

OCCURENCE OF HEXAVALENT CHROMIUM IN THE OPHIOLITE RELATED AQUIFERS OF LOYTRAKI AND SCHINOS AREAS

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Abstract

The main objective of the present study is to assess Cr(VI) concentrations in groundwater and surface water of Loutraki and Schinos areas. Totally, 38 samples were collected from both areas from April to May 2015. Both surface water and groundwater are of bicarbonate-magnesium type ($Mg-HCO_3^-$) and present very high concentrations of Mg^{2+} (up to 266mg/L) whereas the Cr(VI) concentrations vary among the different water groups (<1,6μg/L-120μg/L). Only 2 out of 15 boreholes of Loutraki area have chromium concentrations above the permissible level for drinking water (50μg/L for Cr(tot)) with the maximum Cr(VI) concentration being 74μg/L. In the area of Schinos, three wells have also high concentrations of Cr(VI) ranging from 40μg/L to 120μg/L. The absence of industrial activity in both areas is indicative of the geogenic origin of Cr(VI) in groundwater which is probably related to the dissolution and oxidation of primary Cr bearing minerals derived from ophiolitic rocks of Geraneia Mountains.

Keywords: hydrogeochemistry, geogenic contamination, chromium mobility.

Περίληψη

Η παρούσα εργασία έχει ως στόχο να μελετήσει τόσο τα υπόγεια όσο και τα επιφανειακά ύδατα των περιοχών Λουτρακίου και Σχίνου ως προς τις συγκεντρώσεις τους σε εξασθενές χρώμιο. Η δειγματοληψία πραγματοποιήθηκε κατά τους μήνες Απρίλιο και Μάιο 2015 όπου συλλέχθηκαν συνολικά 38 δείγματα. Τόσο τα επιφανειακά όσο και τα υπόγεια ύδατα είναι πολύ μαγνησιούχα με μέγιστη ανιχνεύσιμη συγκέντρωση τα 266mg/L. Αντιθέτως, οι συγκεντρώσεις Cr(VI) κυμαίνονται από 1,6μg/L έως 120μg/L στα διάφορα δείγματα ανάλογα με την προέλευση τους. Από τις συνολικά 15 γεωτρήσεις του Λουτρακίου μόνο σε 2 ανιχνεύθηκαν συγκεντρώσεις Cr(VI) πάνω από το ανώτατο αποδεκτό όριο (50μg/L για το ολικό χρώμιο) με τη μέγιστη συγκέντρωση να είναι 74μg/L. Στον Σχίνο και στα τρία φρεάτια από τα οποία συλλέχθηκαν δείγματα ανιχνεύθηκαν υψηλές συγκεντρώσεις Cr(VI) μεταξύ 40μg/L και 120μg/L. Η απουσία βιομηχανικής δραστηριότητας στην ευρύτερη περιοχή δείχνει ότι η παρουσία του Cr(VI)

στα υπόγεια ύδατα είναι γεωγενούς προέλευσης και σχετίζεται άμεσα με το γεωλογικό υπόβαθρο της περιοχής που είναι τα υπερβασικά πετρώματα των Γερανείων.
Λέξεις κλειδιά: Υδρογεωχημεία, γεωγενής ρύπανση, κινητικότητα χρωμίου.

1. Introduction

Chromium occurs naturally but also enters the environment through emissions from human activities such as metallurgy and metal-finishing industries as well as from its use as a chemical intermediate. In water, chromium exists in two oxidation states, 3+ (III) and 6+ (VI), but the more thermodynamically stable state is Cr(VI). Hexavalent chromium is far more mobile than Cr(III) and more difficult to remove from water. It is also the toxic form of chromium, being approximately 10 to 100 times more toxic than Cr(III) by the acute oral route. Until recently human activities were considered the only Cr(VI) source in groundwater, however, latest research has shown that relatively high levels of Cr(VI) can also be attributed to natural processes (Kazakis *et al.*, 2015; Dermatas *et al.* 2015; Megremi *et al.*, 2013; Moraitis *et al.*, 2012; Margiota *et al.*, 2012; Oze *et al.* 2007; Fantoni *et al.*, 2002). Weathering and erosion of ultramafic rocks are possibly the main responsible mechanisms for the mobility of chromium from the bedrock to soils and aquifers. According to the Water Framework Directive 2000/60/EC, the upper limit of Cr(tot) in drinking water is 50 µg/L for the countries of European Union including Greece. However, Italy has regulated a maximum permissible level of Cr(VI) in drinking water at 5 µg/L.

