

# GEOCHEMICAL EVIDENCES OF GEOGENIC ORIGIN OF CHROMIUM IN OROPOS PLAIN ATTICA

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**SUMMARY:** Oropos plain exhibits significant concentrations of Cr(VI) in groundwater. Chemical analysis of soil samples show high concentrations of Cr in soils of Oropos plain. Soil fractionation with liquids of high specific gravity that separate soils into heavy and light fractions and subsequent chemical analysis of the fractions showed that the heavy fraction has extremely high concentrations of Cr (11,965 to 15,583 mg/kg). The mineralogical and chemical analysis of those fractions shows strong evidence of ultramafic rock erosion products. The results support the evidence of geogenic origin of hexavalent chromium in soils and groundwater of Oropos Plain. Management of groundwater in the area would require studies that would delineate the anthropogenic from geogenic contamination.

## 1. INTRODUCTION

The emplacement of the last tectonically moved nappe of ophiolites on top of a series of other nappes (Papapnikolaou 2009) in the Greek geological history influenced the mineralogy and geochemistry of soils. The presence of geogenic heavy metals in soils have been recently acknowledged as a significant source of soil and water contamination in Europe and USA (Rodríguez and Reuter 2007, Morrison et al. 2009). Ophiolites consist of ultramafic rocks which are rich in Cr and Ni and their weathering can yield sediments and soils with inherently high

concentrations of Cr and Ni. Geogenic sources of Cr(VI) in groundwater are minerals common in ultramafic rocks such as chromite, serpentine, olivine etc. (Oze et al. 2004b). However other minerals such as clays (chlorites, smectites) and Fe-oxides may contain considerable Cr concentrations (Oze et al. 2004a). A significant number of studies in the scientific literature have reported geogenic origin hexavalent chromium in groundwater that exceed regulatory levels (e.g. Fantoni 2002, Izbicki et al. 2008).

The trivalent chromium is considered essential to humans (taken in the form of chromium picolinate) while the hexavalent chromium is a known carcinogen when inhaled and raises concerns about human health and aquatic quality when drinking water and aquatic quality standards are exceeded. The World Health Organization (WHO) and the European Union-Drinking Water Directive have established a 50 µg/L drinking water standard for total chromium. The United States Environmental Protection Agency (US EPA) has set the standard to 100 µg/L while most of the States have established a standard of 50 µg/L similar to EU and WHO.

The present study has been conducted in Oropos plain where the groundwater has significant concentrations of hexavalent chromium. Asopos River is crossing the plain and carries anthropogenic contamination of heavy metals from the industrial area in the Municipality of Oinofyta. At the same time, ultramafic rocks are outcropping in the area suggesting possible geogenic origin of Cr in soils and groundwater. This study aims at providing geochemical evidence of geogenic origin contamination in Oropos Plain.

## **2. MATERIAL AND METHODS**

### **2.1 Site Description**

The case study is located in northeastern Attica (Oropos municipality). The area is situated on a Neogene sedimentation marine basin, surrounded by outcrops of weathered ultramafic rocks and limestones (Figure 1). The Neogene formations are comprised of two lithological units; one of conglomerates and one of finer sediments with marls and limestones. In one particular area at the site, lignites lenses have been found into the marls. Ultramafic rocks outcrop has been found in the northwestern part of the study area as well as in the northern part of Euvoikos gulf. The study area covers the lower part and the delta of Asopos River basin and is located downstream from the largest industrial park of Greece (Oinofyta Municipality).

### **2.2 Physico-chemical characteristics of soils and groundwater**

27 soil (May 2008), 29 groundwater samples and 4 river samples (February, May and August 2008 and February 2009) was obtained for geochemical analysis. Aqueous samples were analyzed for pH, conductivity, nitrate, ammonia, phosphate, hexavalent and total chromium, cations (Mn, Fe, Ca, Mg, Na, K) and heavy metals. Aqueous samples were analyzed for nutrients with a spectrophotometer HACH 2800DR and for metals with an ICP-MS (Agilent 7500-CX). The Amberlite IR – 120 resin was used for the determination of Cr(VI).

