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Potential Contribution of Geogenic Chromium in Groundwater Contamination of a Greek Heavily Industrialized Area

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This study aims to investigate the potential contribution of geogenic chromium (Cr) to a contaminated aquifer of a heavily industrialized area in Greece. Until recently, high levels of Cr(VI) in the environment have always been attributed to anthropogenic activities, since the wide application of chromium in industry and the neglectful industrial waste disposal has in many cases resulted in serious soil and groundwater contamination incidents. However, a series of publications during the last decade have indicated that chromium might be of natural origin, as well. Therefore, a thorough literature review was performed and a comprehensive monitoring protocol, including a long series of water quality parameters, was adopted. Preliminary results indicate that the Cr(VI) plume in the study area is likely caused by a combination of geogenic and anthropogenic sources.

1. Introduction

Chromium (Cr) is a heavy metal that naturally occurs in the Earth's crust and is commercially produced by chromite ($FeCr_3O_4$) for a variety of metallurgical, refractory and chemical uses. Although Cr can occur in many oxidation states, in groundwater it exists either in the trivalent, Cr(III), or the hexavalent, Cr(VI), form (Richard and Bourg, 1991). Cr(III) is the predominant form in most minerals and is favoured by reducing and strongly acidic conditions, while, Cr(VI) occurs under oxidizing and alkaline conditions (Oze et al., 2004). The Cr form in the environment is very important, since Cr(III) is insoluble at pH > 5, immobile and with relatively low toxicity, while Cr(VI) is very soluble, mobile and a human carcinogen (ATSDR, 2000).

High levels of Cr(VI) in the environment are typically attributed to anthropogenic activities, since the wide industrial application of Cr and neglectful waste disposal have in many cases resulted in serious soil and groundwater contamination incidents. However, it has recently been demonstrated that Cr(VI) might also be produced by geogenic Cr, and particularly by Cr(III) oxidation under appropriate conditions (Oze et al., 2007). Significant naturally derived aqueous Cr(VI) concentrations have been reported in several areas across the globe, such as USA (Gonzalez et al., 2005), Italy (Fantoni et al., 2002) and Greece (Megremi, 2010; Moraetis et al., 2012). Typical geogenic sources of Cr(VI) are ultramafic rocks and serpentinites of ophiolites, where Cr concentrations can be as high as 60,000 mg/kg; Mg and Ni are also typical constituents of this kind of geological formations (Oze et al., 2004).

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When Cr(III) is oxidized to Cr(VI), typically in the presence of Mn oxides, it adsorbs on Fe oxides under neutral to acidic conditions (Izbicki et al., 2008). Mobilization of Cr(VI) can occur when the pH is increased beyond the pH of zero-charge of iron oxides, which is in the range 7.5 to 9 (Fendorf, 1995).

The study presented herein deals with a Greek industrialized region, where most of the typical anthropogenic point and non-point sources of Cr exist. In particular, several different types of Cr-using industries, such as steelworks, metal finishing and Cr-electroplating, were established across the study area during the last three decades, most of them operating with limited or no environmental permits. Additionally, several uncontrolled waste disposal sites and intensive agricultural activity have probably exacerbated the extent and magnitude of Cr(VI) contamination of local aquifers. In order to effectively devise a remediation scheme, the location and relative contribution of Cr(VI) sources needs to be understood. The complex geological background of the area introduces an additional layer of complexity to this end, as the local geology indicates potential geogenic contribution of Cr in the area. Specifically, a group of cherts-ophiolites with shales, limestone layers or lenses and other materials, where ophiolites are mostly serpentinized, is present in the north of the study area, as it is shown in Figure 1. From the viewpoint of hydrogeology there are three different aquifers in the study area, one within the alluvial deposits, one within the pliocene-pleistocene formation and one within the limestone formation, and groundwater is estimated to flow from the south to the north, with slight deviations to NE and NW (Figure 1).

Although high Cr(VI) groundwater concentrations have been sporadically detected in this area, a systematic approach has not been adopted so far and the contribution of geogenic Cr sources is poorly understood. Hence, this study, which is still in progress, was initiated to investigate the potential contribution of geogenic Cr(VI) sources to local groundwater contamination.

