

Geochemical evidences for the sources of the Cr(VI) contamination in groundwater in central Euboea and Assopos-Thiva basins, Greece: Natural versus anthropogenic origin

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Abstract: Analytical data of the water chemistry in central Euboea and the Assopos-Thiva basins, Greece, has revealed high concentrations of Cr(total) and Cr(VI) exceeding, sometimes, the Greek and the EU drinking water maximum acceptable level (50g/L). The case of groundwater contamination in central Euboea related mainly to natural processes (rocks and ores) was compared with that of the neighboring area of Assopos and Thiva basins (areas of Avlida, Thiva, Oropos, Avlona) characterized by widespread industrial activity. The concentrations of Cr(VI) detected in several groundwater samples, ranged from < 2 (below detection limit) to 360µg/L in central Euboea and from < 2 to 185µg/L in Assopos-Thiva basins, Eastern Sterea Hellas, Greece. The ratio of Cr(VI) to Cr(total) ranging from 0,8 to 1 and the excellent correlation ($r^2= 0.98$, $p=0.000$) between Cr(VI) and Cr(total), indicated that hexavalent chromium is the predominant form of dissolved chromium in groundwater of all areas studied, with a pH near to neutral. The concentrations of other elements in the majority of the analyzed water samples in all areas were below the permissible limits for drinking water. Water samples from Assopos-Thiva basins were characterized by lower Si contents compared to those from central Euboea. Based on Na, Ca, Mg, Si and Cr(VI) content of the water samples, several discrimination diagrams have been proposed for the identification of their origin. According to their Na, Ca, Mg, Si and Cr contents, the water samples from central Euboea could be distinguished to a) those influenced by the sea water, having high Na and B concentrations, b) those with lower Na, an average of Cr(total) equal to 25µg/L and Mg/Si ratio approximately to 2.3 and c) those with very high Cr(total) values, up to 360 µg/L. The hydrochemical differences of the water samples from Euboea, have been attributed to natural processes for the (a) and (b) cases, whilst in the case (c) the chromium contamination in groundwater was probably associated with human activities. In the extended area of Assopos-Thiva basins (areas of Avlida, Thiva, Schimatari, Oropos, Avlona) the groundwater samples on the basis of their concentration in Cr(total) were classified into three groups: Group A with Cr(total) concentrations lower than 2µg/L, Group B with Cr(total) concentrations ranging from 2 to 50µg/L and Group C with Cr(total) concentrations higher than 50µg/L. The plots of Cr versus Mg/Ca, Mg/Na versus Ca/Na, B versus Si/(Si+Na) and Mg/Si versus Ca/Si ratios revealed a significant degree of salinization and a wide variation in the Cr content. The spatial association of wells with Cr < 2µg/L and those with high Cr concentrations in the whole region of the Assopos-Thiva basins and central Euboea may be related with the depth of the aquifers. The highest values of Cr(VI), recorded in shallow (alluvial) aquifers, were probably due to the circulation of water in an oxidizing environment, that has been affected by anthropogenic activities.

Keywords: chromium speciation, toxic metals, groundwater contamination, hydrogeochemistry

1. INTRODUCTION

The higher mobility and toxicity of Cr(VI) compared to Cr(III) for biological systems has been extensively documented, due to its strong oxidizing potential (Kotas and Stasicka, 2000, Bielicka et. al., 2005, Wise S. and Wise J., 2012). The speciation and the transport of chromium within the terrestrial and water systems are governed by pH and redox conditions. Three subsystems had been distinguished, considering chromium transport in natural waters: river, lake and ocean water (Bielicka et. al., 2005). In the neutral and alkaline pH conditions the Cr(III) in water has low solubility and readily precipitates as Cr(OH)₃(s) or mixed Cr-Fe hydroxides colloids in pH values greater than 4 (Schlautman and Ihnsup, 2001). The Cr(III) ions have a tendency to bind with the suspended solids and thus are detectable in the sediment (Kotas and Stasicka, 2000). Trivalent chromium is the most stable oxidation state of chromium. In the pH range of natural water (6.5 to 8.5), Cr(VI) exists as chromate CrO₄²⁻, bichromate HCrO₄⁻ and dichromate Cr₂O₇²⁻ ions. These ions

form several Cr(VI) compounds, which are relatively soluble and thus mobile in the environment. The Cr(VI) in groundwater can be reduced to Cr(III) in low pH, under reducing conditions

In contrast, Cr(III), is an essential nutrient required for normal glucose and lipid metabolism in human body, as it enhances the effect of insulin. Chromium enters the human body through inhalation, ingestion and dermal absorption. The general population is exposed to chromium through ingestion from food and water, while occupational exposure occurs predominantly through inhalation and dermal contact. Although Cr(VI) is a known carcinogen through inhalation, the WHO, EU and US agencies have not yet classified it in terms of ingestion (WHO, 2003).

Due to the toxicity of hexavalent chromium, the California Office of Environmental Health Hazard Assessment (OEHHA) developed a Public Health Goal (PHG) for hexavalent chromium of 0,02 µg/L in drinking water (OEHHA, 2011). In all other U.S. states the Federal drinking water standard for total chromium is 100µg/L (WHO, 2003). However, that situation may change as a result of recent research showing elevated levels of Cr(VI) in the drinking water supplies of 31 different cities across the United States. The U.S. Environmental Protection Agency had planned to establish federal limits for Cr(VI) in drinking water in 2012, following the completion of its own risk assessment (OEHHA, 2011). Italy has regulated a maximum permissible level of Cr(VI) in drinking water at 5 µg/L (Fantoni et al., 2002, Stepek, 2002). Most countries, including in the European Union, have currently regulated the limit of 50µg/L for total chromium in drinking water (EC, 1998) which assumes a mixture of hexavalent chromium and trivalent chromium. Greece has adopted the above limit [EC, 1998 Council Directive (98/83/EC)]. Hexavalent chromium and its compounds can originate in the aqueous environment from both anthropogenic (industry wastes and emissions, combustion processes e.t.c.) and natural sources (weathering of chromium bearing minerals). Numerous studies of naturally occurring aqueous Cr(VI) at concentrations up to 73µg/L have been reported in ground and surface waters from New Caledonia, California, Italy and Mexico, associated mainly with serpentine soils and ultramafic rocks (Ball and Izbicki, 2004, Oze et al., 2007, Izbicki et al., 2008, Wise S. and Wise J., 2012).

Given that chromium is a major trace element in both serpentinized ultramafic ophiolitic rocks and Ni-laterites and extended massive serpentinized ultramafic ophiolitic formations and large Ni-laterite deposits are located in the central part of Greece (Lokris and Euboea), (Katsikatsos et al., 1986, Valetton et al., 1987, Eliopoulos and Economou-Eliopoulos, 2000), where previous analytical data had shown significant (several tens of µg/L) Cr(total) concentrations (Megremi 2010), the area of central Euboea had been selected as a case of chromium bearing natural water related to natural processes.