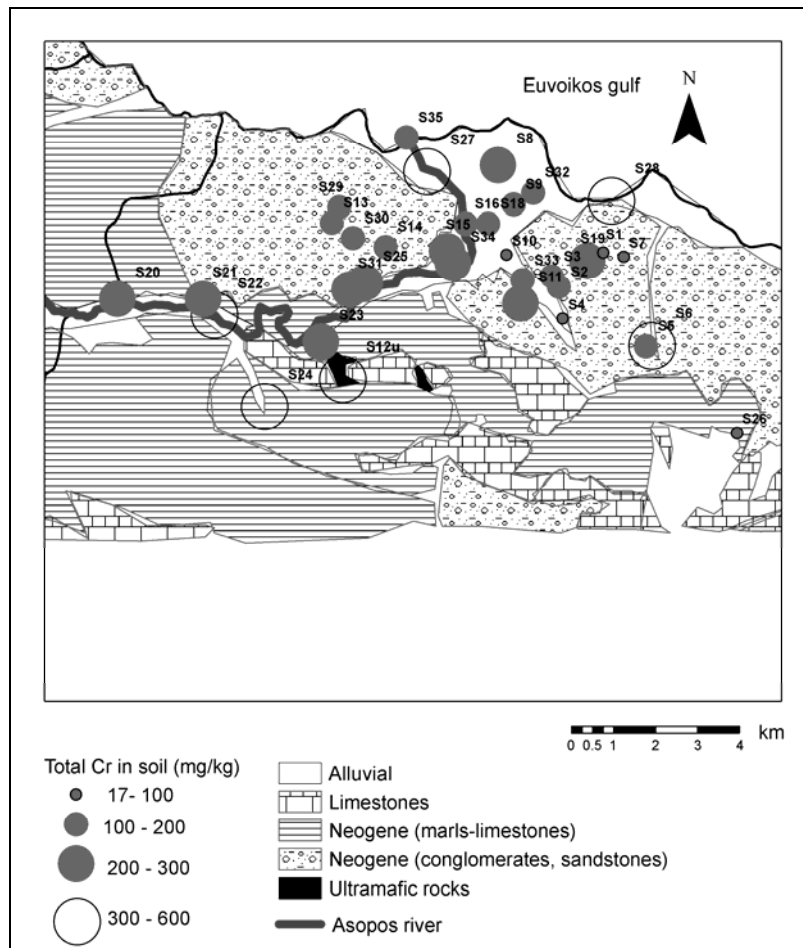


Figure 1. Geology of Oropos area, soil sampling sites in Oropos plain

The mineralogical composition was determined by X-ray diffraction (XRD) techniques using a Bruker D8 Advance powder diffractometer, on samples from the neogene formations, alluvial, ultramafic rocks and serpentine soil. The data were obtained at 35 kV and 35 mA, with a graphite monochromator, using CuK $\alpha$  radiation. A 0.019° scanning step and 32-s scanning time per step was used for the range 4 to 70°. Mineralogical analysis performed for three soils of different lithological origin.

Soil separation into light and heavy classes was performed in soil S23 by using a liquid with specific gravity of 2.8 gr/cm<sup>3</sup> (tetrabromoethane, tetrachloromethane). Mineralogical phases of different density e.g. light minerals like quartz, calcite dolomite (low density) and heavy minerals like magnetite chromite (higher density) were separated. Prior to soil processing, wet sieving was

used to separate the sample into three different fractions  $>500\ \mu\text{m}$ ,  $100\text{--}500\mu\text{m}$ ,  $<100\mu\text{m}$ . Soil processing was performed with a soil grain size of  $>500\ \mu\text{m}$ ,  $100\text{--}500\mu\text{m}$ . After soil processing, the heavy fraction (H) was obtained as the sink material in the liquid for fractions  $>500\ \mu\text{m}$  (500H),  $100\text{--}500\mu\text{m}$  (100H) and the light (L) as the float material (500L, 100L). Mineralogical and chemical analysis was also performed for all derived fractions by using XRD analysis and ICP-MS. Micro-XRF was also applied for all derived fractions using an Orbis micro-XRF elemental analyzer system (EDAX INC). Analysis was performed with an Rh tube at 30 kV/200  $\mu\text{A}$  and each point was analyzed for 30 seconds.

Column studies were used to emulate the mobility of Cr during precipitation and irrigation events and assess the potential of anthropogenic contamination in the area. Column tests were conducted by packing 50 g of soil in columns and successively simulating rain, irrigation and rain again in a continuous round of 12 days. (500 mm of equivalent rainfall- 500 mm of irrigation water with a concentration of 150  $\mu\text{g/L}$  CrVI-rain of 200 mm). All solutions were measured for total Cr using an ICP-MS.

### 3. RESULTS-DISCUSSION

The chemical analysis of ground water revealed a range of Cr(VI) concentrations of 0.18  $\mu\text{g/L}$  to 190  $\mu\text{g/L}$ , pH 7.5 ( $\pm 0.3$ ) and electrical conductivity 1453  $\mu\text{S/cm}$  ( $\pm 462$ ). 28% of the wells investigated exhibited Cr(VI) concentrations close or higher to regulatory levels (50  $\mu\text{g/L}$ ). The use of Amberlite IR – 120 resin showed that Cr in groundwater is mainly in the form of Cr(VI).