Hexavalent chromium contamination in groundwater has been reported at several areas of Greece. Elevated concentrations have been attributed to natural processes within ophiolite related aquifers (Kazakis *et al.*, 2015; Kaprara *et al.*, 2015; Dermatas *et al.*, 2015), anthropogenic activities in industrial zones such as the notorious case of the Oinofyta- Asopos groundwater contamination (Panagiotakis *et al.*, 2015) or a combination of both, such as the ultramafic rock rich area of central Euboea which is also characterized by intensive agriculture (Voutsis *et al.*, 2015; Megremi *et al.*, 2013). Previously published data from the area of Schinos, which is one of study areas of the present study, reported high concentrations of Cr(VI) in a few domestic water wells within the village and attributed contamination to uncontrolled waste disposal (Papadopoulos and Lappas, 2014).

Taking into account that further study is required in order to assess Cr(VI) contamination in areas with suspect to geology, the objective of the present study is to present newly collected data regarding Cr(VI) concentrations in surface and groundwater samples from the area of Loutraki and Schinos and discuss Cr(VI) contamination in the context of the general hydrogeological and hydrogeochemical profile of the study areas.

2. Materials and Methods

2.1 Study Areas

The study areas (Loutraki and Schinos) are located in the Perachora peninsula at the eastern part of Corinthian Gulf (Fig.1). Loutraki lies at the southern part of Perachora peninsula and it is surrounded by the Gulf of Lechaio. The drainage basin of Loutraki covers an area of approximately 53.27 km² and has a perimeter of 35 km. The maximum elevation is 1068 m a.s.l. while the mean elevation is approximately 470 m a.s.l. The main geological formations of Loutraki's drainage basin are carbonate rocks (limestone) which cover an area of approximately 11.8 km², ophiolitic rocks (peridotite and serpentinite) which cover an area of 20.4 km², Neogene carbonate clay formations (marl) which cover an area of 1.1km², functioning as a barrier due to their impermeability controlling the groundwater flow and finally Quaternary conglomerate and alluvial deposits which cover an area of approximately 16km² (Bornovas *et al.*,1969). The above rock formations can be classified as permeable (limestone, quaternary conglomerates and alluvial deposits), partially permeable (marly sandstones and fractured ophiolites) and impervious (clay and marl). The main streams of Loutraki drainage network are Loumpiniaris and Agia Triada. The metallic aquifer is located in the alluvial

deposits consisting of ophiolite material (mainly serpentinite and pyroxenite) from the weathering and erosion of the ophiolite complex of Geraneia Mountains and covers approximately an area of 7.45km² with a maximum depth level of water at 150m (Kounis and Vitoriou, 2003a). The main sources of metallic groundwater are the direct infiltration of precipitation water, the runoff water of the whole drainage basin, the runoff water of ophiolite riverbeds from Geraneia Mountains as well as the underground source of conglomerates aquifer in the southeast part of Loutraki's drainage basin.

The area of Schinos is located in the northeastern part of Perachora peninsula and it is surrounded by the Alkyonides Gulf. The drainage area of Schinos covers approximately an area of 22,4 km² where the main geological formations are Jurassic limestone which is heavily fractured and fissured due to alpine and post-alpine tectonic movements, the Boeotian flysch consisting of rhythmic series of sandstone, clastic limestone and chert, ophiolites (serpentinite and peridotite) and the schist-chert formation at the base of ophiolite mélangé which consists of radiolarites containing thin Mn-layers and reddish or grey limestone with chert (Bornovas *et al.*, 1979). The wider region of Pissia-Schinos is tectonically active with active normal faults of NW-SE and E-W directions and this is depicted at the geomorphology of the whole area with abrupt alternation of slopes. The upper post-alpine formations are alluvial deposits and talus cones where the Schinos aquifer occurs. The aquifer of Schinos is placed in scree for the upper 2m depth and in fractured peridotites until a depth of 100m approximately (Kounis and Vitoriou, 2003b). The quality of groundwater is low due to sea intrusion (Papadopoulos and Lappas, 2014) so it is used mainly for irrigation.

