the rains.

Boron in the atmosphere exists in gaseous forms. The gaseous boron makes up 97% of total boron in the troposphere. Summarising, we can conclude that boron in the atmosphere is mainly derived from sea-spray degassing and fumaroles gases with a boron residence time of approximately one month.

In the hydrosphere, boron dissolves in surface waters, while the most is bound mainly with aluminates. In aqueous solutions, boron is present as $B(OH)_4^-$ ion, undissociated boric acid $B(OH)_3^0$, polyborate ions and borates [(Na-Ca-Mg)$B(OH)_4^+$]. The distribution of these species is controlled by the pH, salinity and specific cation concentrations. Seawater, at temperatures higher than 150 °C, leaches boron from sediments and volcanic rocks (Harder, 1970, 1974; Mosser, 1983; Palmer, 1987). At lower temperatures, boron can be removed from solution by absorption onto clay minerals and incorporation into secondary minerals (Karen and Mezuman, 1981; Seyfried *et al.*, 1984). Biologically, boron is an essential element for both plants and higher animals but when it exceeds a certain threshold, specific for each species, it can be rather toxic for plants and presumably also for humans. Despite the fact that boron is one of the seven most important trace elements for the growth of plants, vegetation is reduced or absent in areas where borates are present at high concentrations. Moreover, many crops are sensitive to high boron levels in irrigation water. Boron can also be detected in human and animals tissues, in which it plays an important physiological role. However, high boron levels in drinking water are considered to bear risks for human health. In animal experiments, high doses of boron affect fertility and pregnancy.

The World Health Organisation guideline value for boron is 0.5 mg/L. The drinking-water standard of the European Community is two times this recommended value but still, in many water resources worldwide, boron concentrations in ground- and surface water exceed this value rendering such water unacceptable according to the European standards.

Boron compounds are widely used in various industrial applications among which in electronics, in nuclear reactors, in metallurgy, in glass making, in pharmaceuticals, in plastics etc. However, the main industrial applications of boron that apparently affect ground water systems are washing powders and agricultural applications of boron-fertilizers and boron-pesticides. In Cyprus, the extremely high boron content of several water sources was the signal for the restriction of the use of washing powders containing boron. Boron contamination is clearly not a major issue in the context of diffuse pollution due to agricultural activities dominated by the problem of nitrates, pesticides and herbicides. Nevertheless, the increase of the concentration of boron is many times indirectly correlated with the development of agriculture, as it presupposes extensive exploitation of high amounts of water resulting therefore in a significant drop of piezometric levels and in the intrusion of salt water.

High levels of boron are also detected in coal and landfills. The main source of boron contamination of the landfills in Germany is the washing powder.

A major boron problem has been identified in Greece. High boron concentrations in Greece water resources make them unusable for irrigation and drinking water purposes. The main goal of the paper is to study boron origin in water resources and to distinguish between natural (geothermal activity, sea water intrusion, evaporate dissolution, mixing with sedimentary brines) and anthropogenic (boron-contaminated surface and ground waters) sources of boron. The used methodology utilise geochemical/isotopic tools. Water samples for chemical, Cl^- and B, and isotopic, ^2H and ^{18}O, analyses were collected. The approach of combining chloride and bromide and ^2H-^{18}O permits the identification of the potential sources of boron (natural and anthropogenic), the origin of salinity and also the origin of water in different environments.

2. Sampling and Analyses

Samples of natural water, spring and boreholes, were collected. Figure 1 shows the locations of the sampling sites of the waters. Temperature was measured directly in the field. The Cl^- content of the water samples is analyzed with ion chromatography. The B content is determined photometrically using the cucrcumin method. The samples are acidified and evaporated to dryness (at 55 °C) in the presence of curcumin. The precipitate is red in colour and can be dissolved in ethyl alcohol. The red alcoholic mixture is photometrically determined at 540 nm. (404A Method of Standard Methods for the Examination of Water and Wastewater, APHA-AWWA-WPCF, 16th edition, 1985).

The $\delta^{18}O$ compositions of water in the samples were determined from CO_2 equilibrated with the water (Epstein and Mayeda, 1953). The δD compositions of water were determined from the H_2 generated by the Zn-reduction method (Coleman *et al.*, 1982).