This study is a compilation of geochemical data on the Cr species from central Euboea (Megremi et al., 2012), and neighbouring Assopos-Thiva basins (Atsarou and Economou-Eliopoulos, 2012, Theodoratou and Economou-Eliopoulos, 2012) presented at the International Conference Protection and Restoration of the Environment, held in Thessaloniki (July 2012) and additional data, in an attempt to create relationships between Cr with other elements determined in natural waters and define the sources of the Cr(VI) contamination (natural processes versus human activities).

2. HYDRO-GEOLOGICAL SETTING

In the central Euboea (Figure 1, sampling area 1), the sampled springs have been issued from the upper Cretaceous limestones and are located near to the contact with the underlying upper Jurassic-lower Cretaceous ophiolitic complex. The ophiolitic complex is consisted by serpentinites, diabases and peridotites. The main aquifer of the wells is hosted into the same ophiolitic complex and it is assumed as a fissured rock aquifer. Alluvial deposits comprise the aquifer of many shallow wells used for agricultural activities. The wells have a depth between 4-180m (Megremi, 2010).

In the extended area of Assopos -Thiva basins (Figure 1, sampling area 2), the wells are sited on a thick Neogene formation (up to over 600 m thick), consisted by intercalations of marles, sands, clays and limestones. The aquifer is porous and is consisted of several sub-aquifers, as the clay

intercalations are impermeable by the water. The wells have a depth between 200-220m and those which are used for the agriculture in that area, have a depth between 15-300m. At the southeast of this basin there are the Mavrosouvala wells (at the edge of the sampling area 1, towards Malakasa town, see Figure 1). Those are sited in middle Triassic to middle Lias, limestone formation (up to over 500 m thick) which is the north extension of the thick Parnis Mountain limestone formation (Vasilatos et al, 2010).

3. MATERIALS AND METHODS

A total of 41 groundwater samples were collected from the extended area of the municipality of Messapia and N. Artaki (areas of N.Artaki – Kastella – Psachna – Makrymalli – Kondodespoti) in central Euboea and 21 groundwater samples from the neighboring area of Assopos-Thiva basins (areas of Oropos and Avlona) (Figure 1).

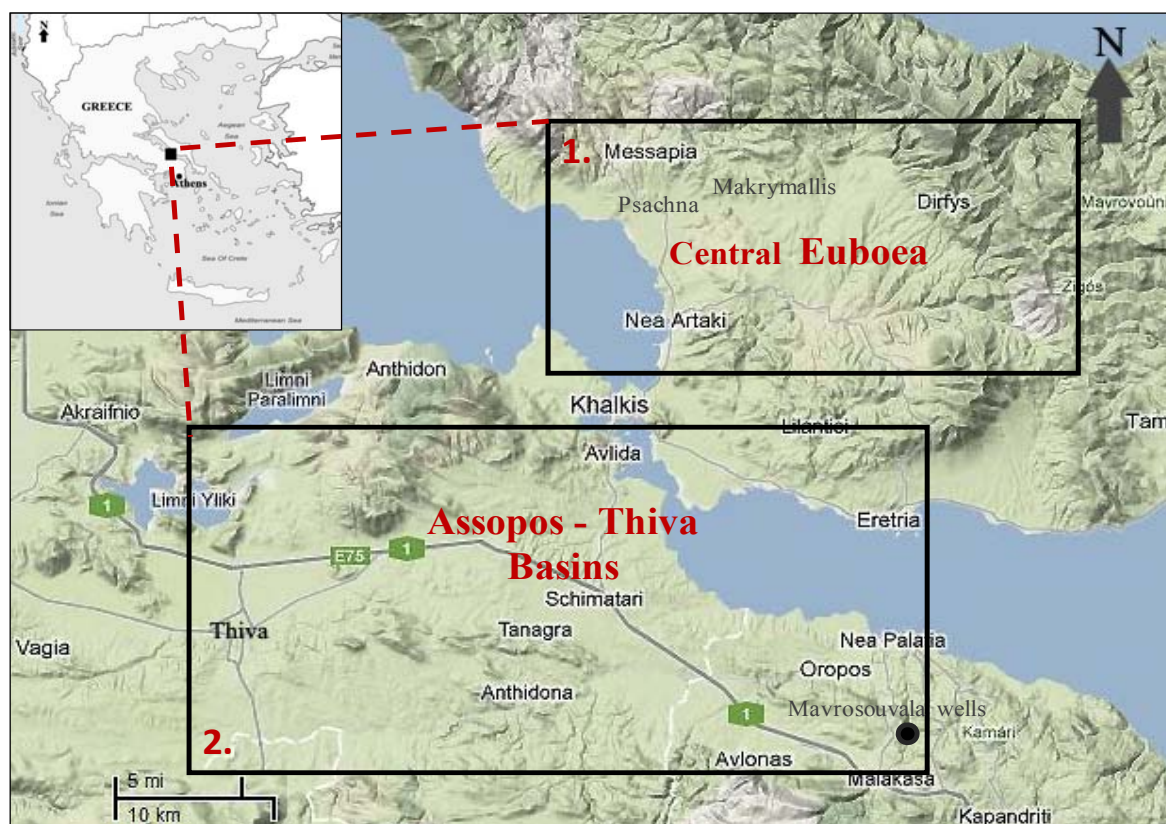


Figure 1. Map of the studied areas. 1. Central Euboea, 2. Assopos-Thiva basins

Physical and chemical sensitive parameters (pH, redox, total dissolved solids, conductivity and temperature) of the water samples were measured in the field using a portable Consort 561 Multiparameter Analyzer. The samples were collected, divided in two portions and each one was stored in polyethylene containers at 4°C in a portable refrigerator. The second portion of each sample was acidified by addition of concentrated HNO₃ acid and stored at 4°C as well.

As the pH reduction could reduce the solubility of hexavalent chromium and any biotic activity could change the valence state of chromium in the samples, the chemical analyses of total and of hexavalent chromium have been performed in the non nitrified portion of the samples, within 24 hours after collection. The analyses of total chromium were performed by GFAAS (Perkin Elmer 1100B). The estimated detection limit of the method was determined at 2 µg/L.

The chemical analyses for Cr(VI) were performed by the 1,5-diphenylcarbohydrazide

colorimetric method, using a HACH DR/4000 spectrophotometer. The estimated detection limit of the method was determined at 4µg/L. The analyses of calcium and magnesium were performed by flame AAS (Perkin Elmer 603). The estimated detection limit of the method was determined at 50µg/L and 20µg/L respectively. All the above analyses were performed at the Laboratory of Economic Geology and Geochemistry in the Faculty of Geology and Geoenvironment of University of Athens.

Other elements (Ni, Mn, Si, Na, K, B, Li, Ba, As, Cd, Co, Cu, P, Pb, S, Se, V and Zn), were analysed, in the acidified portion of the samples, by Inductively Coupled Plasma Mass Spectroscopy (ICP/MS) at the ACME Analytical Laboratories in Canada. The detection limits for those elements are presented along with the analytical results in Table 1.