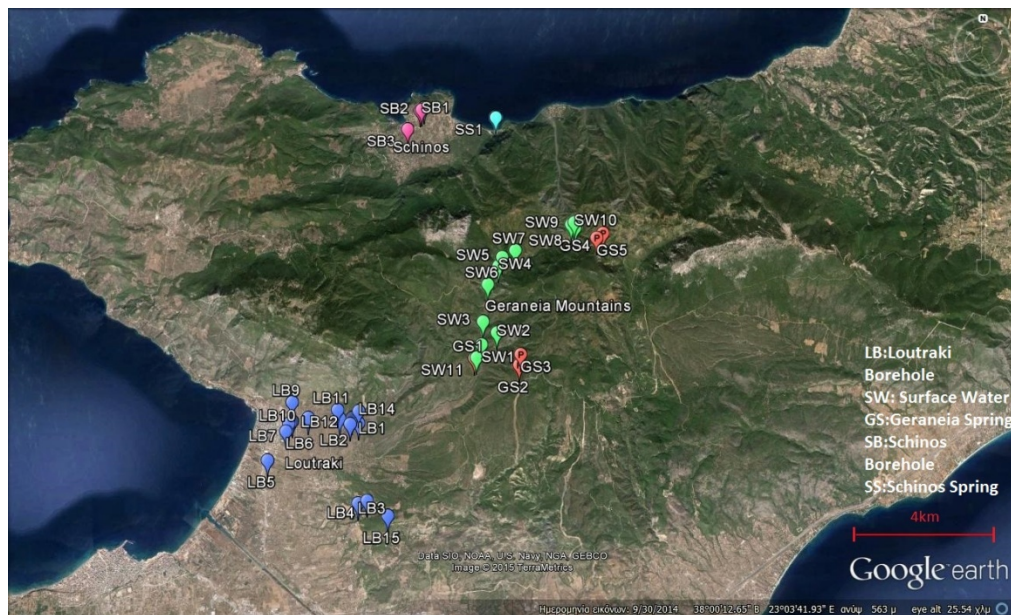


Figure 1 - Google earth map with sampling points.

