

GEOCHEMICAL CHARACTERISTICS OF NATURAL WATERS CONTAMINATED BY HEXAVALENT CHROMIUM, IN EASTERN STEREA HELLAS, GREECE

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Abstract: The chemistry of the groundwater in Eastern Sterea Hellas (central Euboea and Asopos valley), central Greece, has revealed high concentrations of hexavalent chromium in groundwater systems exceeding, sometimes, the Greek and the EU drinking water maximum acceptable level for total chromium. The environmental impact of hexavalent chromium is a controversial issue critical to the protection of groundwater resources. By using the GFAAS for total chromium, diphenylcarbazide-Cr(VI) complex colorimetric method for hexavalent chromium, and flame-AAS and ICP-MS for other toxic elements, their concentrations were investigated in several groundwater samples. According to the results of this analytical work, the geochemical differences of those waters and the origin of the hexavalent chromium are discussed. The contamination of water by hexavalent chromium in central Euboea is mainly linked to natural processes, but there are cases that it is associated with anthropogenic activities. In Asopos valley the hexavalent chromium pollution is associated with the industrial wastes.

Keywords: water chemistry, pollution, hexavalent chromium, toxic elements, Central Euboea, Asopos valley.

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). The speciation of chromium in groundwater is governed by pH and Eh. The Cr(VI) in groundwater can be reduced to Cr(III) in low pH, under reducing conditions. In environmental systems, Cr(VI) exists as oxyanions such as chromate (CrO_4^{2-}), bichromate (HCrO_4^-) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) and has a high solubility in water. In contrast, Cr(III) has a low solubility in water and readily precipitates as $\text{Cr}(\text{OH})_3(\text{s})$ or mixed Cr-Fe hydroxides in pH values greater than 4 (Schlautman and Ihnsup, 2001).

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 northern (Kastoria and Edessa) and central (Lokris and Euboea) parts of Greece (Katsikatsos et al., 1986; Eliopoulos and Economou-Eliopoulos, 2000; Valetton et al., 1987), representative water samples from these

areas were collected and analysed for hexavalent chromium.

Since the preliminary analytical data for Cr(VI) concentration of several water samples throughout Greece, had shown significant (some tens of $\mu\text{g}\cdot\text{L}^{-1}$) Cr(VI) concentrations (Megremi, 2010), and Cr(total) concentrations (Vardaki and Keleperthis, 1999; Megremi, 2010), the area of central Euboea was selected for a systematic investigation for water contamination related to natural processes. Moreover, the widespread industrial activity in Asopos valley with the usage of hexavalent chromium in various industries and the preliminary analytical data presented by Vasilatos et al (2008), has guided us to select that region as a representative area for natural water pollution by Cr(VI) related to anthropogenic processes.

The objective of this study was to compare field and laboratory data on the hexavalent chromium in the groundwaters of central Euboea and Asopos valley, (Fig. 1).



Fig. 1. Map of the studied areas showing the distribution of hexavalent chromium in groundwater. Lower: Asopos Valley, Upper: Central Euboea, (additional data from Vasilatos et al, 2008 and Megremi, 2010).

1.1 Hydro-geological characteristics

In the central Euboea (Fig. 1, upper), 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, con-

sisted of unconsolidated material of sand and rounded-angular pebbles, deposits of loose clayey-sandy material and material and terra rossa with rounded-angular pebbles, comprise also the aquifer of many shallow wells (with a depth up to 15m) used for agricultural activities.

In the Asopos valley (central and north part of the sampling area 1) (Fig. 1, lower), there are the wells for the water supply of the municipalities of Oropos, Oinofyta, and Schimatari. Those 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 for the urban water supply of those municipalities have a depth between 200-220m and those which are used for the agriculture in that area, have a depth between 20-300m.

At the southeast of this basin there are the Mavrosouvala wells (Fig. 1). Those are sited in a 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. These wells are pumping water from a karstic aquifer. The source of groundwater recharge is the Parnis limestone. The water is being used for the municipal water supply of the city of Athens and some of the surrounding towns and villages in the area.

2. Materials and Methods

The water sampling areas, located at the eastern Sterea Hellas, are shown on Fig. 1. The central Euboea is shown in the upper map and Asopos valley (Oropos, Inofyta, Schimatari) which is shown in the lower map. A total of 16 ground water samples were collected from both areas (9 from central Euboea and 7 from Asopos valley).