Sixty eight samples of water were collected for this study: 2 from Nisyros, 6 from Santorini, 8 from Methana, 4 from Milos, 5 from Ikaria, 2 from Mytilini, 3 from Sydirokastro, 7 from Nigrita-Therma, 4 from Lagada, 4 from Nea Appolonia-Volvi-Nymfopetra, 16 from Peninsula of Chalkidika (Nea Triglia,

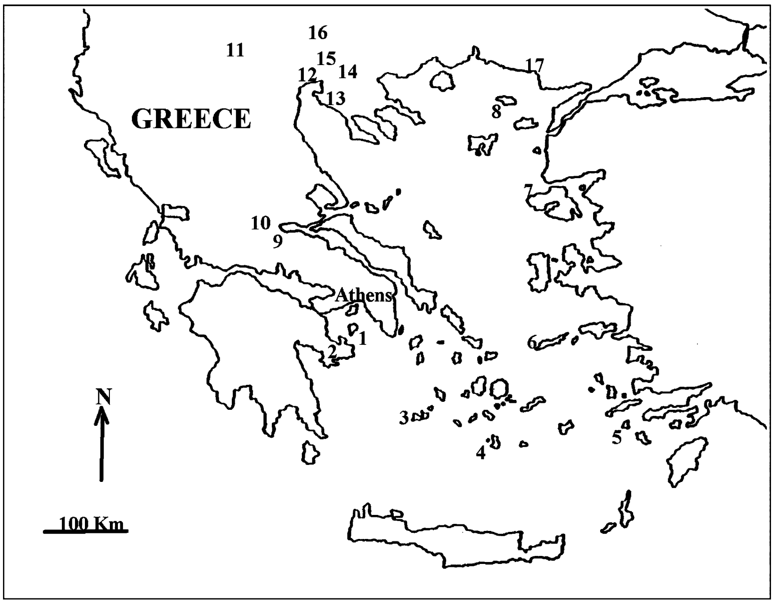

Figure 1. Sampling locations are noted on figure. 1-Egina, 2-Methana, 3-Milos, 4-Santorini, 5-Nisyros, 6-Ikaria, 7-Lesvos, 8-Samothraki, 9-Thermopyles, 10-Ypati, 11-Aridea, 12-Thessaloniki (Sedes), 13-Chalkidiki (Nea Appolonia, N. Triglia, Eleochoria, Nea Tenedos, Petralona), 14-Mygdonia basin (Lagadas, Volvi, Nymfopetra), 15-Nigrita, 16-Sydirokastro, 17-Traianoupoli.

Nea Tenedos, Eleochoria, Petralona, Nea Krini), and one from Thessaloniki, Traianoupoli, Samothraki, Egina, Thermopyles, Aridea, Ypati and seawater. The sampling was carried out between June 2000 and July 2004.

3. Discussion

3.1. ORIGIN AND NATURAL BORON CONTENT

Boron, which is found in ground water systems, can be characterised as either natural or anthropogenic, according to the source from which boron is derived.

The term natural boron includes geothermal boron, boron derived from leaching from a large variety of rocks, volcanic, crystalline, clays and shale, evaporates, or the mixing of ground water with oil field water or connate or fossil brines. The term anthropogenic boron refers to the contents of boron in washing powders, municipal wastewaters, and industrial residues B-pesticides, B-fertilizers, etc.

Greece as a coastal country with a strong geothermal activity combines a variety of potential natural sources of boron and represents an interesting context for the investigation of the provenance of the contaminant. In Greece, we find geothermal fields of low, middle and high enthalpy, a high geothermal gradient, which is due to the volcanic activity of the area and to the active tectonics, which allow the circulation of water in great depths. In these fields or close to them, high concentrations of boron are present. The study of boron content is not only an academic problem interesting to geochemists dealing with geothermal fluids but a necessity for water management in a country that is largely under water stress due to an increasing demand for drinking and irrigation water. The rapid urbanisation of some areas, the tourist industry and the agricultural activities lead to a lowering of water tables and a deterioration of water of quality by the intrusion of seawater.

