

## ORIGIN OF HEXAVALENT CHROMIUM FOUND IN GROUNDWATER: A CRITICAL DECISION-MAKING PARAMETER

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### ABSTRACT

Chromium is a widely used metal in industrial activities, mainly in metallurgy and production of refractory and chemical products. The combination of extended industrial use of chromium with inadequate industrial waste management practices mainly of the past has led to extensive soil and groundwater contamination. However, recent studies indicate that the occurrence of Cr(VI) in groundwater can also be attributed to a geogenic origin. Geogenic Cr(VI) in groundwater comes from minerals which appear in areas with significant presence of ultramafic rocks and ophiolitic complexes. Significant presence of ultramafic rocks and ophiolitic complexes has been reported in several areas worldwide including Greece.

The present study aims at highlighting the origin of Cr(VI) found in groundwater as the most significant decision-making parameter for the rational management of Cr(VI)-contained aquifers. Two different case studies of Cr(VI)-contaminated aquifers, both exceeding the maximum allowable limit of 50 µg/l are presented herein. These two contaminated aquifer cases require diametrically different management approaches due to their differences in Cr(VI) origin and thus concentration. The first aquifer is located in the vicinity of Vergina in northern Greece, where the maximum Cr(VI) concentration measured was 61 µg/L, being one of the highest geogenic concentrations recorded globally in areas with similar geological background. The second aquifer case study presented is the aquifer of Inofyta, a makeshift industrial area north of Athens, where the maximum Cr(VI) concentration is 10 mg/L and is clearly attributed to an anthropogenic origin. In this latter case, the very high Cr(VI) groundwater concentrations are also accompanied by the presence of other contaminants and a significant spatial Cr(VI) concentration variation. Thus, although for the Vergina aquifer, area-wide institutional measures and in some cases pump & treat systems might be sufficient to ensure a safe water supply, this is not the case for the Inofyta aquifer, where a comprehensive remediation scheme should be properly implemented immediately. Therefore the origin of Cr(VI) is an important parameter that must be taken into account for the rational management of aquifers exhibiting significant Cr(VI) concentrations, since completely different technical and institutional actions, with entirely different costs, should be undertaken depending on whether Cr(VI) is of geogenic or anthropogenic origin.

**Keywords:** Chromium, Cr(VI), geogenic, anthropogenic, Vergina, Inofyta

### 1. Introduction

Chromium is a widely used metal in industrial activities, mainly in metallurgy and production of refractory and chemical products (Saha et al. 2011). The combination of extended industrial use of chromium with inadequate industrial waste management practices of the past has led to extensive soil and groundwater contamination. Both concentration and chromium speciation mainly depend on both the specific industrial use entailed and its ultimate disposal environment. Anthropogenic Cr(VI) is typically characterized by significant spatial variation within contaminated areas and the co-existence with other industrial contaminants, such as other heavy metals and organic solvents used in industrial processes.

However, recent studies indicated that the occurrence of Cr(VI) in groundwater can also be attributed to geogenic origin. Geogenic Cr(VI) in groundwater comes from minerals containing Cr,

such as chromite, which appears in areas with significant presence of ultramafic rocks and ophiolitic complexes. Significant presence of ultramafic rocks and ophiolitic complexes has been reported in several areas worldwide and particularly in areas of the Pacific Ocean (California and Mexico) and Eastern Mediterranean (Greece, Italy). Although the solubility of chromite rocks in groundwater is very low, the presence of natural oxidants in the aquifers, and particularly of manganese oxides (MnOs), oxidize Cr(III) to Cr(VI), increasing, thus, the concentration of Cr(VI) in groundwater. This redox process results in achieving significant Cr(VI) concentrations in groundwater, which, however, usually do not exceed 100 µg/L (Fantoni et al. 2002, Izbicki et al. 2008, Morrison et al. 2009, Margiotta et al. 2012) and is rather diffused along the aquifer. In other words, based on this extensive prior research, we can safely conclude that when Cr(VI) concentrations are found to be higher than this upper geogenic threshold of 100 µg/L, it is very likely, even in ophiolitic geological environments, that there is an anthropogenic source. However, there are a few cases worldwide where in the absence of any anthropogenic activity, Cr(VI) concentrations well above this 100 µg/L threshold have been detected.