The soil pH, electrical conductivity (E.C.) organic matter (OM %) and Cr concentration ( $\text{HNO}_3$  digestion) are depicted in Table 1. The average Cr concentration is slightly higher than the lower Cr concentration level determined in serpentine soils (Oze et al. 2004a, 2004b), in addition 40% of the soils exhibited Cr concentration higher than 200 mg/kg. Table 1 presents the results from samples that exhibit unique characteristics (lignite lense-S6, Neogene Limestones-S26, ultramafic rocks, Serpentinite-S12d and in situ serpentine soil S12u).

Table 1. Cr concentration in Oropos soils (S1-S30) lignite lens (S6), serpentine soil (S12u), ultramafic rock (S12d), Neogene limestone (S26)

	Soils (S1-S30)	S6	S26	S12u	S12d
pH	8.07	3.28	8.75	8.06	8.54
E.C. $\mu\text{S/cm}$	355 (340) <sup>a</sup>	6310 (134) <sup>b</sup>	150 (32) <sup>b</sup>	83 (21) <sup>b</sup>	88 (19) <sup>b</sup>
Cr mg/kg	212 (62) <sup>a</sup>	442 (32) <sup>b</sup>	54 (4) <sup>b</sup>	567 (23) <sup>b</sup>	1900 (76) <sup>b</sup>

O.M.%	1.7 (0.7) <sup>a</sup>	11.84 (0.4)	0.1 (0.05) <sup>b</sup>	2.11 (0.01) <sup>b</sup>	-
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-: Not detected

<sup>a</sup>: Parentheses depict standard deviation due to spatial variability

<sup>b</sup>: Parentheses depict standard deviation of the measurement

PCA analysis was performed using all the samples for the following chemical parameters: Cr, Mn, Fe, Al, Mg, K, pH, and electrical conductivity (E.C). Figure 2 presents the score plot for the two first components, whereas the first three principal components describe 97% of the total variation. Soils (S1-S27) are grouped into group A, whereas S6, S12d and S26 are excluded due to different geochemical characteristics. S6 and S12d are lignite lenses and ultramafic rock respectively whereas S26 is a neogene limestone and exhibits low Cr content. Soils in Oropos plain exhibit identical geochemical characteristics and have high Cr content.

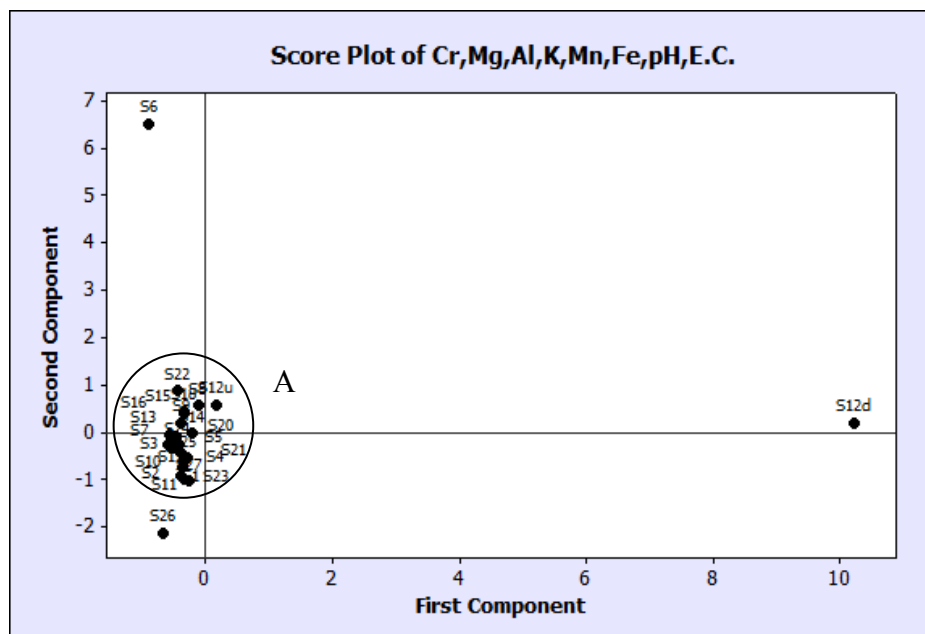


Figure 2. Principal component analysis of soil geochemistry (Cr, Mg, Al, K, Mn, Fe, pH, E.C.) for samples S1-S27.