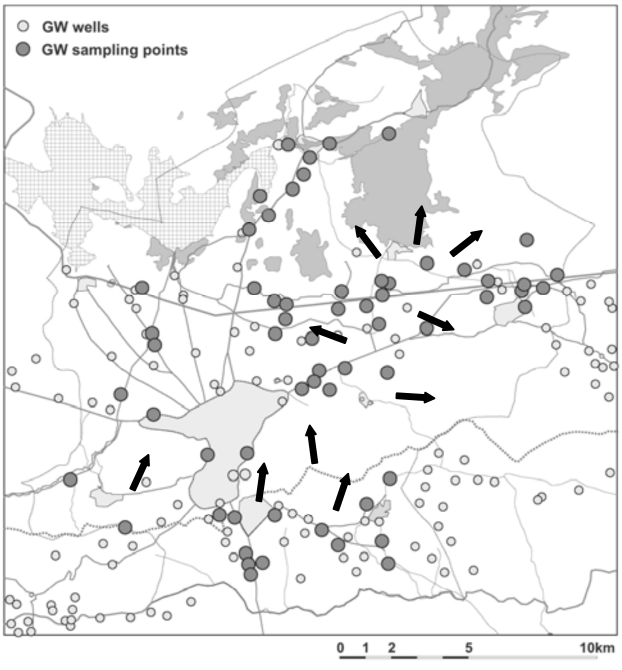

Figure 1. Spatial distribution of cherts-ophiolites with shales (grey) and estimated groundwater flow directions within the study area.

2. Materials and methods

The contribution of geogenic Cr was investigated through a field study with detailed chemical analyses of groundwater samples, in conjunction with a literature review and desktop analysis of existing information. The hydrological background of the study area was first determined, the available data of previous chemical groundwater analyses were reviewed and the local industries were identified and placed on the created maps. An extensive monitoring program was then implemented, during which a series of 61 existing wells (12 used for drinking water, 31 for irrigation and 18 for industrial purposes) were monitored between June and September of 2010, covering an area of 250 km^2. The parameters that were measured included: temperature, pH, dissolved oxygen (DO), electrical conductivity (EC), SO_4^{2-}, NO_3^-, Cl^-, HCO_3^-, Cr_{tot}, Cr(VI), Mg, Ca, K, Na, TOC, B, Ni, Zn, Ba, Si, total petroleum hydrocarbons (TPH), volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), benzene, toluene, ethylbenzene and xylene (BTEX), methyl butyl-tert ether (MTBE), polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). Metal concentrations were measured using Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES), while ions and Cr(VI) were measured using ultraviolet-visible spectrophotometry. Finally, VOCs, SVOCs, BTEX, MTBE, PAHs and PCBs were measured using Gas Chromatography - Mass Spectrometry (GC-MS). Contour maps of the parameter measured were created by using the Kriging method, a geostatistical technique applied to interpolate a value of a parameter at a location from known values of this parameter at nearby locations.

3. Results and discussion

Table 1 illustrates the average values ± 95 % confidence interval and range of the most significant chemical parameters measured in samples taken from the monitoring wells. Groundwater in this area is generally alkaline (pH = 8.2 ± 0.1) and oxic (DO = 6.2 ± 0.3 mg/L), with significant concentrations of Cr_{tot} (28.5 μg/L on average), which occurs almost exclusively in the hexavalent form Cr(VI) (25.3 μg/L on average). Although Cr_{tot} concentrations were lower than 50 μg/L in the majority of the monitoring wells, a few wells yielded values up to 190 μg/L, most of which occurred as Cr(VI) (160 μg/L). Additionally, NO_3^- (21.8 mg/L) and Mg (65.6 mg/L) were also found in significant concentrations, while Ca/Mg ratio was low and equal to 0.52. The presence of elevated NO_3^- concentrations complies with the intense agricultural activity, while the high Mg concentrations and the low Ca/Mg ratio with the presence of ophiolitic background within the study area (Figure 1) (Oze et al., 2004). The concentrations of TPH, VOCs, BTEX, MTBE, PAHs and PCBs were measured below the method detection limits in all samples.

In order to identify spatial trends in the obtained data, contour maps of the distribution of water table elevation and chemical parameters concentrations (EC, pH, DO, Mg, NO_3, Cl, Na, TOC, Cr_{tot}, Cr(VI), Ni, Zn, Ba, B and Si) were created. Among them, the most interesting results emerged from the contour maps of Cr(VI) concentrations (Figure 2) and pH values (Figure 3). As it is shown in Figure 2, the highest Cr(VI) concentrations are located approximately in the center of the study area between two clusters of industries, while a third hot-spot of Cr(VI) is located further away to the south, in an area close to another cluster of industries, with much lower Cr(VI) concentrations, though. Figure 3 revealed two hot spots of high pH values at the east of the Cr(VI) plume, where the two clusters of industries are located, implying a potential release of alkaline waste. It is also possible that these industrial clusters directly release Cr(VI) into the groundwater; the geogenic contribution remains unclear based on this analysis.