4. RESULTS - DISCUSSION

Concentrations over the maximum acceptable level for Cr (total) in drinking water (50 µg/L, according to the EU Directive), (EC, 1998) were found in 39% of the total groundwater samples from central Euboea and the Assopos-Thiva basins, which are characterized by widespread industrial activity (Table 1). Relatively high Cr(VI) concentrations have been determined in the groundwater samples, from central Euboea up to 360 µg/L. The ratio of Cr(VI) to Cr(total) ranging from 0.8 to 1 and the very good correlation ($r^2=0.98$, $p=0.000$) between Cr(total) and Cr(VI) indicated that Cr(VI) was the predominant form of dissolved Cr in the areas studied. With the exception of Cr(total), Cr(VI) and in some cases of Zn, and As (Vasilatos et al., 2008, 2010), all the other elements in ground water samples, were detected in concentrations below the maximum permissible limits for human usage (EC, 1998). The range of pH (7.1-7.9) and Eh (-62 to 16mV) measurements of the groundwater indicated slightly alkaline and almost neutral redox conditions, suitable for the stability of Cr(VI) in solution.

The spatial associations of Cr-free (lower than the detection limit of 2µg/L) wells with those with high-Cr concentrations was a common feature in both central Euboea and the Assopos-Thiva basins (Figure 2). On the basis of their concentration in Cr(total) the groundwater samples from the area of Assopos-Thiva basins could be classified into three groups: Group A with Cr(total) concentrations lower than 2µg/L, Group B with Cr(total) between 2 to 50µg/L and Group C with Cr(total) higher than 50µg/L (Figure 2). Although chromium concentrations in the Thiva basin were relatively low, up to 37µg/L (Giannoulouopoulos et al., 2008; Vasilatos et al., 2008; Economou-Eliopoulos et al., 2012), elevated Cr concentrations up to 210µg/L in some irrigation wells northwards of Thiva town were recently presented (Tziritis et al., 2012).

With respect to the source of Cr(VI) contamination it has been suggested (Stamatis et al., 2012) that in the Assopos basin, concentrations lower than 50µg/L are mainly related with the weathering products of the ultramafic rocks whilst Tziritis et al. (2012) concluded that the high Cr values in the Thiva basin are related with anthropogenic activities. In general, literature data suggest that soil geochemistry and mineralogy may be major factors controlling the kinetics and mechanisms of Cr(III) and Cr(VI) solid-phase interactions (Izbicki et al., 2008). In addition, it has been suggested that chromium fate and transport could be described by sorption processes, that may be kinetically controlled or in equilibrium with the soil solution and that although Cr(VI) is strongly sorbed by Fe-oxides at acidic and near neutral pH it is not strongly sorbed at higher pH (Izbicki et al., 2011).

Available data on the groundwater from central Euboea and the Assopos-Thiva basins indicated that it has either Ca-HCO₃ or Mg-HCO₃ composition and that there is a wide variation in various trace element concentrations (Megremi, 2010; Theodoratou, 2011; Atsarou, 2011).

Table 1. Trace elements concentrations in groundwater from central Euboea and Assopos-Thiva basins.

Location	Samples	µg/L											
		Cr(total)	Cr(VI)	Ca	Mg	Ni	Mn	Si	Na	K	B	Li	
Central EUBOEA (*)	E1	33	32	30200	50200	1.6	<0.05	12800	22300	1230	30	2.7	
	E2	130	128	17700	81200	4.2	<0.05	19800	72700	12400	146	6.8	
	E3	53	51	31960	76300	5.1	0.11	16900	37600	1670	38	4.1	
	E4	60	59	33100	74500	4.4	0.11	16300	38000	1600	35	4	
	E5	114	110	63700	103100	3.6	<0.05	17400	40200	4800	61	5.8	
	E6	70	68	16500	113600	1.8	0.13	24500	52700	3900	68	6.8	
	E7	360	360	64000	124800	4.8	<0.05	27700	31700	1950	42	7.3	
	E8	70	64	64000	154600	5.8	<0.05	20300	97900	1060	79	16.4	
	E9	86	83	59100	88900	3	0.07	19300	44300	1790	47	11.1	
	E10	105	104	64500	114600	4.6	<0.05	15400	37600	910	35	4.6	
	E11	68	63	113000	86900	3.6	0.26	13300	38800	2470	36	6.3	
	E12	75	62	75300	56100	0.5	0.93	12900	25100	2750	28	5.6	
	E13	56	56	141500	133600	5.4	<0.05	13000	79400	4530	88	9.1	
	E14	16	16	15300	59000	8.9	<0.05	24100	15800	600	25	2.4	
	E15	25	25	19900	52300	2.1	<0.05	24300	19600	500	21	3.8	
	E16	18	18	35300	28400	0.3	<0.05	10000	12400	450	10	0.2	
	E17	37	36	7400	66800	0.8	<0.05	33000	21000	320	19	4.3	
	E18	33	32	94000	44900	5.2	1.18	19800	19400	670	19	2	
	E19	32	32	95000	45400	5.8	0.8	18800	19300	650	19	2	
	E20	16	12	98600	51600	11	1.56	23200	22300	460	25	2.7	
	E21	13	12	121700	28600	33	0.52	14300	18800	480	22	2.1	
	E22	52	51	77800	83100	3.8	1.11	27900	29900	320	29	3.5	
	E23	15	15	9500	79600	1	0.5	34100	14700	380	15	1.6	
	E24	14	14	17800	81500	4.5	<0.05	34100	35100	1220	16	2.3	
	E25	37	36	8900	67500	0.9	<0.05	32000	21600	350	21	4.5	
	E26	31	30	48600	74100	1.9	0.08	30700	21700	350	23	3.7	
	E27	33	32	47600	74200	2.3	0.13	29900	21600	350	23	3.4	
	E28	27	26	94400	43400	4.1	<0.05	20700	19100	670	17	1.9	
	E29	26	25	65400	69900	2.4	0.43	26500	22600	580	17	2.7	
	E30	18	18	36600	26900	6.8	<0.05	15400	15300	2300	19	1.6	
	E31	17	12	113000	26400	11	0.06	14100	16000	1770	24	1.6	
	E32	15	15	68200	55800	7.2	0.8	23700	15500	460	26	2.1	
	E33	<2	<4	98000	5200	1.5	0.18	4090	12000	450	10	1.4	
	E34	<2	<4	46200	7700	1.4	<0.05	5600	14200	1070	13	0.7	
	E35	2	<4	53400	11100	0.1	<0.05	6800	15400	680	11	2.2	
	E36	3	<4	43600	9700	0.7	<0.05	6400	14000	470	11	0.9	
	E37	<2	<4	51100	4400	0.1	<0.05	3900	12000	410	8	1	
	E38	5	<4	118000	12900	1.9	0.23	6900	10800	360	10	0.7	
	E39	22	20	84900	421006	0.9	0.35	7600	65500	2040	24	3.7	
	E40	23	20	85400	43000	0.6	0.19	7500	66500	2010	23	3.5	
	E41	23	19	86200	43600	0.7	<0.05	7500	65600	1990	23	3.7	
AVLONA (**)	Avlo 2W	4	<4	77000	64000	4	2	13000	78000	3000	60	10	
	Avlo 3W	20	16	41000	61000	1	5	22000	32500	1500	50	15	
	Avlo 4W	50	48	44000	56000	8	3	19000	33000	700	40	10	
	Avlo 5W	55	52	35000	66000	5	4	19000	33000	1000	30	10	
	Avlo 6W	32	30	59000	58000	4	9	16500	29000	2000	30	10	
	Avlo 7W	45	40	39000	71000	7	7	19000	31000	1000	35	10	
	Avlo 8W	56	50	62000	61000	3	3	16000	35000	1100	30	10	
	Avlo 9W	58	50	40000	95000	10	5	23000	104000	1200	420	20	
	Avlo 10W	25	20	25000	132000	14	9	22000	80000	2500	95	20	
	Avlo 13W	76	65	37000	63000	3	2	20000	24000	700	30	6	
	Avlo 14W	90	85	40000	60000	<0.2	2	22000	28000	600	30	10	
	Avlo 15W	<2	<4	56000	11000	<0.2	<0.05	5000	7000	400	9	1	
	OROPOS (***)	D1	137	121	48300	89500	1.3	20	13400	126500	1580	120	24
		D2	138	118	49200	92150	1.6	20	13100	115400	1570	130	23
		XV	58	53	43700	69450	1.1	0.88	9550	117500	1500	120	23
XD		54	46	46200	72000	0.3	0.34	9800	115900	1600	120	24	
XX1		10	4	32400	46600	0.4	<0.05	8900	109100	2400	130	20	
GN		32	25	123200	118700	8.6	<0.05	12100	114500	2350	78	14	
GM		55	49	202600	185500	7.1	0.18	12700	84200	2200	78	16	
GSR		23	11	71300	77000	3.9	0.12	18900	55000	1200	58	19	
GK	52	45	119400	172900	7.9	<0.05	19300	168700	2160	200	31		
Detection Limits		<2	<4	50	50	0.2	0.05	1	50	50	5	0.05	
Parameter values(****)		50µg/L			20µg/L		50µg/L	200mg/L		12mg/L	1.0mg/L		
Data from (*)Megremi, 2010, (**)Atsarou, 2011, (***)Theodoratou, 2011													
Parameter values (****) according to EC (1998), Council Directive (98/83/EC)													