The B and Cl^- concentrations can be used for the comprehension of the provenance of boron contents in water resources. Cl^- is regarded as a conservative element even in geothermal environments. Its behaviour is thus particularly interesting in studies of the origin of salinity. In seawater boron concentrations range between 4.5 and 5 mg/L and B/Cl ratio is 2×10^{-4} (Table I). In fossil brines, of seawater origin, boron concentrations range between 47.6 and 1379 mg/L and B/Cl ratio range between 5.6×10^{-4} and 9.9×10^{-3} (Valyashko, 1956; Herrmann *et al.*, 1973). In rainwater, boron concentration is approximately 0.01 mg/L, while in fresh and uncontaminated surface water this concentration is in general less than 0.05 mg/L with a B/Cl ratio of 1.3×10^{-3}. In waters, which are contaminated by domestic waters and other anthropogenic sources (derived from Na or Ca–borates), the concentrations of boron are significantly elevated. In these waters B/Cl ratio is much higher than that of the sea.

The concentrations of boron in oil fields waters are greater than 100 mg/L. Connate waters are also enriched in boron, with values that often exceed 350 mg/L (Rittenhouse *et al.*, 1969) and B/Cl ratios that range from 5×10^{-3} to 4×10^{-2}. In thermal waters, which contain juvenile water boron is present at various concentrations and the ratio of B/Cl ranges from 2×10^{-2} to 0.4 (White and Warning, 1963). In general, the distribution of boron among hydrothermal waters depends on the provenance, temperature, vapour pressure and the lithology of water bearing rocks.

3.2. GROUNDWATER ORIGINS RELATED TO CHLORIDE, BORON AND STABLE ISOTOPE CONTENTS

The samples collected all over Greece (Figure 1), represent cold and hot waters collected from springs and boreholes. The areas from which the samples were collected cover a wide range of typical aquifers. Many samples come from the NE islands of Greece [Ikaria, Lesvos (Mytilini), Samothrace], from the areas and islands of the volcanic arch (Methana, Milos, Santorini, Nisyros, Egina) and from the continental Greece (Thermopiles, Ypati, Trajanoupolis, Aridea, Nigrita, Sidirokastro, Lagada, Nymphopetra, Nea Appolonia, N. Triglia, Eleochoria, Nea Tenedos, Sedes, Petralona). In order to carry out the present project we used geochemical methods and isotopic techniques. The quality of the waters, collected from the islands (islands

TABLE I

B and B/Cl contributions in the water

	B (mg/L)	B/Cl	References
Meteoric water	0.01	$\approx 2 \times 10^{-4}$ to 5×10^{-3}	Harder (1973)
Fresh water	<0.05	1.3×10^{-3}	Harder (1973), Dotsika *et al.* (2002)
Sea Water	4.5–5	2.3×10^{-4}	Harder (1973), Dotsika *et al.* (2002)
Salt water intrusion	Varies	$<8 \times 10^{-4}$	Harder (1973), Dotsika *et al.* (2002)
Fossil brine (Sea water evaporated, $d = 1{,}106$)	47.6	5.6×10^{-4}	Valyashko (1956), Herrmann *et al.* (1973)
Fossil brine (Sea water evaporated, $d = 1{,}131$)	63.8	5.9×10^{-4}	Valyashko (1956), Herrmann *et al.* (1973)
Fossil brine (Sea water evaporated, $d = 1{,}225$)	120	6×10^{-4}	Valyashko (1956), Herrmann *et al.* (1973)
Fossil brine (Sea water evaporated, $d = 1{,}270$)	601	2.9×10^{-3}	Valyashko (1956), Herrmann *et al.* (1973)
Fossil brine (Sea water evaporated, $d = 1{,}290$)	889	3.9×10^{-3}	Valyashko (1956), Herrmann *et al.* (1973)
Fossil brine (Sea water evaporated, $d = 1{,}305$)	949	3.6×10^{-3}	Valyashko (1956), Herrmann *et al.* (1973)
Fossil brine (Sea water evaporated, $d = 1{,}325$)	1379	9.9×10^{-3}	Valyashko (1956), Herrmann *et al.* (1973)
Non-marine brine		$>8 \times 10^{-4}$	Rittenhouse *et al.* (1969)
Hydrothermal fluids	Often by 0.5 to 20	$\ggg$Marine ratio	White and Warning (1963)
Hydrothermal fluids with juvenile water	Varies	2×10^{-2}–0.4	White and Warning (1963)
Connate water	>350	5×10^{-3} to 4×10^{-2}	Harder (1973)
B is derived from Na or Ca–borates		$\gg$Marine ratio	Vengosh (1998), Vengosh *et al.* (1999)
Oil field waters	>100	$>$Marine ratio	White *et al.* (1963)

of the volcanic arch and islands of the NE Greece), has been degraded by both the elevated salinity and the high boron levels ($B = 0.1$–2.6 mg/L). Moreover, the thermal waters from the same areas show very high concentrations of B ($B = 1$–12 mg/L), a fact that is probably related to the high temperature ($T = 30$–$55\,^{\circ}$C) leading to enhanced water-rock interaction and leaching of boron. The waters of the continental Greece have also a high temperature, a B/Cl ratio much greater than that of seawater (10^{-2}) and a Cl^- concentration less than 200 mg/L.