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.

Knowing that 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 not 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 1 µg.L⁻¹. The chemical analyses for Cr(VI) were performed by the 1,5-diphenylcarbohydrazide colorimetric method, within 24 hours after sampling, using a HACH DR/4000 spectrophotometer. The estimated detection limit of the method was 4 µg.L⁻¹. The analyses of calcium and magnesium were performed by flame AAS (Perkin Elmer 603). The estimated detection limit of the

method was determined at 50 µg.L⁻¹ and 20 µg.L⁻¹ 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.

The other elements (Ni, Mn, Zn, Si, Na, K, B, Li, As, Cd, Co, Cu, P, Pb, S, Se, V, Fe), were analysed, in the acidified portion of the samples, by Inductively Coupled Plasma Mass Spectroscopy (ICP/MS) at the ACME Analytical Laboratories in Canada.

For the statistics, the spatial distribution of hexavalent chromium and the interpretation of those results, additional data published by Megremi, (2010) for central Euboea groundwaters and by Vasilatos et al. (2008) for the Asopos valley groundwaters have been used.

3. Results and Discussion

The analytical results for the analyzed groundwater samples are presented in tables 1 and 2. The water samples from both areas were classified into 3 groups according to the observed differences in their hexavalent chromium compound [$<4 \mu\text{g.L}^{-1}$, $<50 \mu\text{g.L}^{-1}$, $>50 \mu\text{g.L}^{-1}$] (Fig 1). Concentrations over the maximum acceptable level for total Cr in drinking water (50 µg/L, according to the EU Directive (EC, 1998), were found in several groundwater samples from central Euboea and from Asopos valley as well.

The contamination of natural waters in central Euboea, with hexavalent chromium, may be mainly linked to the Cr-extraction and oxidation from Cr-bearing serpentinite in ophiolitic rocks that host along with the limestone the aquifer and lesser to chromite [FeCr₂O₄] and to Cr-bearing goethite [FeO(OH)] which is abundant in Fe-Ni laterite deposits. The serpentine and chlorite are the most common minerals in the ophiolitic rocks.

The above suggestion for the origin of hexavalent chromium is enhanced by the good positive correlation coefficients between Cr(total) versus Mg (0.70) and Cr(VI) versus Mg (0.68) and between Mg versus Si (0.92) (Fig.2). These strongly correlated elements discriminate these water samples from those coming from Asopos valley, where no correlation between these elements was observed (in respect with the mineralogical and the chemical composition of the host rocks) (Fig.2).

Table 1. Concentrations of chemical constituents (in $\mu\text{g.L}^{-1}$) and other physical and chemical parameters of water samples of central Euboea.

	E1	E2	E3	E4	E5	E6	E7	E8	E9
Cr	100	51	111	<2	<2	3	15	12	25
Cr(VI)	98	49	97	<4	<4	<4	12	10	24
Ca	17610	31870	63800	46220	53360	43650	98680	121820	65300
Mg	81160	76210	103180	7780	11000	9790	51660	28710	69760
Ni	4,1	4,9	3,4	1,4	<.2	0,7	9,5	31	2,1
Mn	<.05	0,9	<.05	<.05	<.05	<.05	1,49	0,51	0,4
Zn	2,1	0,5	0,5	<.5	<.5	1,1	48	45	0,5
Si	19760	16860	17490	5640	6700	6430	23240	14240	26440
Na	72610	37590	40250	14270	15290	14060	22340	18690	22580
K	12320	1650	4840	1120	620	480	480	475	550
B	140	36	63	11	10	12	24	21	15
Li	6,6	3,9	5,6	1,1	2	0,7	2,4	2,2	2,6
As	0,6	0,8	0,9	1,8	0,7	<.5	<.5	<.5	<.5
Cd	<.05	<.05	<0.5	<.05	<.05	<.05	0,06	<.05	<.05
Co	0,14	0,11	0,23	0,07	0,02	0,06	0,22	0,12	0,06
Cu	1,1	0,5	0,8	0,2	0,2	0,3	5,8	1,3	0,4
P	<20	<20	<20	<20	<20	<20	35	36	32
Pb	<.1	<.1	<.1	<.1	<.1	<.1	10	0,2	<.1
S	40000	27000	70000	8000	6000	6000	25000	11000	5000
Se	1,5	1,1	2,3	0,5	0,7	0,5	1,7	1,2	1,1
V	2,9	2,3	2,9	1,2	1,3	0,8	1,6	0,8	0,8
Fe	16	12	<10	48	<10	25	428	481	238
pH	7,23	7,48	7,72	7,35	7,25	7,06	7,28	7,10	7,71
Eh (mV)	-30	-38	-52	-31	-25	-15	-25	-15	-49
CND(mS/cm)	1,30	1,99	1,43	0,53	0,53	0,83	0,88	0,76	0,80
TDS (g/l)	0,69	1,06	0,76	0,28	0,28	0,44	0,44	0,39	0,40