Table 1. Continued

Location	Samples	µg/L										mg/L
		Ba	As	Cd	Co	Cu	P	Pb	Se	V	Zn	S
Central EUBOEA (*)	E1	13	0.9	<0.05	0.11	0.4	<20	0.05	0.9	1.9	0.25	15
	E2	8	0.7	<0.05	0.16	1.1	<20	0.05	1.5	3.1	2.2	41
	E3	10	0.8	<0.05	0.12	0.5	<20	0.05	1.2	2.5	110	29
	E4	15	0.8	<0.05	0.09	1.0	<20	0.05	1.2	2.5	10	28
	E5	45	0.9	<0.05	0.22	0.6	<20	0.05	2.1	2.7	0.5	68
	E6	2	1.4	<0.05	0.2	0.8	<20	0.05	3.5	4	0.9	27
	E7	9	0.7	<0.05	0.29	1.3	<20	<0.01	1.6	2.1	0.7	44
	E8	25	2	<0.05	0.15	1.1	<20	<0.01	5.4	5.8	3.9	58
	E9	23	1.3	<0.05	0.07	0.8	<20	<0.01	2.2	4.3	2.6	32
	E10	10	0.6	<0.05	0.21	0.8	<20	<0.01	1.1	2.2	5.7	52
	E11	30	1.6	<0.05	0.05	1	<20	<0.01	2.1	2.2	89	57
	E12	38	1.7	0.09	<0.02	0.5	<20	1.1	1.4	1.8	527	13
	E13	59	1.4	<0.05	0.19	1.9	<20	<0.01	3.5	2.1	1.2	110
	E14	1	0.5	<0.05	0.04	0.4	<20	0.05	0.7	3	1.9	7
	E15	9	0.7	<0.05	0.02	0.3	<20	0.05	0.25	6.1	0.25	6
	E16	4	<0.5	<0.05	0.04	0.3	<20	0.05	0.5	1	0.25	3
	E17	2	0.5	<0.05	<0.02	0.3	<20	0.05	0.8	8.4	0.25	1
	E18	15	<0.5	<0.05	0.12	24.8	30	1.5	1.4	1	55	19
	E19	15	<0.5	<0.05	0.13	3	32	0.6	1.3	1	48	17
	E20	20	<0.5	0.08	0.24	5.9	37	10.6	1.7	1.7	2637	29
	E21	16	<0.5	<0.05	0.11	1.4	35	0.2	1.1	0.7	48	13
	E22	20	<0.5	<0.05	0.25	1.1	43	0.05	2.5	2.3	2.2	35
	E23	0	2.6	<0.05	0.03	0.3	<20	0.05	0.8	3.4	0.6	8
	E24	3	1.5	<0.05	0.02	0.5	<20	0.05	1.4	6.8	0.25	13
	E25	2	0.5	<0.05	<0.02	0.3	<20	0.05	1	9.3	0.25	1
	E26	19	<0.5	<0.05	0.03	0.5	35	0.05	1.2	6.1	0.9	5
	E27	19	<0.5	<0.05	0.05	0.6	33	0.05	1.3	6.2	0.7	4
	E28	15	<0.5	<0.05	0.1	0.4	34	0.05	1.4	1.1	0.25	19
	E29	21	<0.5	<0.05	0.06	0.4	33	0.05	1.1	0.8	0.6	5
	E30	6	0.5	<0.05	0.06	0.2	<20	0.05	0.25	1	0.25	6
	E31	8	<0.5	<0.05	0.08	0.4	75	0.05	0.8	0.7	0.25	5
	E32	11	<0.5	0.07	0.04	2.5	34	2.1	1.5	1.9	6086	7
	E33	24	<0.5	<0.05	0.03	7.1	34	0.2	0.5	0.4	32	5
	E34	13	0.6	<0.05	0.07	0.2	<20	0.05	0.5	1.2	0.25	6
	E35	11	0.7	<0.05	0.02	0.2	<20	0.05	0.7	1.3	0.25	5
	E36	8	<0.5	<0.05	0.06	0.3	<20	0.05	0.7	0.5	1.1	5
	E37	7	0.5	<0.05	0.02	0.3	<20	0.05	0.5	0.7	0.25	4
	E38	6	<0.5	<0.05	0.03	1.1	34	0.05	0.5	0.4	0.8	4
	E39	30	1.8	<0.05	0.06	3.5	<20	0.05	2.2	2.5	25	13
	E40	22	2	<0.05	0.05	2	<20	0.05	2.3	2.3	16	11
	E41	26	2	<0.05	0.06	1.5	<20	0.05	2.4	2.1	0.5	12
AVLONA (**)	Avlo 2W	120	1	<0.05	0.06	1.2	<20	<0.1	1	3	1	35
	Avlo 3W	15	4	<0.05	<0.02	1.1	<20	<0.1	1	8	1	4
	Avlo 4W	18	1	<0.05	<0.02	1.2	<20	<0.1	1	4	1	7
	Avlo 5W	21	1	<0.05	0.04	0.6	<20	<0.1	1	5	<0.5	7
	Avlo 6W	78	2	<0.05	0.03	1.1	<20	<0.1	1	5	<0.5	7
	Avlo 7W	28	1	<0.05	0.06	0.2	<20	<0.1	2	5	<0.5	6
	Avlo 8W	51	3	<0.05	<0.02	0.7	<20	<0.1	1	6	<0.5	8
	Avlo 9W	12	1	<0.05	1.34	0.7	<20	<0.1	1	8	1	20
	Avlo 10W	23	2	<0.05	2.58	0.6	<20	<0.1	3	8	1	35
	Avlo 13W	14	1	<0.05	0.19	1.2	<20	<0.1	1	4	1	5
	Avlo 14W	29	3	<0.05	<0.02	0.4	<20	<0.1	1	8	<0.5	4
Avlo 15W	9	1	<0.05	<0.02	0.7	<20	<0.1	<0.5	1	<0.5	3	
OROPOS (***)	D1	100	1.6	<0.05	0.05	1.5	<20	0.5	4.5	4.3	502	13
	D2	110	1.6	<0.05	0.05	1.5	<20	0.7	3.9	4.4	368	13
	XV	67	2.6	<0.05	<0.02	2.4	<20	<0.1	4.7	3	55	14
	XD	58	2.9	<0.05	<0.02	1.6	<20	<0.1	4.5	3.3	4	16
	XX1	49	2.2	<0.05	0.37	1.6	<20	<0.1	2.7	1.6	3.1	14
	GN	120	3.7	<0.05	0.41	1.7	<20	<0.1	4.3	4.8	0.5	51
	GM	81	4.2	<0.05	0.28	1.3	<20	<0.1	6.8	4.8	27	97
	GSR	43	1.4	<0.05	<0.02	0.8	<20	<0.1	2.8	4.3	1	8
GK	50	4.1	<0.05	0.33	2.3	<20	<0.1	8.9	7.5	1	71	
Detection Limits		0.05	0.5	0.05	0.02	0.1	20	0.1	0.5	0.2	0.5	1
Parameter values(****)		10µg/L		5.0µg/L		2mg/L		10µg/L		10µg/L		
Data from (*)Megremi, 2010, (**)Atsarou, 2011, (***)Theodoratou, 2011												
Parameter values (****) according to EC (1998), Council Directive (98/83/EC)												