The contour maps of other parameters did not provide any meaningful spatial correlations with the Cr(VI) plume (data not shown), with the exception of Ni, Mg and B, which follow a similar pattern to Cr(VI). This relationship was quantified through the correlation coefficients between these chemical parameters and Cr(VI) for the plume area alone and the entire study area, which are presented in Table 2. The correlation coefficient between Cr(VI) and Cr_{tot} concentrations was equal to 0.99 in both columns, implying that a very strong relationship exists in the entire study area between those two parameters. However, the analysis of Cr(VI)/Mg, Cr(VI)/Ni and Cr(VI)/B showed negligible or very weak correlation in the entire study area, while in the Cr(VI) plume area correlation of Cr(VI)/Mg (r = 0.33), Cr(VI)/Ni (r = 0.58) and Cr(VI)/B (r = 0.65) was weak, moderate and strong, respectively. This geochemical profile agrees with the presence of ophiolites within the study area (Figure 1), since they are possible natural sources of Mg, Ni and Cr.

Although these results do not definitely support the geologic origin, they lend credence to the hypothesis that there is at least partial contribution of geogenic Cr to the Cr(VI) plume. The missing link in the geogenic Cr(VI) scenario is the oxidation mechanism of Cr(III), which is the form of Cr included in the minerals. Cr(III) oxidation is only mediated by the presence of certain Mn oxides, while oxygen has been found to be an inefficient oxidant (Schroeder and Lee, 1975). The presence of Mn oxides in the local rocks has not been established to date, but it cannot be excluded either. Further analyses of the local geology and mineralogy are necessary to this end.

Table 1: Average values ± 95 % confidence interval and range of chemical parameters measured in samples taken from monitoring wells.

Parameter	Total	Range
Temperature (ºC)	22.8 ± 0.8	17.7 - 32.8
pH	8.2 ± 0.1	7.4 - 9.6
DO (mg/L)	6.2 ± 0.3	1.8 - 8.1
EC (µS/cm)	786.1 ± 85.6	435 - 3000
SO_4^{2-} (mg/L)	16.3 ± 6.5	1.0 - 131.0
NO_3^- (mg/L)	21.8 ± 4.8	1.3 - 77.5
Cl^- (mg/L)	74.5 ± 42.2	15.0 - 1,300.0
HCO_3^- (mg/L)	428.6 ± 21.3	282.5 - 652.0
Mg (mg/L)	65.6 ± 3.9	18.0 - 96.6
Ca (mg/L)	57.1 ± 4.9	25.0 - 152.0
K (mg/L)	1.2 ± 0.9	≤ 24.6
Na (mg/L)	40.7 ± 27.5	2.0 - 831.0
TOC (mg/L)	2.8 ± 0.4	≤ 5.9
Cr_{tot} (µg/L)	28.5 ± 9.3	≤ 190.0
Cr(VI) (µg/L)	25.3 ± 8.4	≤ 160.0
B (µg/L)	57.8 ± 6.8	≤ 130.0
Ni (µg/L)	8.4 ± 1.0	≤ 18.0
Zn (µg/L)	31.1 ± 5.2	15.0 - 130.0
Ba (µg/L)	29.2 ± 6.6	5.0 - 110.0
Si (µg/L)	25.8 ± 2.4	4.0 - 39.0

Table 2: Correlation coefficients of chemical parameters measured within the entire study area and the Cr(VI) plume area.

Parameters	Entire study area	Cr(VI) plume (≥ 50 µg/L)
Cr(VI)/Cr_{tot}	0.99	0.99
Cr(VI)/Mg	0	0.33
Cr(VI)/Ni	0.16	0.58
Cr(VI)/B	0.35	0.65

Note: 0 < r < 0.2 negligible correlation, 0.2 < r < 0.4 weak correlation, 0.4 < r < 0.6 moderate correlation, 0.6 < r < 0.8 strong correlation, 0.8 < r < 1.0 very strong correlation.