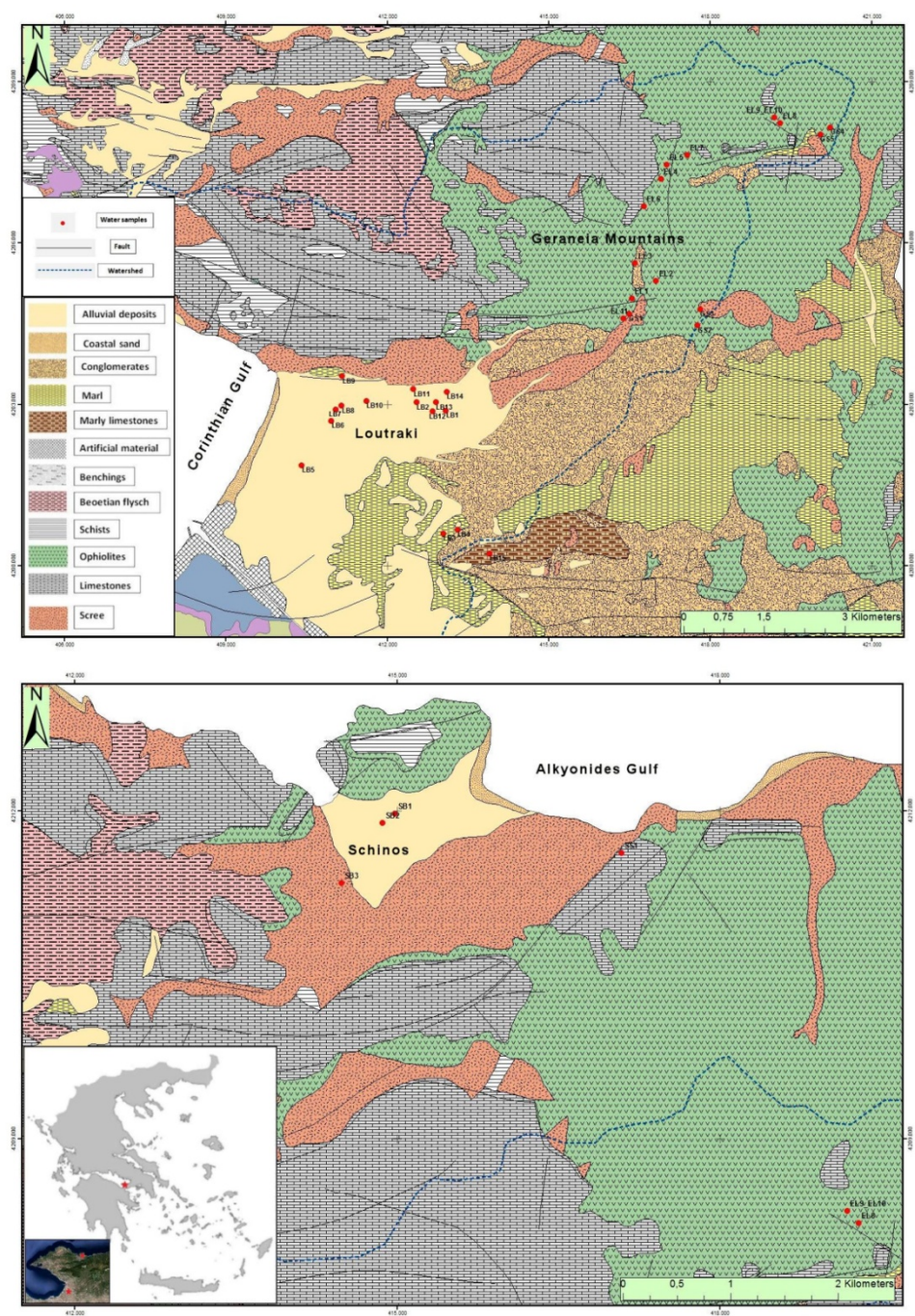


Figure 2 - Geological map of Loutraki and Schinos areas and location of sampling points.

2.2 Water Sampling and Analysis

A total of 38 water samples were collected from April to May 2015 (Fig. 1). Groundwater samples were collected from 15 boreholes from Loutraki area (LB) used to cover mainly the drinking water demands of Loutraki's residents. In addition, 5 groundwater samples (GS) were collected from natural springs of Geraneia Mountains, 11 surface water samples from the streams of Geraneia Mountains (SW), 1 surface water sample from the area of Sousaki (SSW) and 6 from the area of Schinos including 3 samples from wells (SB), 2 from springs (SS) and 1 from a borehole (SBF). In each sampling station three sub-samples were collected in separate bottles; one for cation analysis, one for Cr(VI) analysis and one for anion analysis. The water samples for cation and Cr(VI) analysis were filtered through 0.45 μm membrane filters *in situ* in order to collect only the soluble phases. The samples for cation analysis were acidified to $\text{pH} < 2$ by adding a few drops of HNO_3 . All samples were refrigerated during their transfer to laboratory. *In situ* measured parameters included pH, electrical conductivity (EC), total dissolved solids (TDS) and temperature. All major ions and trace elements were analyzed shortly after sampling in the laboratories of Environmental Chemistry, and Economic Geology and Geochemistry, University of Athens. In particular, Cr(VI) was determined by the DPC colorimetric method according to the ELOT-EN-ISO 18412 Standard (2006). The absorbance was determined at 540 nm on a double beam UV-vis Carry 1E spectrophotometer. The Method's Detection Limit (MDL), determined according to the EPA CRF 40B procedure (EPA 2008), is 0.6 $\mu\text{g L}^{-1}$. Nitric anions were measured with a photometric method which is based on the reduction of nitrates to nitrous using a cadmium column in a buffer solution and then the nitrous are measured according to the Griess-ilosvay process. Sodium and K^+ were determined by flame photometry, Mg^{2+} and Ca^{2+} were determined by means of Flame Atomic Adsorption Spectrometry (Varian SpectrAA-200) and finally the concentration of HCO_3^- was calculated by measuring the alkalinity of the samples through titration with H_2SO_4 1.16N using a HACH digital titrator.

3. Results and Discussion

3.1 Hydrogeochemical Features

The chemical analyses were tested for charge balance errors. Calculated charge balance errors were found to be less than or equal to $\pm 10\%$ for the majority of samples, which is an acceptable error for the purposes of the present study (Güler *et al.*, 2002). Only 3 samples balance errors were above $\pm 10\%$. In general, the different water samples are classified into 6 groups according to their type (springs, boreholes, surface water) and physicochemical properties (Table 1). Among the different groups, mean pH values range from 7.5 to 9, conductivity (EC) ranges from 0.65 to 2.63 ms/cm, total dissolved solids (TDS) range from 0.33g/L to 1.34g/L and total hardness (CaCO_3) ranges from 329 mg/L to 606 mg/L. Relatively elevated values of conductivity have been measured at a Loutraki borehole, LB5 (13mS/cm) and at three Schinos boreholes-wells (SB1,SB2,SB3) ranging from 1.44 to 3.81mS/cm. These values are indicative of seawater intrusion because the same samples present elevated concentrations of Na^+ and Cl^- . As is shown in Figure 3, most samples are characterised by high concentrations of Mg^{2+} exceeding 100 mg/L whereas Ca^{2+} concentrations are significantly lower, ranging from 2 to 40 mg/L for most samples.