In the diagram Cl^- versus B (Figure 2), two linear correlations appear between B and Cl^-, suggesting a different origin for both elements. The trend, with the

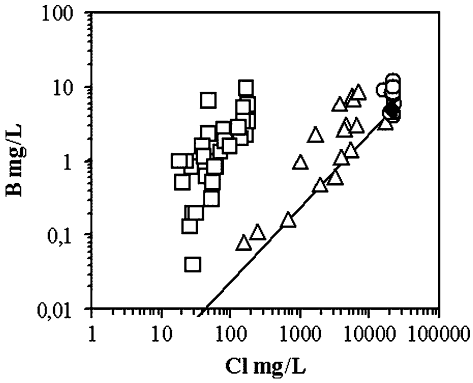

Figure 2. B concentrations vs chlorinity. *Squares*: Thermopiles, Ypati, Trajanoupolis, Aridea, Nigrita, Sidirokastro, Lagada, Nymphopetra, Nea Appolonia, N. Triglia, Eleochoria, Nea Tenedos, Sedes, Petralona. *Triangles*: Methana, Milos, Santorini, Nisyros, Egina. *Circles*: Ikaria, Mytilini Therma, Methana Therma. *Black Rhombus*: Seawater, *Line*: seawater dilution line.

lower slope, that that is defined by all the waters samples coming from the islands, is an ideal line mixing between seawater and fresh water. This suggests that Cl^- and B derive from seawater, which is more or less diluted by fresh water and that the supply of these ions by rock leaching is negligible.

The trend, with the higher slope, is a mixing line between cold water and deep thermal water. The hot member is water, with temperature less than 62 °C, coming from Nigrita, Sidirokastro, Aridea and Chalkidika and the cold water coming from the same areas. The values of the ratio B/Cl of these waters, coming from the continental Greece, are different from those of the seawater (the B/Cl ratio of sea water collected is 2×10^{-4}) suggesting a non-marine origin of the B. Generally in fresh waters, B/Cl ratios are higher than those of seawater. With increasing temperature these ratios become progressively higher. For the water of the continental Greece the B content of fresh and hot water is higher than seawater and increase with temperature.

In the figure B/Cl *versus* Cl^- (Figure 3), representing the values of all the samples, two main groups can be distinguished: the Cl^- concentration of the first group is less than 200 mg/L and its B/Cl ratio less than 200. In the second category fall waters with Cl^- concentrations exceeding 700 mg/L and a B/Cl ratio greater than 800.

To the first category belong the waters which were sampled from the areas of the continental Greece, in particular Aridea, Nigrita, Sidirokastro, Langadas, Nymphopetra, Nea Apollonia, Sedes, Eleochoria, Nea Triglia, Petralona and Nea Tenedos. Most of the waters of this category have a high temperature, a B/Cl ratio much higher than that of seawater (2×10^{-4}) and are freshwaters with Cl^- concentrations less than 200 mg/L. The measured Cl^- concentration indicates mainly a meteoritic origin of water and thus the possible boron contamination

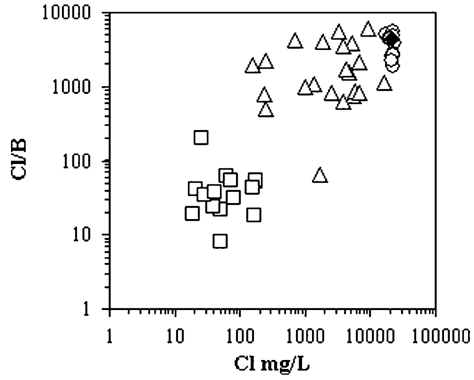

Figure 3. Cl/B ratio vs Cl. For symbols see Figure 2.