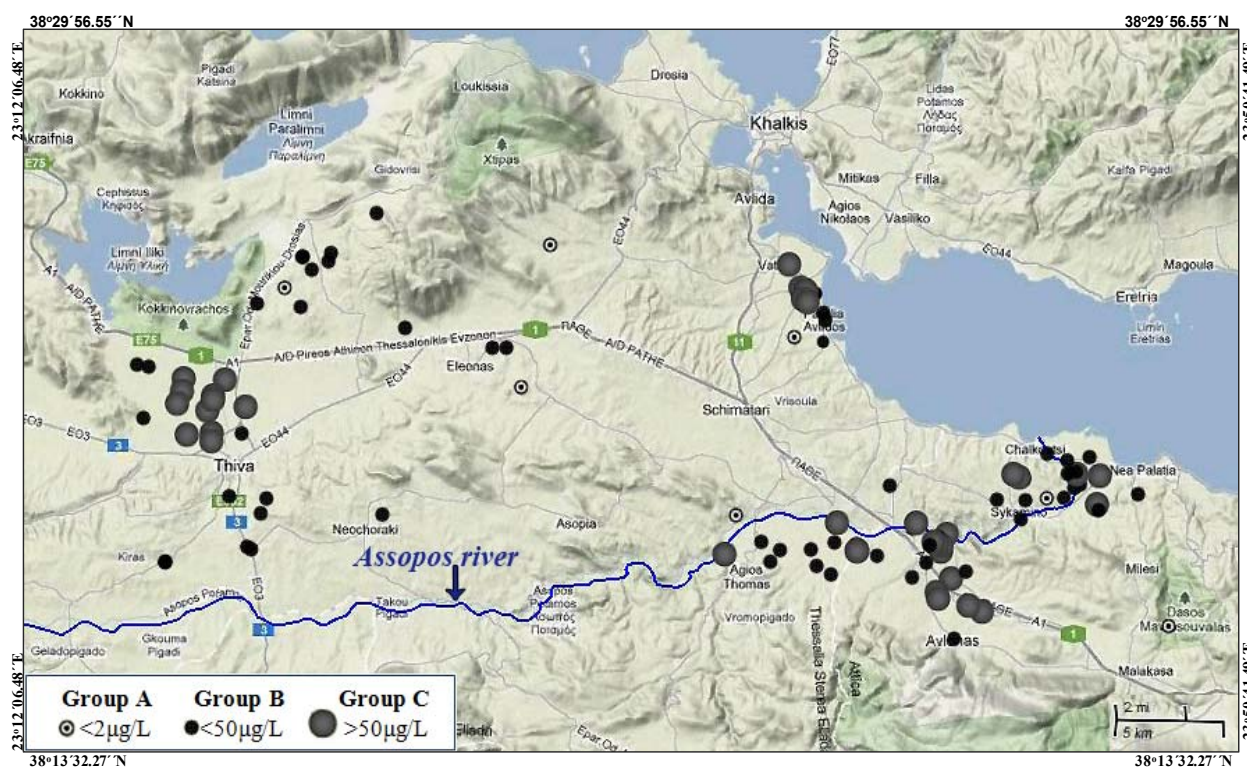


Figure 2. Distribution of the Cr(total) concentrations (in $\mu\text{g/L}$) throughout the extended areas of Assopos and Thiva basins. (Data from Giannouloupoulos, 2008; Vasilatos et al., 2008; Atsarou, 2011; Theodoratou, 2011; Economou-Eliopoulos et al., 2012; Tziritis et al., 2012).

Since Ca, Mg, Na, Si and B are common components of water, rocks and sea-water the plots of Mg/Si, Mg/Na versus Ca/Na, B versus Si/(Si + Na) and B versus Ma/Si ratios are given (Figure 3) in order to evaluate the role of the water-rock interaction and the degree of the sea-water contribution into the groundwater aquifer.