As a result it is concluded that the groundwater as well as surface water chemical composition is directly influenced by their interaction with ultramafic rocks and serpentinites. This is also justified by the high ratios of Mg/Ca for the different water groups (Table 1). The surface water samples (SW) are enriched in Mg^{2+} compared to Loutraki's alluvial aquifer groundwater (LB). The only sample with Mg/Ca ratio below 1 (0.15) is GS5 and this shows that probably this spring is related to the karstic aquifer. The highest Mg/Ca ratio is 149 and characterizes the spring Prathi (GS4). Plotting the samples' composition on a Piper plot (Fig. 4) revealed that all water samples are of bicarbonate magnesium type (Mg-HCO_3). Elevated concentrations of NO_3^- ranging from 16 mg/L to 207mg/L have been detected in certain samples within the built areas of Loutraki (LB5) and

Schinos (SB1,SB2,SB3) indicating most probably the deterioration of the water quality by wastewater i.e., contribution of organic effluents in water chemistry.

Table 1 - Mean values of physicochemical parameters and major ions in water samples.

Water groups	pH	EC ms/cm	TDS g/L	Ca ²⁺ mg/L	Mg ²⁺ mg/L	Mg/Ca	K ⁺ mg/L	Na ⁺ mg/L	HCO ₃ ⁻ mg/L	NO ₃ ⁻ mg/L	Cr(VI) µg/L
LB (n=15)	8.1	0.69	0.42	10.4	89.2	27.9	1.4	24.6	402	7.6	22.8
GS (n=5)	8.1	0.89	0.48	28	145	33.6	1.4	16.8	739	1.8	7.4
SW (n=11)	8.6	0.69	0.35	20.2	126	26.5	1.2	17.3	660	3.1	1.8
SSW (n=1)	8.3	1.1	0.54	35.8	145	6.7	1.5	27	825	1.3	3.5
SB (n=3)	7.5	2.63	1.34	59.9	225	7	1.86	254	676	107	65.3
SS (n=2)	9	0.65	0.33	2.07	105	55.3	1	20.6	580	1.3	1.3

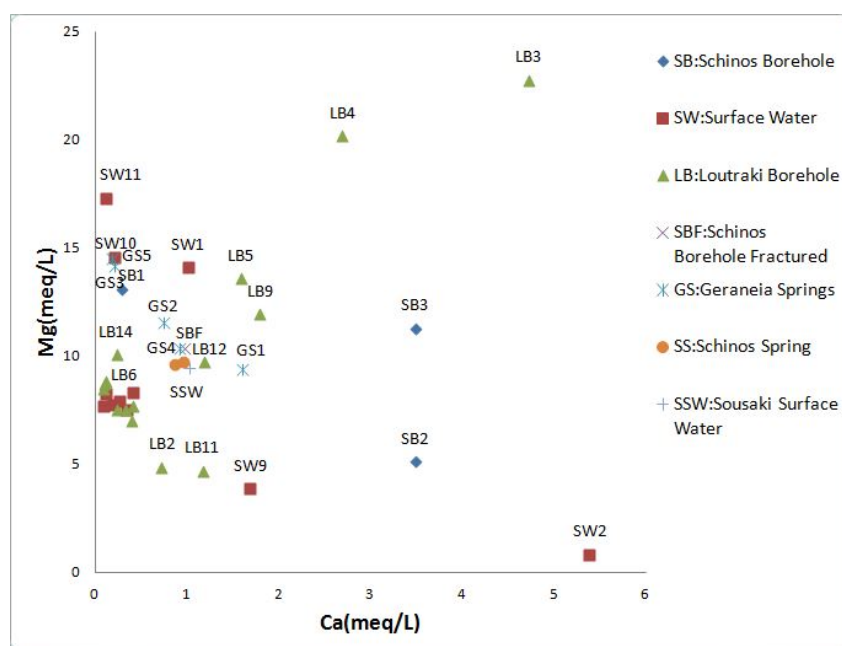


Figure 3 - Plot of Mg vs Ca.