It is worthy mentioning lignite lenses (S6) exhibit high Cr content and this has been reported also by others and demonstrates that soil solutions rich in Cr content influenced lignite lenses before and/or after lignite lenses formation (Kaupenjohann and Wilcke 1995). The S12u is a serpentine soil on top of ultramafic rock (S12d) and exhibits high Cr concentration (567 mg/kg). The soil S12u exhibits 70% less Cr compared to the parent material S12d which is an indication of Cr leaching through erosion and or weathering processes.

The mineralogical analysis were applied to soils S12u (serpentine soil), S23 (neogene sediments) S8 and S15 (alluvial). Mineralogy analysis was also performed for rock sample S12d for comparison reasons with S12u soil. The samples S23, S8 and S15 contain calcite and quartz as primary mineralogical phases whereas chlorite, illite and montmorillonite were also identified. S12u contains serpentine and quartz. S12d contain also serpentine which is characteristic mineral for ultramafic rocks. Valley soils S8, S15 and S23 have typical mineralogical phases of soils developed in sedimentary parent material (alluvial and neogene formations).

The separation of heavy fraction (H) and light fraction (L) in soil S14, S22, S23 and S24 was applied in grain size  $>500\text{ }\mu\text{m}$  and  $500\text{-}100\text{ }\mu\text{m}$ . Chemical analysis of heavy fraction 500H and 100H exhibit on average 11,965 mg/kg and 15,583 mg/kg of Cr respectively. Light fractions 500L and 100L also exhibit high Cr concentration 402 mg/kg and 427 mg/kg respectively. The results from the mineralogical analysis for soil S23 and 100H and 500H are shown in Figure 6. Fractions 100H and 500H contained aluminium chromite, magnesium chromite and hematite magnetite. Light minerals were also present in 100H and 500H like quartz and dolomite, probably related to iron coatings and/or aggregates of iron oxide and quartz which make the quartz grains heavier. The bulk soil mineralogical analysis for S23 (2 mm) is identical with that described previously for other soils of Oropos plain. Finally the light fractions contained minerals like quartz, calcite, and minor minerals like montmorillonite and illite.

A representative micro-XRF picture for sample S23 and fraction 100H is presented in Figure 5. The chemical analysis is also shown in addition to a diagram of Al versus Cr that shows that soils in Oropos fall on the theoretical line which describes the isomorphous substitution of Al to Cr in a typical chromite (Oze 2004a).

Finally, column experiments results simulating rain and irrigation events for soil S7 are presented in Figure 6. Column experiments showed low potential of Cr(VI) release from soils after a simulated rain event and high retention of chromium when simulated irrigation took place.

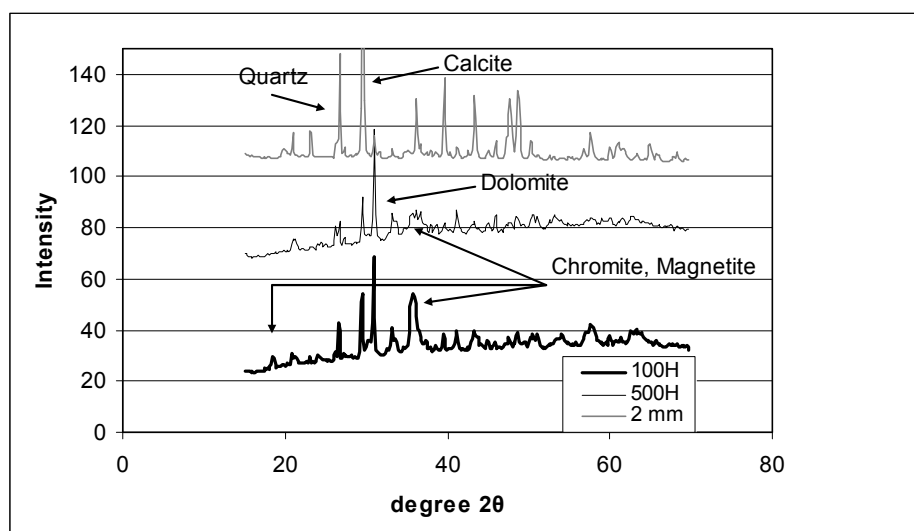


Figure 4. Mineralogical analysis of processed soil fractions S23 (100H, 500H) and bulk soil fraction S23 (2mm).