A water-rock interaction model has been applied by Fantoni et al. (2002) and concluded that magnesium-rich water is normally produced through interaction of meteoric water with ultramafic rocks. Such an origin of chromium in groundwater of central Euboea by natural processes seems to be consistent with the strong correlation coefficients between Cr(total) and Mg ($r^2=0.56$, $p=0.000$), Cr(total) and Si ($r^2=0.52$, $p=0.000$) and Mg - Si ($r^2=0.96$, $p=0.000$), in contrast to the water samples from the Assopos basin with high Cr(VI) concentrations, and low values of the correlation coefficients between Cr(total)-Mg ($r^2=0.03$, $p=0.409$), Cr(total)-Si ($r^2=0.12$, $p=0.119$) and Mg-Si ($r^2=0.23$, $p=0.021$). Therefore, the above correlations between elements which are components of ophiolitic rocks seem to be consistent with the Cr(VI) origin in groundwater of central Euboea mainly from the ophiolitic rocks. As any correlation between Cr(total) and Ni or Fe concentrations in groundwater is lacking, the enrichment of waters from central Euboea in Cr(VI), may be linked mainly with Cr-extraction from Cr-bearing silicate minerals (serpentinite and chlorite) hosted in ophiolitic rocks and its subsequent oxidation rather than Fe-oxides.

On the basis of the geochemical data (Table 1, Figure 3c,d) an assessment of the degree of salinization is given. More specifically, the plots of B vs Si/(Si+Na) and Mg/Na vs Ca/Na (Figure 3c,d) provide evidence for the degree of the sea water contribution into the groundwater aquifer (salinization) throughout the Assopos-Thiva basins. The highest degree of the water salinization was recorded in the Avlida area. Also, based on the Na, B, Mg and Cr concentrations, the water samples from central Euboea can be distinguished to (a) those influenced by the sea water, having high Na, K and B concentrations and (b) those with lower B and Na concentrations and a great variation as far as Cr(total) concentrations.

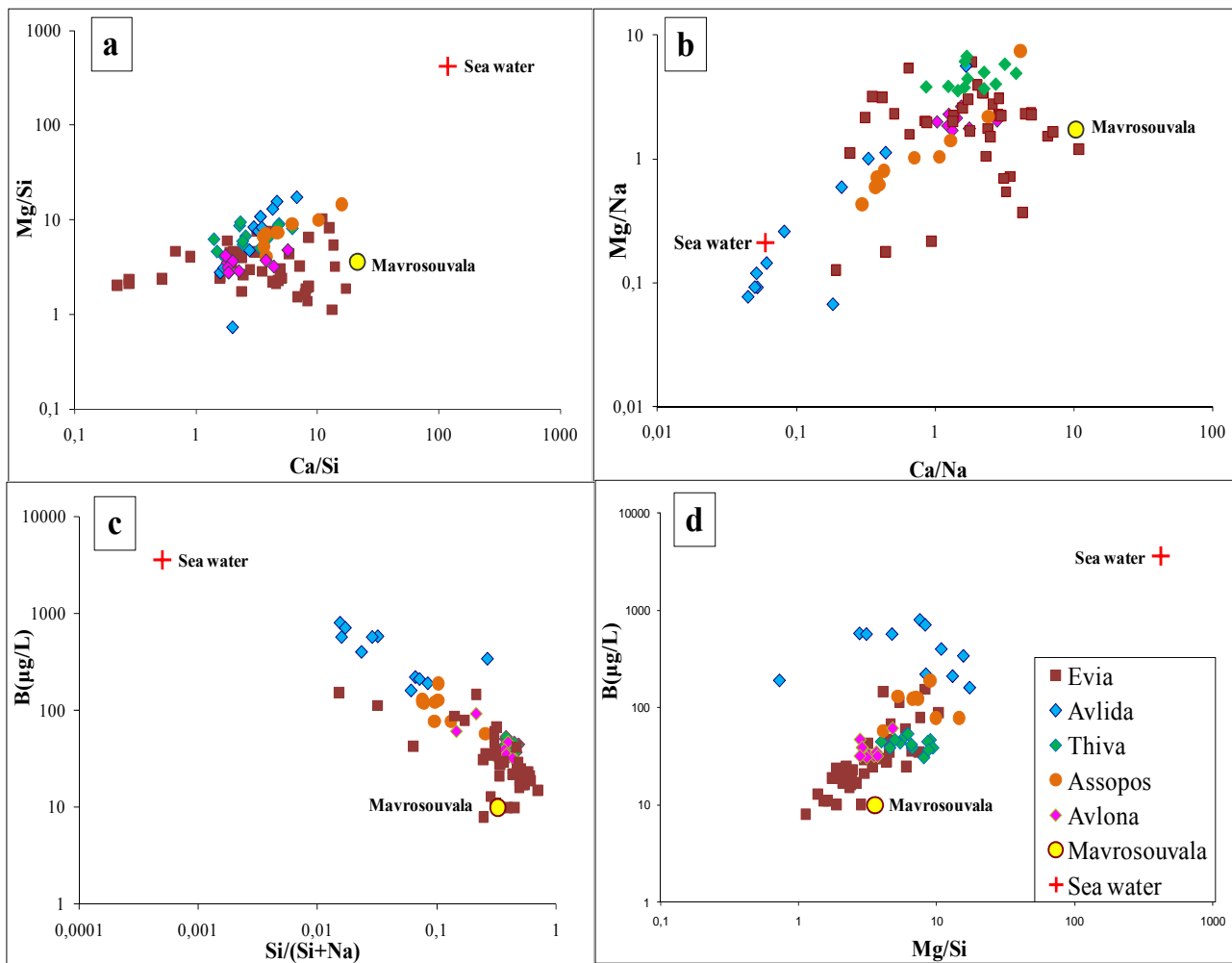


Figure 3. Variation of Mg/Si vs Ca/Si (a), Mg/Na vs Ca/Na (b), B vs Si/(Si+Na) and Mg/Si (c, d) in groundwater wells from Oropos, Avlona, Avlida (Assopos), Thiva and Central Euboea. Data: Vasilatos et al. (2008), Megremi, (2010), Moraki, (2010), Atsarou (2011), Theodoratou (2011), Economou-Eliopoulos et al. (2012).

The most salient feature concerning the composition of groundwater at central Euboea is the presence of a group of wells located exclusively within peridotites with average value for Cr(total) equal to $25\mu\text{g/L}$, and Mg/Si ratio value equal to 2,3 (Figure 4), in contrast to the Mg/Si ratio in the water samples exhibiting high Cr concentrations, ranging from 3,9 to 10,2. Also, due to the absence of anthropogenic sources of Cr, relatively high Cr(VI) concentrations ($5 - 73\mu\text{g/L}$) in groundwater have been attributed (Fantoni et al., 2002) to the associated serpentinized ultramafic ophiolites. Thus, data published by Fantoni et al., 2002 for groundwater interacting with ophiolitic rocks, exhibit similar value of the Mg/Si ratio (mean value equal to 2.03) and are projected in the same field to that of central Euboea samples with a mean value of Cr(total) equal to $25\mu\text{g/L}$ (Figure 4).