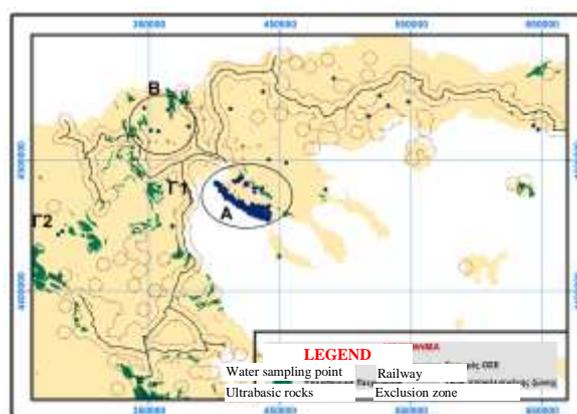
The origin of Cr(VI) is an important parameter that must be taken into account for the rational management of aquifers exhibiting significant Cr(VI) concentrations, since completely different actions, with completely different costs, should be undertaken depending on whether Cr(VI) is primarily geogenic versus anthropogenic. While in the case of anthropogenic origin several remediation alternatives can be undertaken by applying the appropriate technologies to effectively address the contamination problem, this is not possible in the case of geogenic origin, due to the great areal extension of Cr(VI) presence in the entire aquifer and due to the dissolution of Cr-bearing minerals, which will in turn continuously feed the groundwater with Cr(VI). Thus, in the case of geogenic origin applying mainly institutional measures, such as providing alternative water supply that is free of Cr(VI), is the only reasonable alternative to ensure safe water end uses. In some cases, pump & treat systems, mainly for irrigational purposes, might be applied at a cost, in order to ensure a safe water supply.

This study aims at highlighting the origin of Cr(VI) as the most important decision-making parameter for the rational management of Cr(VI)-contaminated aquifers in Greece.

## 2. Chromium in greek aquifers

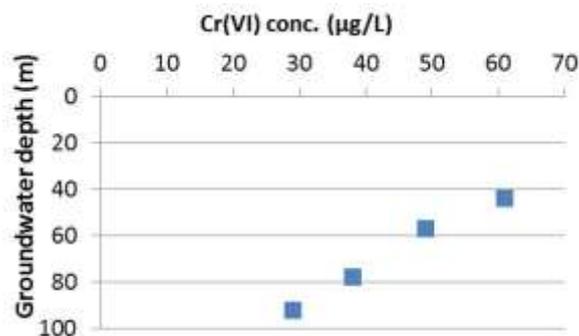
### 2.1. Geogenic chromium in groundwater

Greece is characterized by the presence of ophiolitic complexes (Papanikolaou 2009). A recent study highlighted the geographic areas where the detected Cr(VI) in groundwater is probably of geogenic origin (Tettas 2012, Panagiotakis et al. 2012). This study was based on three (3) main criteria for highlighting the respective areas: a) the presence of consistent and systematic monitoring of Cr(VI) groundwater concentrations as recorded by previous studies, b) the absence of any anthropogenic activities related to primary chromium release to the environment and c) the geological background being ophiolitic. The areas that were mainly highlighted after this screening process were Chalkidiki-Thermi (A), Edessa (B), Vergina (Γ1) and Grevena (Γ2) (Figure 1).