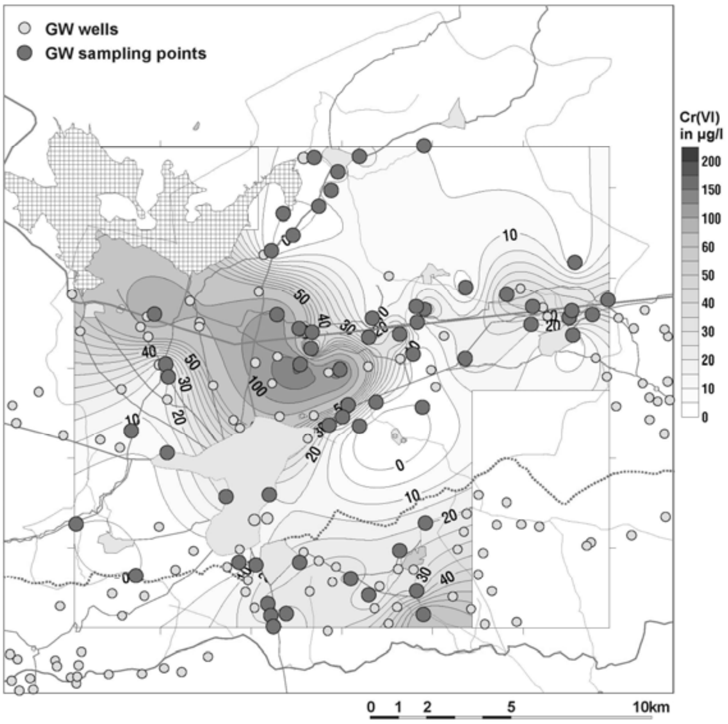

Figure 2. Contour maps of Cr(VI) concentration using the Kriging method.

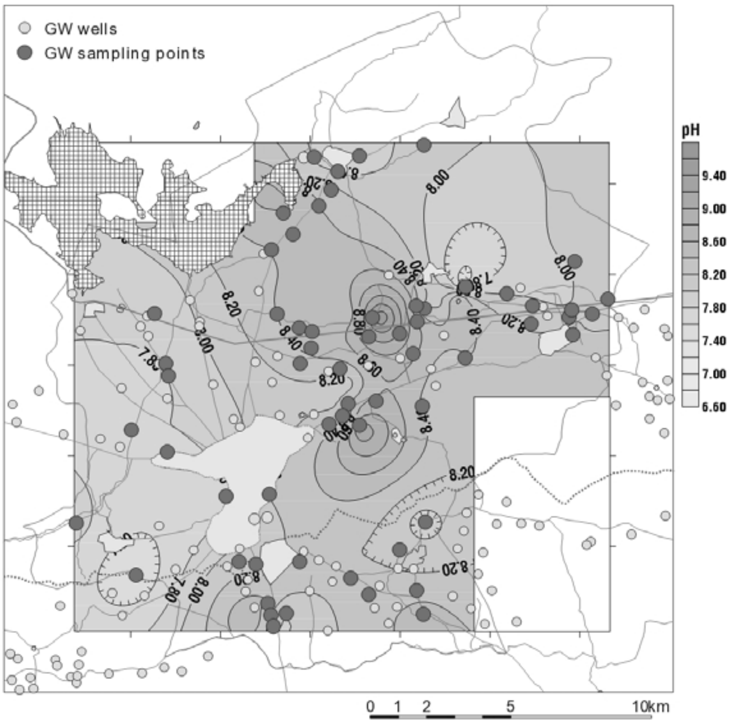

Figure 3. Contour maps of pH values using the Kriging method.

4. Conclusion

The initial results of the present study show that the Cr(VI) plume detected in an industrialized area in Greece is likely caused by a combination of geogenic and anthropogenic sources. In particular, the present study indicates that: a) a cluster of industries are located in the center of a high pH plume, b) the high pH plume is located upstream of the main Cr(VI) plume and c) the Cr(VI) plume is also spatially correlated with high Mg and Ni concentrations. These three elements are indicative of the dissolution of indigenous rocks and specifically of ophiolites, well-known sources of geogenic Cr, which are present to the north of the study area and typically contain elevated concentrations of Ni, Mg and Cr. Furthermore, the alkaline and oxidizing conditions of the aquifer favor the presence and mobility of Cr(VI) in groundwater. Although the direct anthropogenic contribution of Cr by the industries cannot be excluded, this geochemical profile suggests that geogenic contribution is likely. Future work will focus on the mineralogical analysis of rocks and soils in the area and specifically on the identification of Mn oxides, which are a necessary catalyst for Cr(III) oxidation.

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