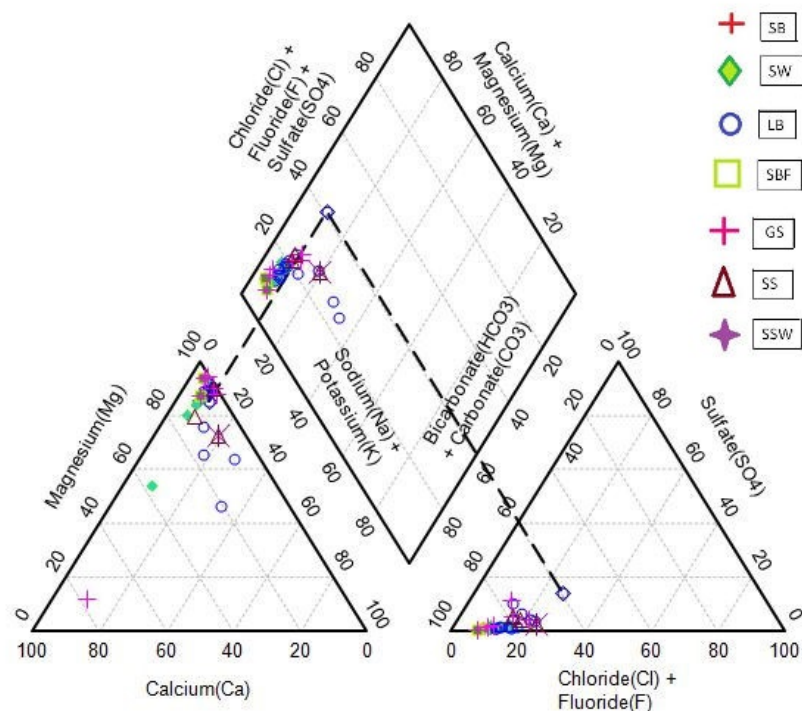


Figure 4 - Piper plot of different water groups indicating a bicarbonate magnesium water type.

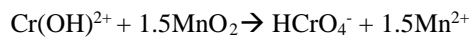
3.2 Occurrence of Cr(VI) in water

The concentration of Cr(VI) in groundwater samples of Loutraki boreholes group (LB) were moderate to high ranging from 1.8 $\mu\text{g/L}$ to 74 $\mu\text{g/L}$ with a mean value of 23 $\mu\text{g/L}$. Only 2 out of 15 samples had concentrations above the permissible level for drinking water. Dermatas *et al.* (2015) and Kazakis *et al.* (2015) have also found similar concentrations of Cr(VI) in the areas of Vergina (up to 64 $\mu\text{g/L}$) and Anthemountas (up to 70 $\mu\text{g/L}$) which also have an ophiolite-influenced geological background and aquifers which are related to ultramafic rocks. Furthermore, Dermatas *et al.* (2015) have reported much higher Cr(VI) concentrations, reaching 10 mg/L in groundwater from the area of Oinofyta where industrial activity is intense. The absence of industrial activities in the areas of Loutraki and Schinos as well as the concentrations levels of Cr(VI) are indicative of the natural source of this toxic element in water.

The highest Cr(VI) concentration of 120 $\mu\text{g/L}$ was measured in one of the three water samples collected from domestic wells within the Schinos village. This is in agreement with data reported previously by Papadopoulos and Lappas (2014) who had measured up to 460 $\mu\text{g/L}$ Cr(VI) in a water well at Schinos village. In contrast to domestic water wells Cr(VI) concentrations in the borehole sample of the area (SBF) as well as the two springs SS1 and SS2 which are the drinking water sources of Schinos village did not exceed 1.85 $\mu\text{g/L}$. Moderate concentrations have been found in Geraneia springs (GS) with a maximum value of 14 $\mu\text{g/L}$ Cr(VI) while low concentrations of Cr(VI) have been detected in surface water samples of Geraneia streams (SW) with a maximum concentration of approximately 4 $\mu\text{g/L}$. The water samples with moderate to low concentrations of Cr(VI) (GS,SW,SBF,SS) are related to the aquifer of fractured ultramafic rocks of Geraneia Mountains, whereas the water samples with higher concentrations (GL, BS) are related with Loutraki's and Schino's alluvial aquifers. It is noted that alluvial sediments consist mainly of eroded ophiolite material derived from the upland areas surrounding the plains (Fig. 2). The enrichment of

alluvial aquifers in Cr(VI) has been also observed by Kazakis *et al.* (2015), Megremi *et al.* (2013) and Voutsis *et al.* (2015). Finally, Kelepertzis *et al.* (2013) have found that in Thiva basin which has a similar geological background, Cr(III) is mainly bounded within inherited chromite and to a lesser extent with Cr-magnetite and Cr silicates like enstatite, a conclusion which is in accordance to recent observations for this study.