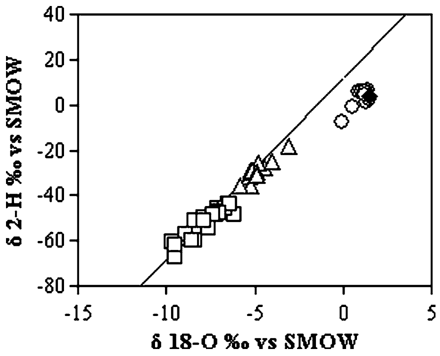

Figure 4. δ^2H vs δ^{18}O diagram. Line: Local meteoric water line. For symbols see Figure 2.

by seawater intrusion cannot be excluded. In fact in Figure 4, which presents the relationship between oxygen-18 and D contents of the samples (Table II), and the range of local meteoric line water (IAEA, 1981; Leontiadis *et al.*, 1996, 1997, 1999), for the samples from this first category a strong meteoric contribution appears.

So, boron contamination can be attributed to either anthropogenic or natural reasons. If boron originated from B-fertilizers, B-pesticides and industrial and urban wastewater, the elevated amount of boron would be accompanied by high amounts of other ions (high amount of Ca^{2+}, Na^+ and NO_3^- compared to the unpolluted fresh waters of the areas), a fact that is not observed (Dotsika *et al.*, 2002). Therefore, the above results indicate a geothermal origin for boron, meaning that the boron content is due to the interaction between water and rock. In this category, water sampled from the Northern Greece (Dotsika *et al.*, 2002) area is also included: the temperature of this water is less than 24 °C and can be utilized for water supplies and irrigation.

TABLE II

B, Cl, B/Cl and stable isotopes contents in water

Sampling region	Sampling site	*t* (°C)	Cl (mg/L)	B (mg/L)	B/Cl	δ^{18}O (H_2O) (‰ SMOW)	δD (‰ SMOW)
1	Egina Souvala	24	3300	0.6	1.8×10^{-4}	−4.9	−29.5
2	Methana	32	22260	8.7	3.6×10^{-4}	−4.8	−26
	Loutra	32	21900	7.7	3.5×10^{-4}	1	6
	EOT spring A	31	21000	8.3	3.9×10^{-4}	1.1	6
2	Methana	32	21970	8.3	3.8×10^{-4}	1.3	6
	Loutra	32	21580	9.8	4.5×10^{-4}	1.2	6
	EOT spring B						
2	Methana	36	3940	1.1	2.7×10^{-4}	−5.3	−32
	Agios Nikolaos	37	4700	3.0	6.4×10^{-4}	−5.2	−29
		35	4380	2.6	5.9×10^{-4}	−5.2	−29
3	Milos Charou	46	1000	1.0	1×10^{-3}	−5.1	−29.2
3	Milos Thiafes Charou	24	1380	1.3	9×10^{-4}		
3	Milos Rapanaki Irrigation water	24	1700	2.3	1.3×10^{-3}	−5.2	−35.7
3	Milos Gaitanis Irrigation water	35	2520	3.1	1.2×10^{-3}	−4.9	−31.3
4	Santorini Palea Kameni	35	23280	6.0	2.5×10^{-4}	−4.4	−27.5
4	Santorini Plaka	34	5300	1.42	2.6×10^{-4}	−4	−25
4	Santorini Monolithos A Irrigation water	24	250	0.11	4.4×10^{-4}		
4	Santorini Vlichada Irrigation water	31	1900	0.48	4.4×10^{-4}	−5	−31
4	Santorini Preka	26	690	0.16	2.3×10^{-4}		
4	Santorini Monolithos B Irrigation water	24	250	0.5	2×10^{-3}		
5	Nisyros Avlaki	55	22000	12.0	5.4×10^{-4}	1.4	6.5
5	Nisyros Mandraki	42	16000	9.0	5.6×10^{-4}		
6	Ikaria Agia Kiriaki	38	9300	1.5	1.6×10^{-4}	−3.1	−18.2
6	Ikaria Agia Kiriaki	34	17200	3.4	1.9×10^{-4}	−0.1	−7.6
6	Ikaria Spileo	53	19600	4.5	2.3×10^{-4}	1.3	0.9
6	Ikaria Apollons	52	22250	4.0	1.8×10^{-4}	1.5	2.6
6	Ikaria Kratsa	50	22040	4.5	2.0×10^{-4}	1.2	4.6
7	Mytilini Thermis	48	19700	4.4	2.2×10^{-4}	0.5	−0.6
7	Mytilini Polychnitos	90	6700	3.1	4.6×10^{-4}	−5.8	−35.6
8	Samotraki Therma	54	6800	8.4	1×10^{-3}	−6.2	−48.5