**Figure 1.** Areas with geogenic Cr(VI) in groundwater in Greece.

The above results were verified by further research aiming at investigating the origin of Cr(VI) in groundwater where a new borehole of 100 m depth was constructed in the Vergina area (Γ1, Figure 1), one of the areas listed above. Our new results verified the presence of elevated Cr(VI) groundwater concentrations and Cr(III) in soils (Dermatas et al. 2015). In particular the maximum detected Cr(VI) concentration in groundwater was 61 µg/L, which is one of the highest concentrations measured globally in areas with similar geological background, and this value was decreased with sampling depth (Figure 2). Cr(VI) in soil was similarly decreased with respect to increasing depth (0.7-7.5 mg/kg), although the concentration of total chromium was generally increased (1410-12.137 mg/kg). These results were supported by the decreased mass of Cr(III) which is available for oxidation to Cr(VI) with increasing depth, since rock erosion decreased and pH values increased with increasing depth. Finally, the extensive agricultural activity in the area, resulted in high nitrate concentrations in groundwater (≈80 mg/L), which probably also contribute to the rise of Cr(VI) mobility in groundwater (Mills et al. 2011, Dermatas et al. 2015).



**Figure 2.** Cr(VI) concentration in groundwater in relation to sampling depth in Vergina aquifer.

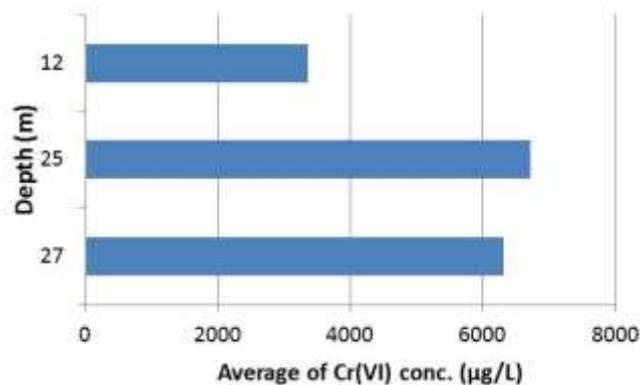
## 2.2. Anthropogenic chromium in groundwater – the case study of Inofyta industrial area

The most representative case of anthropogenic groundwater contamination in Greece is the makeshift industrial area of Inofyta, which still suffers from inadequate waste management practices. Until recently the detected concentrations of Cr(VI) in local groundwater did not exceed 160 µg/L, with the vast majority of the recorded concentrations being under the 50 µg/L national limit. In the handful of cases where Cr(VI) measured higher than the 100 µg/L upper geogenic threshold, they could not be solely attributed to the industrial activities, since the ophiolitic geological background in the area is also likely contributing to the detected Cr(VI) concentrations. In addition, these recorded values were obtained from sampling at pre-existing, mainly irrigational wells with unknown technical characteristics, extending over several shallow aquifer zones down to the targeted, higher discharge, productive deep aquifer. Moreover, sampling was performed by conventional sampling methods, overlooking the fact that several aquifer zones were simultaneously tapped during sampling. Anthropogenic activities will first adversely impact aquifer zones closer to the soil surface and therefore the majority of anthropogenic Cr(VI) will be encountered in these relatively shallow groundwater aquifer zones. In the case of the Inofyta, prior to our study sampling, sampled wells extended at significantly greater depths where the, mainly limestone, productive aquifer zones are located, since they were initially constructed to mainly cover the areas' perceived irrigational needs. This fact made groundwater sampling unreliable, since groundwater samples were obtained by pumping from multiple aquifers, with the groundwater pumped from the deepest, higher discharge aquifer effectively diluting the Cr(VI) concentration groundwater pumped from the much lower discharge shallower contaminated aquifer zones, thus concealing the real size and source of the contamination in the final values being recorded. The fact that in some cases there are undocumented reports of deep groundwater injection of industrial waste in this area only further complicates this issue.