Figure 5 presents a plot of Cr(VI) against Mg^{2+} concentrations in water samples. It is obvious that the increase of soluble Mg^{2+} does not influence soluble Cr(VI). This is probably explained by different sources of the two elements i.e., olivine for Mg and chromite for Cr as well as different processes affecting their release into the water, i.e. congruent dissolution of olivine and other silicate minerals for Mg and release of Cr(III) from chromite with subsequent oxidation to Cr(VI). According to the literature the release of Cr(VI) in the aqueous environment depends on several parameters such as the redox potential, the presence of MnO_2 and Fe_2O_3 , the level of dissolved O_2 etc. Manganese oxides are likely to be responsible for chromium oxidation in aquatic environments through the following reaction (Fendorf, 1995):



Also worth noting in Fig. 5 is the clustering of water samples according to their respective groups with stream water samples showing the lowest Cr(VI) concentrations and groundwater samples showing the highest Cr(VI) concentrations. This, indicates that the residence time of groundwater is a significant factor affecting Cr(VI) release into the water. Finally, the samples with relatively high conductivity (LB5,SB1,SB2,SB3) have also high concentrations of Cr(VI) ranging from 37 $\mu g/L$ to 120 $\mu g/L$.

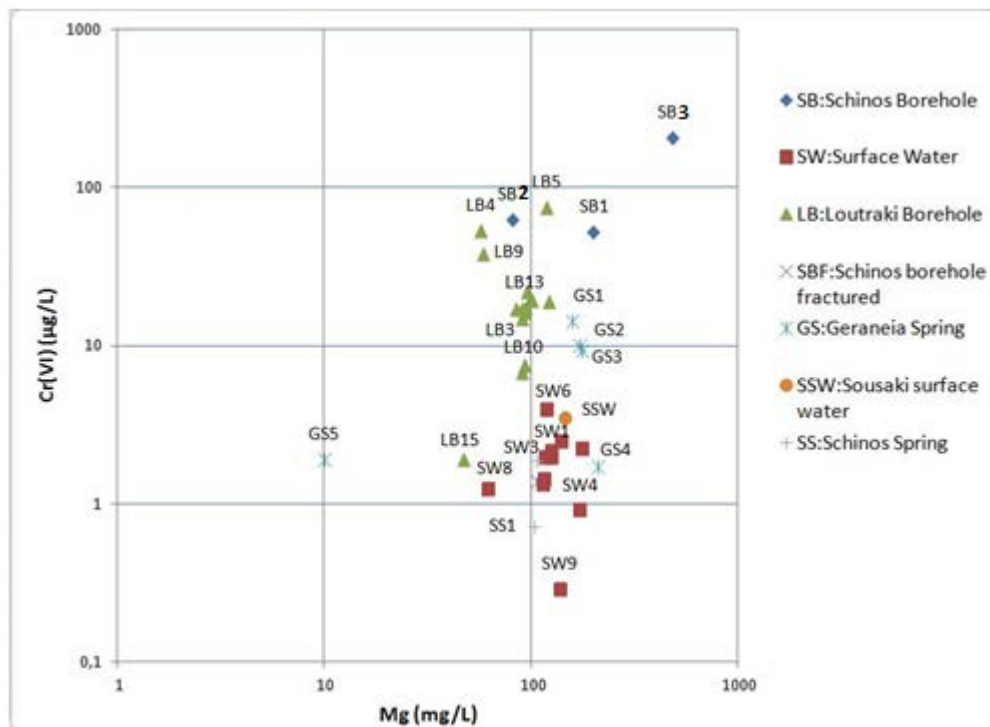


Figure 5 - Plot of Cr(VI) vs Mg.

4. Conclusions

Hexavalent chromium contamination of surface and groundwater in the areas of Loutraki and Schinos has been accessed in the context of local geology and hydrogeochemistry. Based on the data presented in the previous paragraphs the following conclusions have been drawn:

- The general chemical composition of all water samples is of $\text{Mg}\cdot\text{HCO}_3$ type due to the interaction of both surface and groundwater with serpentinized ultramafic rocks that characterize the local geology.
- The release of Cr(VI) in groundwater is probably linked to natural processes and it is reflective of water–rock interaction within the ophiolite related aquifers in the study area.
- Alluvial aquifers present moderate to high concentrations of Cr(VI) in contrast to ophiolite fractured aquifers where the lowest Cr(VI) concentrations were measured.
- Groundwater of alluvial aquifers is enriched in Mg^{2+} and Cr(VI) in contrast to surface water which has only high concentrations of Mg^{2+} .
- Groundwater samples with higher conductivity exhibit the highest concentrations of Cr(VI).

Further research, looking into the mineralogy and weathering regime of chromium bearing phases in the serpentinized rocks as well as the hydrogeological features at local scale is needed in order to clarify the processes affecting Cr(VI) release into the water.