(*Continued on next page*)

TABLE II
(*Continued*)

Sampling region	Sampling site	t (°C)	Cl (mg/L)	B (mg/L)	B/Cl	$\delta^{18}O$ (H_2O) (‰ SMOW)	δD (‰ SMOW)
9	Thermopyles Leonidas	32	5670	7.5	1.3×10^{-3}	−7	−47.5
10	Ypati	30	3800	6.0	1.5×10^{-3}	−7.9	−50
11	Aridea	25	170	9.5	5.5×10^{-2}	−9.7	−60.4
12	Sedes Thessaloniki	30	170	2.2	1×10^{-2}		
13	NeaTriglia, Eleochoria	33	183	5.7	3×10^{-2}	−7.1	−45.5
13	Nea Triglia, Nea Tenedos	40	155	5	3×10^{-2}	−7	−47.1
13	Nea Triglia, Driking water						
	DW 1	22	101	1.8	1.7×10^{-2}	−6.5	−44
	DW2	23	144	2	1.7×10^{-2}	−6.7	−45.5
	DW3	20	86	1.8	2×10^{-2}	−7	−47.1
	DW4	19	47	0.6	1×10^{-2}	−6.4	−44
	DW9	20	30	0.2	6×10^{-3}	−7.2	−48.2
	DW10	24	54	0.3	5×10^{-3}		
	DW11	22	56	0.5	8.9×10^{-3}	−7	−47.5
	DW12	23	63	0.8	1.2×10^{-2}	−7.6	−54.3
	DW13	22	60	0.8	1.2×10^{-2}		
13	Nea Triglia Irrigation water						
	IW5	23	100	1.6	1.6×10^{-2}		
	IW6	22	156	3.3	2×10^{-2}	−7.3	−47.2
	IW7	22	133	2.8	2×10^{-2}	−7.4	−48.2
13	Nea Krini Irrigation water	21	32	0.2	6×10^{-3}	−7.9	−51
13	Petralona irrigation water	22	155	0.08	5×10^{-4}		
13	Nea Appolonia Irrigation water	34	42	1.1	0.03	−9.5	−61.8
13	Nea Appolonia Loutra	49	72	1.3	0.02	−9.5	−67.3
14	Volvi Lac	25	112	0			
14	Lagada Chrisavgi Irrigation water	19	28	0.8	0.028	−8.4	−59.6
14	Lagada Mouries Irrigation water	20	23	1.0	0.04	−8.6	−60.2
14	Lagada Lac		238	0.3	0.001		
14	Lagada Irr. W.	39	21	0.5	0.023	−8.4	−51.4

(*Continued on next page*)

TABLE II

(*Continued*)

Sampling region	Sampling site	t (°C)	Cl (mg/L)	B (mg/L)	B/Cl	$\delta^{18}O$ (H_2O) (‰ SMOW)	δD (‰ SMOW)
14	Nymfopetra	41	19	1.0	0.05		
14	Lagada Chrisavgi Irrigation water	19	28	0.8	0.028	−8.4	−59.6
15	Nigrita Therma	62	177	3.4	1.9×10^{-2}	−8.8	−59.2
15	Nigrita Therma	47	177	3.3	1.8×10^{-2}	−8.4	−56.1
15	Nigrita Driking water	24	80	2.6	3.2×10^{-2}	−8.8	−57.2
15	Nigrita borehole N2 Irrigation water	27	39	1.6	4×10^{-2}		
15	Nigrita borehole N4 Irrigation water	19	26	0.13	5×10^{-3}		
15	Therma Nigrita Source	50	156	3.6	1.3×10^{-2}		
15	Therma Visy	17	63	1.0	1.5×10^{-2}		
16	Sidirokasrto Loutra	42	50	6.5	0.13		
16	Sidirokastro Agia Barbara	46	50	2.3	4.6×10^{-2}		
17	Traianoupoli Evrou	50	5900	6.9	1×10^{-3}		

The waters of the second category come mainly from the islands and the geothermal fields of the volcanic arch. The positions of the points (Figure 3) representing these waters, show the participation of seawater (seawater or fossil brine of marine origin) in the deep hydrothermal system indicating a marine provenance of boron. The B/Cl ratio of these waters is either very similar to that of seawater (2×10^{-4}) or slightly greater (6×10^{-3}), indicating therefore a possible mixing with the geothermal water of meteoric origin. In fact in the Figure 3 the position of samples, coming from the islands [Methana (is a peninsula), Nisyros, Thermopyles, Ikaria, Mytilini, Samothraki, Egina, Santorini], is very close to that of mean seawater (SMOW) confirming its purely marine origin. The position of some samples under the local meteoric water area could reflect mixing between seawater and fresh water.