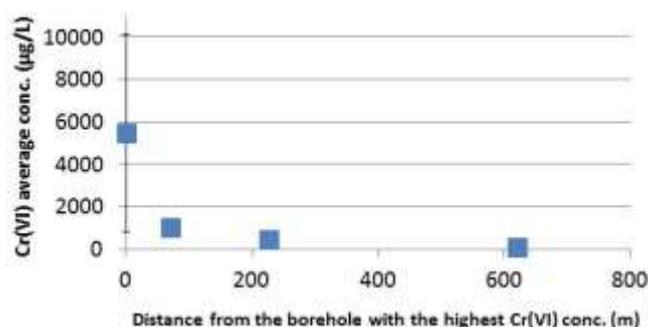
Conversely, as demonstrated by the LIFE+ CHARM project, the actual size and source of the problem was very different from what was demonstrated until recently. Groundwater sampling from new boreholes within the industrial area using the discrete sampling method showed Cr(VI)

concentrations as high as 10 mg/L, 100 times above the geogenic origin upper threshold value, which is thus indisputably of anthropogenic origin. This anthropogenic origin is further supported by the tremendous spatial variations observed in Cr(VI) concentrations, contrary to what was observed at the Vergina aquifer, where Cr(VI) concentrations presented a uniform distribution along the aquifer. These results would not be obtained if the discrete sampling method was not applied, by which groundwater sampling from known depths and thus specific and distinct aquifer zones is achieved. Needless to say that our study confirmed the above stated hypothesis, that the vast majority of anthropogenic Cr(VI) was indeed encountered in the relatively shallow groundwater aquifer zones characterized by a much lower discharge as compared to the deep limestone aquifer zones.

More specifically, in the borehole where the highest Cr(VI) level was detected, the average Cr(VI) groundwater concentrations during three (3) successive sampling campaigns increased with increasing depth: from 3 mg/L at 12 m to 7 mg/L at 25 m (Figure 3), while it sharply decreased to 1/10 and to 1/20 of the maximum concentration within a distance of less than 100 m and 250 m from this borehole, respectively (Figure 4). Additionally, the anthropogenic origin of Cr(VI) in groundwater is further supported by two other parameters which are: a) the high concentrations of chloride ions (up to 440 mg/L) and b) the presence of other pollutants (mainly synthetic organic compounds) in the groundwater.



**Figure 3.** Variation of the average Cr(VI) groundwater concentration for three successive sampling campaigns in relation to the sampling depth in the borehole with the highest Cr(VI) levels at Inofyta aquifer.



**Figure 4.** Variation of the average Cr(VI) groundwater concentration in relation to the distance from the borehole with the highest Cr(VI) levels at Inofyta aquifer.

Therefore, the combination of: a) the very high concentrations of Cr(VI) far above the upper geogenic threshold of 100 µg/L, b) the tremendous spatial Cr(VI) concentration fluctuations and c) the presence of other contaminants in the groundwater leads undoubtedly to the conclusion that Cr(VI) detected in the Inofyta aquifer is of anthropogenic origin. The very high levels of Cr(VI) contamination detected render the undertaking of immediate remedial actions imperative.

### 3. Conclusions

Cr(VI) in groundwater can be either of geogenic or anthropogenic origin. Greece is characterized by the significant presence of ultramafic rocks, which result in elevated geogenic Cr(VI) concentrations in groundwater, that might exceed the maximum allowable level of 50 µg/L. As demonstrated by the LIFE+ CHARM project, Cr(VI) concentrations up to 61 µg/L were detected in the area of Vergina. These values are among the highest that have been recorded globally in areas with similar geological background. Regarding anthropogenic origin, the Inofyta area is the most representative case study in Greece. The presence of a makeshift industrial area, lacking the necessary infrastructure for waste management, results in uncontrolled disposal of industrial waste and consequently in groundwater contamination. Until recently, the available data were not adequate for attributing the Cr(VI) concentrations detected in the Inofyta aquifer directly to anthropogenic activities. However, the present study conducted within the LIFE+ CHARM project framework reliably established the actual size of the problem, since Cr(VI) concentrations up to 10 mg/L in groundwater were detected. Although both of these sites demonstrated above the allowable national limit Cr(VI) groundwater concentrations, it is obvious that they require totally different management approaches. Thus, although for the Vergina aquifer, institutional measures and pump & treat systems might be sufficient to ensure safe water supply to cover the mainly irrigational local needs, this is not the case for Inofyta aquifer, where a comprehensive remediation scheme should be properly implemented immediately.

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