In addition, the case of central Euboea, could be compared with that of the neighbouring area of Assopos-Thiva basins (Eastern Greece) where the impact of anthropogenic activities on groundwater quality is more intense. The analytical data of groundwater values from Assopos-Thiva basins of the present study were projected along with published data for the same area (Vasilatos et al., (2008),(2010), Moraki, 2011, Atsarou 2011, Theodoratou, 2011) in a bivariate plot of the Ca/Si versus Mg/Si ratios (Figure 5). The groundwater samples from the Assopos-Thiva basins that are characterized by high Cr concentrations fall in the same field that comprise the groundwater samples of elevated Cr concentrations from Euboea, exhibiting a similar variability in Mg/Si ratio (2.9 to 10.3), and probably linked to the industrial activities in the area. In contrast, the Mg/Si ratio is lower in central Euboea samples with a mean value of Cr(total) equal to $25\mu\text{g/L}$ due to the elevated concentrations of Si as a result of water interaction with the Mg-rich silicate minerals of ophiolitic rocks.

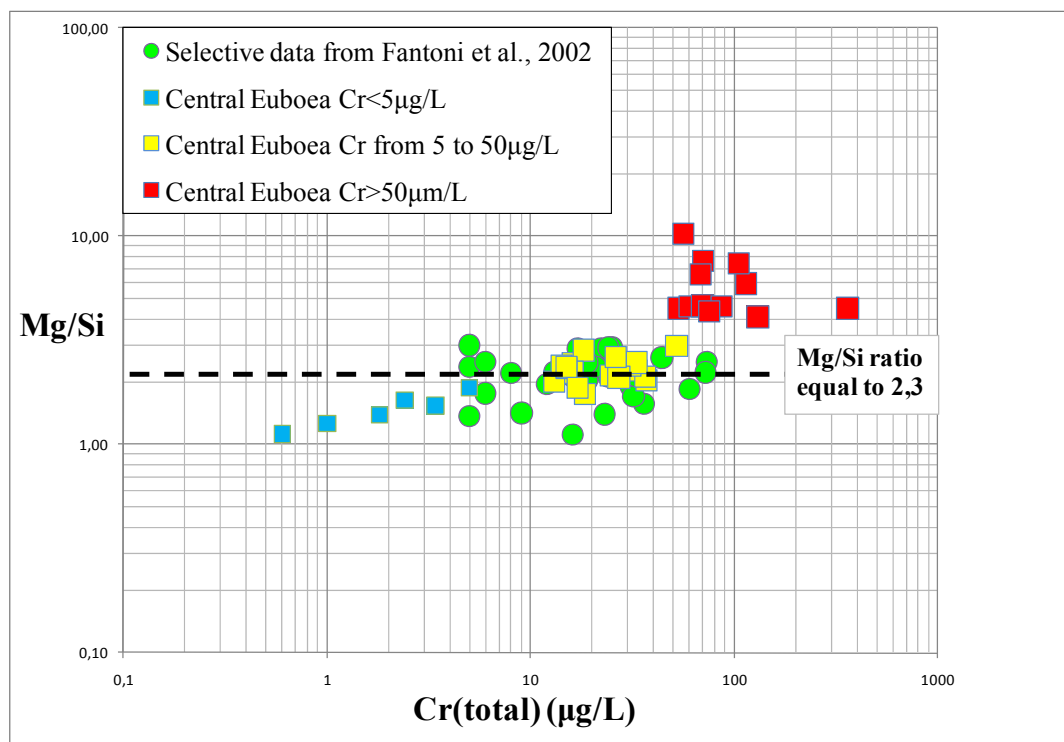


Figure 4. Bivariate plot of Mg/Si versus Cr showing the trends and the variations of the chemical composition of the water samples from central Euboea in comparison with international data (the dashed line corresponds to the value of Mg/Si ratio equal to 2,3). Data from Megremi (2010), Fantoni et al. (2002).

The majority of water samples show a wide variation in the Cr concentration throughout the whole region of the Assopos – Thiva basins and central Euboea, but it seems likely that in the latter the highest values of Cr(VI) were recorded in alluvial aquifers, and fall into the field of shallow wells. In contrast deep wells of karst-type are characterized by Cr concentrations below detection limit (Figure 5). Moreover, the Ca/Si ratio (Figure 5) of the samples from the karstic limestone Mavrosouvala aquifer is higher than the ratio of the rest samples from the Assopos-Thiva basins and the samples from central Euboea as well, due to the host rocks which are mainly composed by limestone.

Although the presented plots (Figures 3, 4, 5 & 6) are not necessarily discrimination diagrams they provide some evidence for the source of the Cr contamination in groundwater. In particular, the bivariate plot of Ca/Si versus Mg/Si has been successfully used for the discrimination and the identification of the origin of the water samples from central Euboea and Assopos -Thiva basins, related mostly to natural processes the former, and anthropogenic origin the latter.

In addition, the available analytical data (Megremi, 2010; Atsarou, 2011) indicated that higher Cr concentrations in groundwater fall into the field of shallow wells, whilst deep wells of karst-type are characterized by Cr concentrations below detection limit (Figure 6).

Since the common oxidation stage of chromium in rock-forming minerals is mostly Cr(III), its release into aqueous solutions requires oxidation to Cr(VI). Besides the source of chromium in soils (alluvial formation) and the possibility of its oxidation by various electron acceptors, such as Mn-oxides, oxidation driven by atmospheric oxygen may facilitate the oxidation of chromium as well. Thus, the Cr(III) oxidation, in particular in cultivated soils, may be a major controlling factor for the elevated Cr(VI) values in the shallow irrigation wells, representing circulation water within relatively oxidation conditions.

Since the contamination of the domestic and irrigation wells, by either Cr(VI) and seawater, may affect directly the human health and the quality of the crops in the cultivated areas and in turn the human food-chain, the proposed solution of the crucial environmental problem in central Euboea

and the Assopos-Thiva basins is the use of the deep karst-type aquifer instead the shallow-Neogene ones.