In the diagram $\delta^{18}O$ *vs* Cl^- and in a δ^2H *vs* Cl^- (Figures 5 and 6) the positions of the spots, which are related to waters with B/Cl ratio lower to that of the seawater, are distributed along different lines, between seawater and geothermal water of meteoric origin, corresponding to different sampling zones. If these lines were mixing lines their x-axis intercepts would represent the $\delta^{18}O$ and δ^2H contents of the meteoric

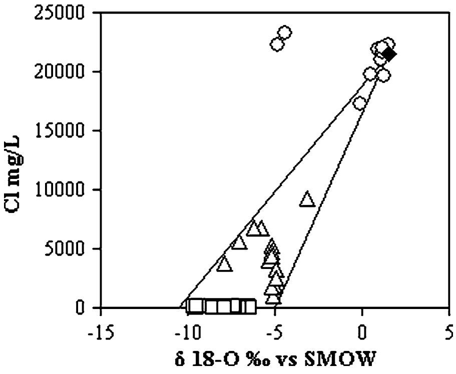

Figure 5. δ^{18}O vs Cl. For symbols see Figure 2.

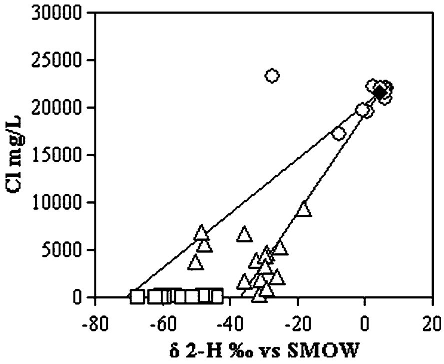

Figure 6. δ^{2}H vs Cl. For symbols see Figure 2.

component of the mixtures. These correspond to about -6.5 in δ^{18}O and -45 in δ^{2}H for the Chalkidika peninsula (N. Triglia, N. Tenedos.) sample and -9.5 in δ^{18}O and -67 in δ^{2}H for the continental N. Greece (Nigrita, Sydirokastro, Lagada.). These variations could reflect differing recharge altitudes: Recharge altitude varies by about 800 m between the continental N. Greece and the Chalkidika peninsula. In general, the waters belonging to this category were sampled from the volcanic arch (Nisyros, Santorini, Melos, Methana), among with the waters sampled from Ikaria, Lesbos, Samothrace and Egina (Dotsika and Michelot, 1992; Michelot *et al.*, 1993). The high boron content of the waters from the volcanic arch can be attributed mainly to the temperature, which is mostly responsible for the formation of salt geothermal water. In Ikaria ($B/Cl = 2 \times 10^{-4}$), the provenance of boron is clearly related to the intrusion of marine water (Dotsika and Michelot, 1992). On the contrary, the high boron contents of water from Lesbos, Samothrace and Egina, are attributed to both the elevated temperatures and the intrusion of marine water.

4. Conclusion

In all the sampled water, the boron concentration exceeds the former WHO limit of 0.3 mg/L and in many waters in regions with high geothermal activity, boron is higher than 1 mg/L, which is the acceptance value for the human consumption in the EU. Moreover, in the irrigation water examined, the boron concentration exceeds the value of 0.75 mg/L, which is the limit for sensitive crops. About the origin of B, both the boron concentrations and the B/Cl ratios of waters indicate, generally, that their enrichment in boron is due to their vicinity of geothermal fields and/or to the intrusion of seawater. Especially the elevated B concentrations in some water samples from the N. Greece (Aridea, Nigrita, Sidirokastro, Langadas, Nymphopetra, Nea Apollonia, Sedes, Eleochora, Nea Triglia, Petralona and Nea Tenedos) may be related with the geothermal field of Central Macedonia, in Northern Greece. The B contents of water samples from the islands can be attributed mainly to the temperature (Nisyros, Santorini, Milos, Methana), and to the intrusion of marine water (Ikaria, Lesbos, Samothrace and Egina).

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