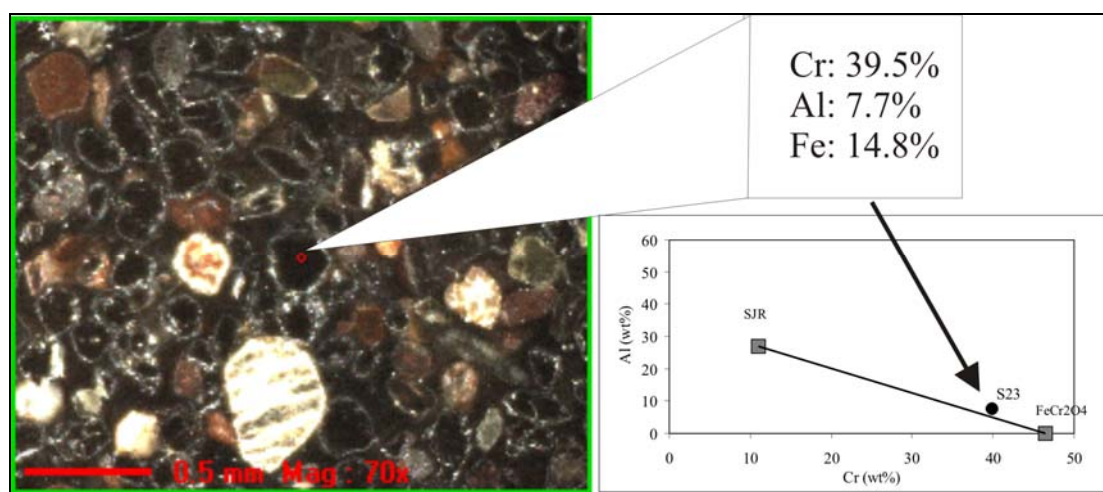


Figure 5. Picture of black grain for 100H fraction of soil S23 and point micro-XRF analysis (Cr, Al, Fe), Al and Cr diagram with the theoretical line connecting SJR Chromite chemistry for serpentine in Jasper Ridge and FeCr<sub>2</sub>O<sub>4</sub> stoichiometric chemistry of chromite.

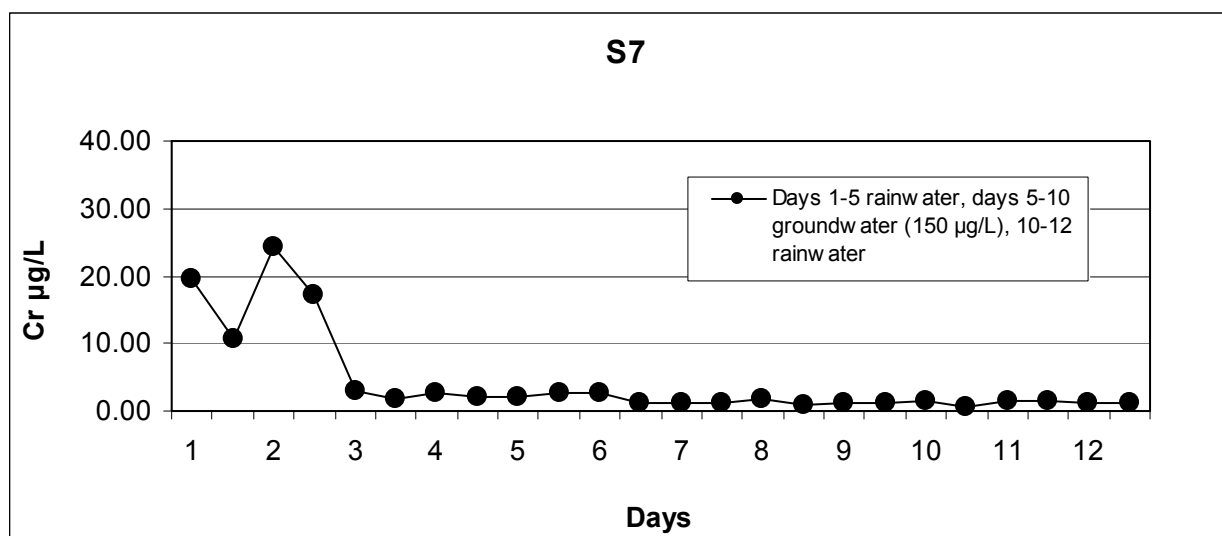


Figure 6. Column experiments for soil S7 simulating 500 mm of annual rain, 500 mm of irrigation water, and 200 mm of rain after irrigation. Circles depict Cr average concentration.

## CONCLUSIONS

The results support the evidence of geogenic origin of hexavalent chromium in soils and groundwater of Oropos Plain. The soils in the area are erosion products of ultramafic rock. Management of groundwater in the area would require studies that would delineate the anthropogenic from geogenic contamination.

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