With the exception of Fe, the concentrations of the rest chemical elements analysed, are below the regulated parametric values given by the EC, (EC, 1998) for drinking water. High Fe concentrations, above the permeable limit [$200 \mu\text{g.L}^{-1}$, (EC, 1998)], were detected in some water samples of central Euboea.

Moreover the much higher values of Fe in these samples from those in natural waters from Asopos valley could be used as another indicator factor for their discrimination, as it is presented in the triangular plot of Fe-Mg-Ca (Fig.3f). Silicon distribution in groundwaters from both areas could be also used as a discriminator factor, as it is shown in the triangular plot of Cr(total)-Mg-Si (Fig.3e) and the diagrams of correlation coefficients (Fig.2).

According to Cr(total), Mg, Si and Ca composition of ground waters samples from central Euboea, the “below detection limit” values of Cr(VI) ($<4 \mu\text{g.L}^{-1}$) and its high concentrations ($>50 \mu\text{g.L}^{-1}$), detected in the shallow wells cited on the alluvial deposits of the area (Megremi, 2010), are also being discriminated from its intermediate values as it is presented in the ternary plots of Mg-Si-Ca (Fig.3b), Mg- Cr(total)-Ca (Fig.3d) and Cr(total)-

Mg-Si (Fig.3e).

The ratio of Cr(VI)/Cr(total), is between 0.7 to 1 and their excellent correlation (0.88 to 1,00) in both areas, (fig. 2), indicates that hexavalent chromium is the predominant form of dissolved chromium in natural waters.

The contamination of groundwater by Cr(VI) that was found in the majority of groundwater samples in Asopos valley has been related to the widespread industrial activity for the last 40 years and the usage of hexavalent chromium in various processes. In the water samples from the Mavrosouvala wells both the hexavalent and total chromium were found below detection limit.

The discrimination between water samples from the Asopos valley and from the Mavrosouvala wells according to the differences of their chemical composition are presented by the triangular plots of Mg-Si-Ca (Fig. 2a) and Mg-Cr-Ca (Fig. 2c).

The water samples from Mavrosouvala wells were characterized by higher Ca/Fe and Ca/Mg ratios compared to those coming from the rest of the Asopos valley. The different mineralogy and the chemistry of the rocks that hosts the aquifers might

be the cause for this difference. The marle and the clay rocks of Asopos valley are containing minerals with high Fe and Mg compounds such as chlorite $[(Mg,Al,Fe)_{12}(Si,Al)_8O_{20}(OH)_{16}]$, micas $[(K,Na,Ca)_2(Al,Mg,Fe)_{4-6}(Si,Al)_8O_{20}(OH,F)_4]$, smectites $[(Na,Ca)_{0.5}Al_2(Si_{3.5}Al_{0.5})O_{10}(OH)_2 \cdot n(H_2O)]$, e.t.c. In contrast, the limestone is composed mainly by calcite $[CaCO_3]$. The absence of hexavalent chromium in the samples from the Mavrosouvala wells might be interpreted by the insignificant indus-