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6. References

- Bornovas, J.I., Eleutheriou, A. and Gaitanakis, P., 1970-1980. Map of IGME Kaparellion.
- Bornovas, J., Lalechos, N. and Filippakis, N., 1969. Map of IGME Korinthos.
- Dermatas, D., Mpouras, T., Chrysochoou, M., Panagiotakis, I., Vatsieris, C., Linardos, N. and Sakellariou, L., 2015. Origin and concentration profile of chromium in a Greek aquifer, *Journal of Hazardous Materials*, 281, 35-46.
- Fantoni, D., Brozzo, G., Canepa, M., Cipolli, F., Marini, L., Ottonello, G. and Zuccolini, M., 2002. Natural hexavalent chromium in groundwaters interacting with ophiolitic rocks, *Environmental Geology*, 42(8), 871-882.
- Fendorf, S.E., 1995. Surface reactions of chromium in soils and waters, *Geoderma*, 67(1), 55-71.
- Güler, C., Thyne, G.D., McCray, J.E. and Turner, K.A., 2002. Evaluation of graphical and multivariate statistical methods for classification of water chemistry data, *Hydrogeology journal*, 10(4), 455-474.
- Kaprara, E., Kazakis, N., Simeonidis, K., Coles, S., Zouboulis, A.I., Samaras, P. and Mitrakas, M., 2015. Occurrence of Cr (VI) in drinking water of Greece and relation to the geological background, *Journal of hazardous materials*, 281, 2-11.
- Kazakis, N., Kantiranis, N., Voudouris, K.S., Mitrakas, M., Kaprara, E. and Pavlou, A., 2015. Geogenic Cr oxidation on the surface of mafic minerals and the hydrogeological conditions influencing hexavalent chromium concentrations in groundwater, *Science of the Total Environment*, 514, 224-238.
- Kelepertzis, E., Galanos, E. and Mitsis, I., 2013. Origin, mineral speciation and geochemical baseline mapping of Ni and Cr in agricultural topsoils of Thiva valley (central Greece), *Journal of Geochemical Exploration*, 125, 56-68.
- Kounis, G. and Vitoriou-Georgouli, A., 2003a. Water balance of Loutraki's metallic aquifer.
- Kounis, G. and Vitoriou-Georgouli, A., 2003b. Hydrogeological survey of Schinos area with implementation of pumping tests.
- Margiotta, S., Mongelli, G., Summa, V., Paternoster, M. and Fiore, S., 2012. Trace element distribution and Cr (VI) speciation in Ca-HCO₃ and Mg-HCO₃ spring waters from the northern sector of the Pollino massif, southern Italy, *Journal of Geochemical Exploration*, 115, 1-12.

- Megremi, I., Vasilatos, C., Atsarou, A., Theodoratou, C., Economou-Eliopoulos, M. and Mitsis, I., 2013. Geochemical evidences for the sources of the Cr (VI) contamination in groundwater in central Euboea and Assopos-Thiva basins, Greece: natural versus anthropogenic origin, *European Water*, 41, 23-34.
- Moraetis, D., Nikolaidis, N.P., Karatzas, G.P., Dokou, Z., Kalogerakis, N., Winkel, L.H.E. and Palaogianni-Bellou, A., 2012. Origin and mobility of hexavalent chromium in North-Eastern Attica, Greece, *Applied Geochemistry*, 27(6), 1170-1178.
- Oze, C., Bird, D.K. and Fendorf, S., 2007. Genesis of hexavalent chromium from natural sources in soil and groundwater, *Proceedings of the National Academy of Sciences*, 104(16), 6544-6549.
- Panagiotakis, I., Dermatas, D., Vatsaris, C., Chrysochoou, M., Papassiopi, N., Xenidis, A. and Vaxevanidou, K., 2015. Forensic investigation of a chromium (VI) groundwater plume in Thiva, Greece, *Journal of Hazardous Materials*, 281, 27-34.
- Papadopoulos, K. and Lappas, I., 2014. Groundwater quality degradation due to Cr⁶⁺ presence in Schinos area, prefecture of Corinth, Central Greece, 10th International Hydrogeological Congress of Greece, Thessaloniki.
- Richard, F.C., and Bourg, A.C., 1991. Aqueous geochemistry of chromium: a review, *Water Research*, 25(7), 807-816.
- Voutsis, N., Kelepertzis, E., Tziritis, E. and Kelepertzis, A., 2015. Assessing the hydrogeochemistry of groundwaters in ophiolite areas of Euboea Island, Greece, using multivariate statistical methods, *Journal of Geochemical Exploration*, 159, 79-92.