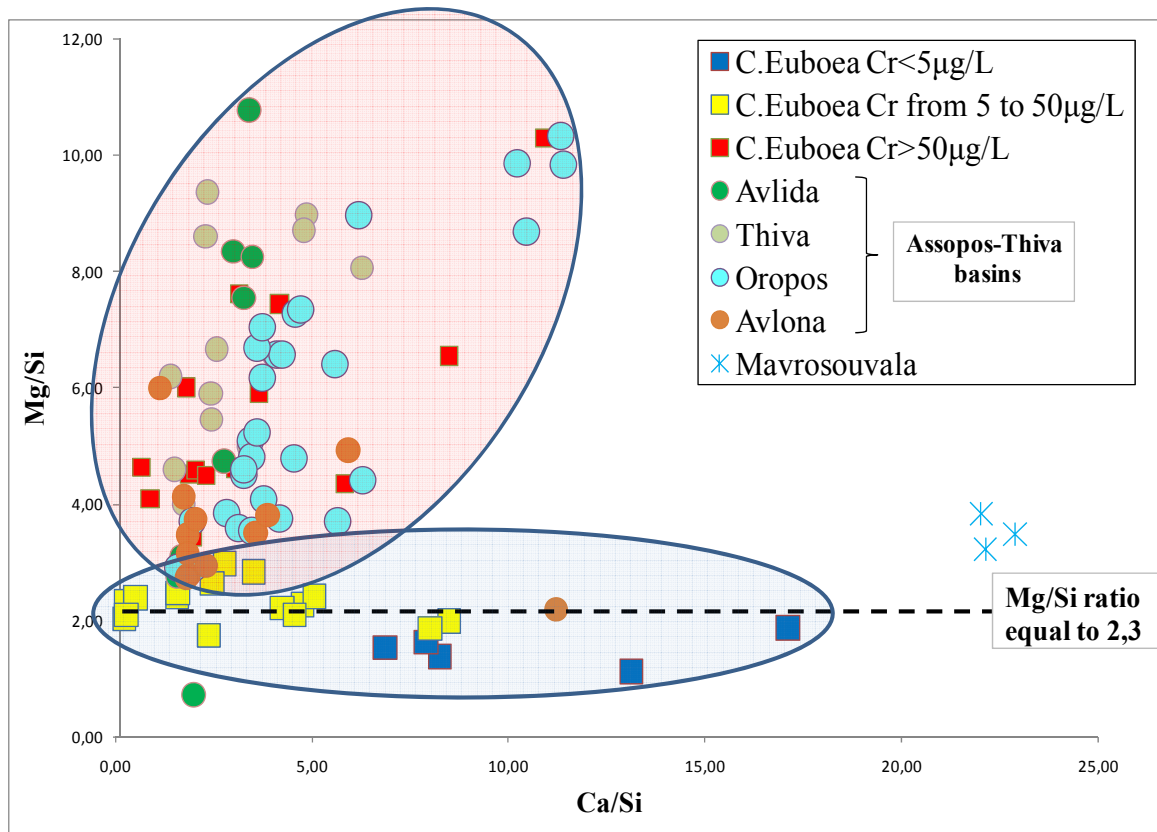


Figure 5. Bivariate plot of Ca/Si vs Mg/Si showing the different trends and the variations of the chemical composition of the water samples from central Euboea, Assopos-Thiva basins and Mavrosouvala (data from Vasilatos et al. (2008), Megremi, (2010), Moraki, (2011), Vasilatos et al. (2011), Economou-Eliopoulos et al. (2012))

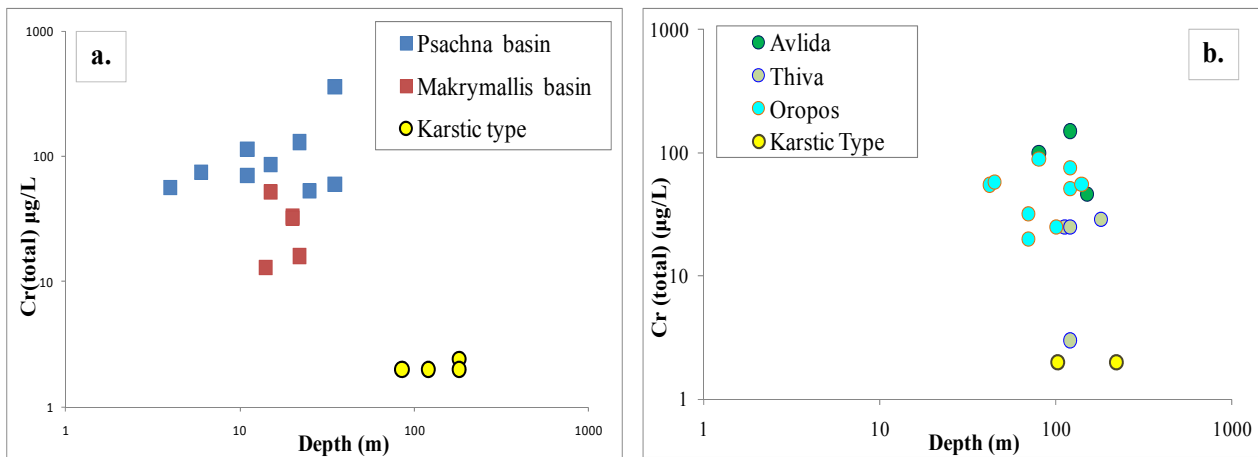


Figure 6. Bivariate plot of wells depth from a) central Euboea and b) the extended area of Assopos -Thiva basins versus their Cr (total) concentrations. Data from Vasilatos et al. (2008), Megremi (2010), Moraki (2011), Theodoratou (2011), Economou-Eliopoulos et al. (2012).

5. CONCLUSIONS

The geochemical data of water samples evaluated in accordance with the local geological settings from central Euboea and the Assopos-Thiva basins lead to the following conclusions:

- Significant concentrations over the maximum acceptable level of total Cr in drinking water have been detected in both areas.

- The spatial associations of Cr-free (lower than the detection limit of 2 µg/L) wells with those with high-Cr concentrations is a common feature in both central Euboea and the Assopos-Thiva basins
- The bivariate plot of Ca/Si versus Mg/Si has been successfully used for the discrimination and the identification of the origin of the water samples from central Euboea and Assopos-Thiva basins.
- The contamination by Cr(VI) of the groundwater in central Euboea may be mainly linked to the chromium extraction and oxidation from the Cr-bearing silicate minerals of serpentinites of the ophiolitic rocks and lesser to chromite and to Cr-bearing goethite which is abundant in Fe-Ni laterite deposits.
- The composition of groundwater in central Euboea with Cr(total) values ranging from 5 to 50 µg/L (mean value equal to 25µg/L) and Mg/Si ratio up to 2,3 is attributed to natural processes of water interactions with the silicate minerals of ultramafic rocks.
- The water samples from central Euboea and the Assopos-Thiva basins exhibiting high Cr(VI) concentrations, up to 360 µg/L and a variability in the value of Mg/Si ratio, is probably related to human activities.
- Regardless the source of the groundwater contamination by Cr(VI) it seems likely that deep wells of karst-type could be used to supply water instead of the alluvial deposits strongly affected by probably both anthropogenic activities and natural processes.
- The contamination of the irrigation wells throughout the Assopos-Thiva basins, by either Cr(VI) and seawater may affect the quality of the crops in the cultivated areas and in turn the human food-chain.

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