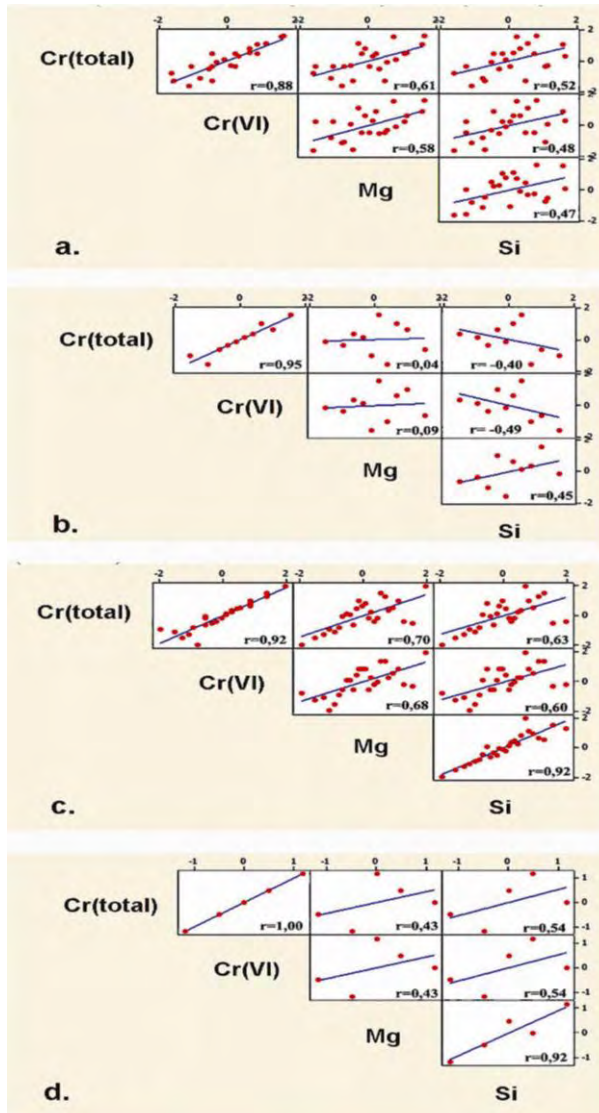


Fig. 2. Correlation coefficients and trend line plots of Cr(total), Cr(VI), Mg and Si of the ground water samples from Asopos valley and central Euboea: a. Asopos area, groundwater samples with Cr(VI) < 50 $\mu\text{g.L}^{-1}$ (n=23*), b. Asopos area, groundwater samples with Cr(VI) > 50 $\mu\text{g.L}^{-1}$ (n=10*), c. Euboea's groundwater samples with Cr(VI) < 50 $\mu\text{g.L}^{-1}$ (n=26**), d. Euboea's groundwater samples with Cr(VI) > 50 $\mu\text{g.L}^{-1}$ (n=5**), (*)additional data from Vasilatos et al. (2008) (**)additional data from Megremi (2010)

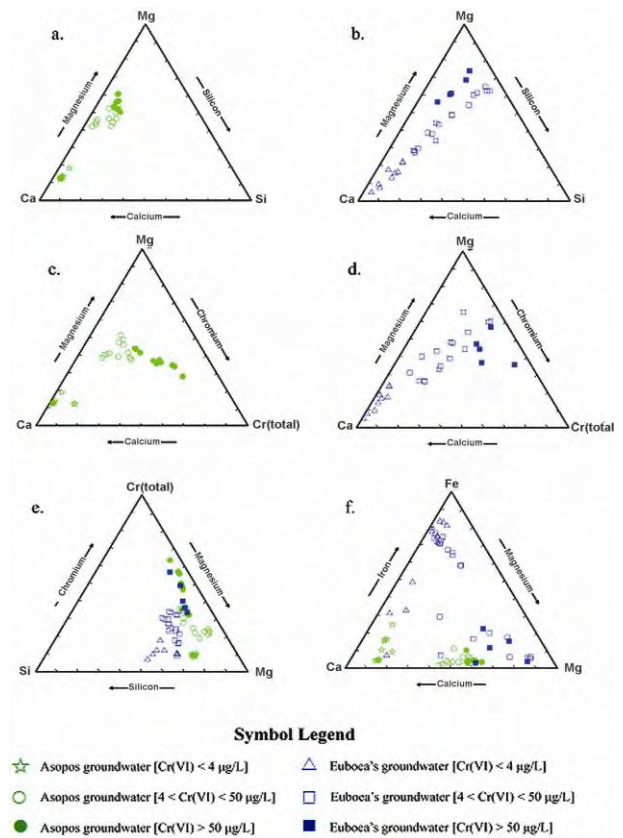


Fig. 3. Ternary diagrams for the water samples on the basis of their chemical compounds. a. Mg-Si-Ca triangular plot for the ground water samples from Asopos valley. b. Mg-Si-Ca triangular plot for the ground water samples from central Euboea. c. Mg-Cr(total)-Ca triangular plot for the ground water samples from Asopos valley. d. Mg-Cr(total)-Ca triangular plot for the ground water samples from central Euboea. e. Cr(total)-Mg-Si triangular plot for the ground water samples from Asopos valley and central Euboea. f. Fe-Mg-Ca triangular plot for the ground water samples from Asopos valley and central Euboea.

trial activity in the surrounding area of the wells and by the fact that the aquifer has different hydrogeological characteristics: it is hosted in a karstic limestone formation with tremendous water potential and the source of groundwater recharge is the thick Parnis Mountain limestone formation at the southwest of the basin.

4. Conclusions

Concentrations over the maximum acceptable level of total Cr in drinking water and high Cr(VI) values have been found in both central Euboea area and Asopos valley as well.

The presence of a few tens of $\mu\text{g.L}^{-1}$ in majority of the groundwater samples from central Euboea, may be linked to the ultramafic rocks and the Ni-Fe laterites of the area.



Fig. 4. Map presenting the suggested origin of Cr(VI) in the aquifers at Eastern Sterea Hellas. Lower: Asopos Valley, Upper Central Euboea (additional data from Vasilatos et al, 2008, and Megremi, 2010) .

However the high concentrations of Cr(VI) in both areas ($>50 \mu\text{g}\cdot\text{L}^{-1}$), and even the lower concentrations in Asopos valley are mainly linked to anthropogenic impact. The triangular plots of Mg-Si-Ca, Mg-Cr(total)-Ca, Cr(total)-Mg-Si and Fe-Mg-Ca, have been successfully used for the discrimination and the identification of the origin of the water samples from the studied areas.

Moreover, according to their Ca, Mg, Si and Cr content, there is a geochemical discrimination within the water-group from Asopos valley, be-

tween the groundwater samples from the karstic aquifer of the Mavrossouvala wells, which are free of Cr(VI) and the samples from the clay - marle - limestone porous aquifer in the rest of the basin, which has higher Cr(total) and Cr(VI) values. Figure 4 presents the spatial distribution of the hexavalent chromium contamination of groundwaters according to its value.

In addition to the fact that the Cr(VI) compounds are much more soluble, than the major Cr(III) oxides under natural conditions, the ratio of Cr(VI)/

Table 2. Concentrations of chemical constituents (in $\mu\text{g}\cdot\text{L}^{-1}$) and other physical and chemical parameters of water samples of Asopos valley.

	Or 1	Or 2	Or 3	Or 4	Or 5	Or 6	Or 7
Cr	<1	<1	<1	160	46	71	68
Cr(VI)	<4	<4	<4	153	34	62	61
Ca	83330	94660	92380	52080	73300	45160	46960
Mg	13890	13830	14080	85690	68440	62000	65620
Ni	<.2	<.2	<.2	1,6	2,1	<.2	<.2
Mn	<.05	<.05	<.05	23	1,47	<.05	0,47
Zn	<.5	<.5	<.5	277	<.5	2,2	<.5
Si	4390	4280	4040	13870	20550	10580	10510
Na	8870	7890	8250	117380	50690	113270	115670
K	575	550	480	1570	1100	1450	1460
B	9	8	8	120	58	110	100
Li	1,2	0,9	0,8	21	16	19	18
As	1,5	1,4	1	1,2	1,5	2,4	2,3
Cd	<.05	<.05	<.05	<.05	<.05	<.05	<.05
Co	<.02	<.02	0,02	0,06	0,02	<.02	<.02
Cu	0,1	0,2	0,1	1,1	0,4	1	0,9
P	<20	<20	<20	<20	<20	<20	<20
Pb	<.1	<.1	<.1	1,3	<.1	<.1	<.1
S	2000	2000	2000	14000	7000	14000	14000
Se	0,6	0,5	<.5	4	2,8	4	3,9
V	1	0,9	0,7	4,1	4,9	2,9	3,3
Fe	<10	21	35	<10	<10	12	<10
pH	7,63	7,28	7,33	7,36	7,19	7,55	7,47
Eh (mV)	-48	-27	-29	-31	-22	-43	-39
CND(mS/cm)	0,54	0,54	0,54	1,35	1,02	1,16	1,22
TDS (g/lt)	0,29	0,29	0,29	0,72	0,56	0,62	0,65

Cr(total), has been assessed close or up to 1, and the excellent correlation of Cr(VI) to Cr(total), indicate that hexavalent chromium is the predominant form of dissolved chromium in groundwaters.

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