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Geogenic Cr oxidation on the surface of mafic minerals and the hydrogeological conditions influencing hexavalent chromium concentrations in groundwater

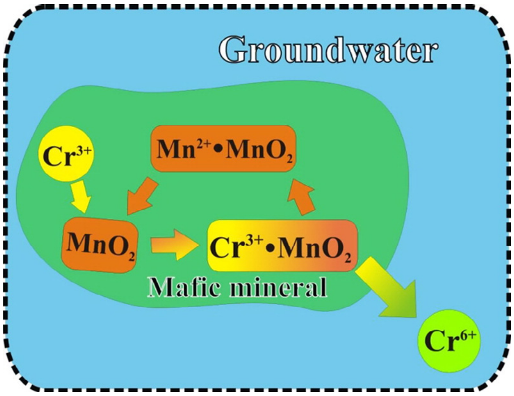
N. Kazakis [a,*], N. Kantiranis [b], K.S. Voudouris [a], M. Mitrakas [c], E. Kaprara [c], A. Pavlou [a]

[a] Aristotle University of Thessaloniki, School of Geology, Lab. of Engineering Geology and Hydrogeology, 54124 Thessaloniki, Greece
[b] Aristotle University of Thessaloniki, School of Geology, Dept. of Mineralogy, Petrology and Economic Geology, 54124 Thessaloniki, Greece
[c] Aristotle University of Thessaloniki, Department of Chemical Engineering, 54124 Thessaloniki, Greece

HIGHLIGHTS

- Fe–Mn oxides are located on the surface of mafic minerals and coexist with Cr.
- Cr(VI) is released directly from serpentine, chlorite, amphibole and pyroxene.
- Higher Cr(VI) concentrations are detected in shallow porous aquifer (<150 m).
- Low groundwater velocity favors Cr(VI) generation in sedimentary aquifer.

GRAPHICAL ABSTRACT



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ABSTRACT

This study aims to specify the source minerals of geogenic chromium in soils and sediments and groundwater and to determine the favorable hydrogeological environment for high concentrations of Cr(VI) in groundwaters. For this reason, chromium origin and the relevant minerals were identified, the groundwater velocity was calculated and the concentrations of Cr(VI) in different aquifer types were determined. Geochemical and mineralogical analyses showed that chromium concentrations in soils and sediments range from 115 to 959 mg/kg and that serpentine prevails among the phyllosilicates. The high correlation between chromium and serpentine, amphibole and pyroxene minerals verifies the geogenic origin of chromium in soils and sediments and, therefore, in groundwater. Manganese also originates from serpentine, amphibole and pyroxene, and is strongly correlated with chromium, indicating that the oxidation of Cr(III) to Cr(VI) is performed by manganese–iron oxides located on the surface of Cr–Mn-rich minerals. Backscattered SEM images of the soils revealed the unweathered form of chromite grains and the presence of Fe–Mn-rich oxide on the outer surface of serpentine grains. Chemical analyses revealed that the highest Cr(VI) concentrations were found in shallow porous aquifers with low water velocities and their values vary from 5 to 70 μg/L. Cr(VI) concentrations in ophiolitic complex aquifers ranged between 3 and 17 μg/L, while in surface water, karst and deeper porous aquifers, Cr(VI) concentrations were lower than the detection limit of 1.4 μg/L.

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[*] Corresponding author.
E-mail address: kazanera@yahoo.com (N. Kazakis).

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1. Introduction

The average concentration of Cr in the Earth's crust is about 100 mg/kg, although significant variations are observed depending on bedrock (Nriagu, 1988; Richard and Bourg, 1991). Higher concentrations of Cr occur in ultramafic rocks (1800 mg/kg), while considerably lower ones are found in sandstones (35 mg/kg), granites (22 mg/kg) limestones (11 mg/kg) (Faure, 1992; Fantoni et al., 2002). In the natural environment, chromium exists in two oxidation states: Cr(III) and Cr(VI) (Bartlett and James, 1979; Ball and Nordstrom, 1998). Cr(VI) has been recognized as a carcinogen and irritant via inhalation and is about 100–1000 times more toxic than Cr(III) when ingested (Salnikow and Zhitkovich, 2007; Stout et al., 2008; Linos et al., 2011). The origin of hexavalent chromium in soils, sediments and groundwater has been the subject of extensive research during the past decades in many regions of the world, such as the Leon basin in Mexico (Robles-Camacho and Armientac, 2000), the La Spezia Province in Italy (Fantoni et al., 2002), the Uraina State of Sao Paolo in Brazil (Bourette et al., 2009), and Davis in the southwestern Sacramento Valley of California, USA (Mills et al., 2011).

The majority of minerals containing Cr(III) belong to the Cr-spinel group. These include chromite ($FeCr_2O_4$) and magnesiochromite ($MgCr_2O_4$), while the mineral phases of Cr(VI), crocoite ($PbCrO_4$) and iranite ($PbCr_4OH_2O$), are rarer (Palmer and Wittbrodt, 1990). Chromium is also present as an element in clay minerals and can be an important source of chemically mobile and bioavailable Cr (Oze et al., 2004; Morrison, 2010). Weathering and erosion of ultramafic rocks have also been determined to be a natural source of chromium in sediments and groundwaters (Chung et al., 2001; Cooper, 2002; Garnier et al., 2006; Morrison et al., 2009; Economou-Eliopoulos et al., 2011; Moraetis et al., 2012). Anthropogenic activities that pollute the natural environment with hexavalent chromium include paint manufacturing, tannery industry, mining activities, phosphate fertilizer manufacturing (Molina et al., 2009), and the combustion of coal and fly ash deposits (Jacobs and Testa, 2004). Even in heavily industrialized areas Cr and specifically Cr(VI) contamination in soils, sediments, plants, surface and groundwaters is due to both natural processes and human activities and depends, among other things, on rock chemistry, mineral chemistry, the organic or inorganic affinity of Cr to the different metallic and industrial mineral deposits that are exploited by humans and the bioavailability of Cr (Papastergios et al., 2011; Petrotou et al., 2012; Megalovasilis et al., 2013; Skordas et al., 2013).

In the common pH range of natural waters (6.5–8.5) the solubility of Cr(III) is comparably low (<5 μg/L) (Rai et al., 1987) within the Cr(VI) form is expected to dominate whenever increased levels of naturally leached chromium occur (Gonzalez et al., 2005; Kaprara et al., 2015). Natural oxidation of Cr(III) to Cr(VI) in aquatic systems is related to the presence of manganese oxides which are considered as direct oxidizing agents or as catalysts (Eary and Rai, 1987).

The high toxicity of Cr(VI) and its ability to cause various cancers and DNA damage (Barceloux, 1999; Linos et al., 2011) classifies Cr(VI) as a significant groundwater pollutant worldwide.

This study focuses on: 1) the role of Mn oxides in Cr(III) oxidation in natural environments, and 2) the hydrogeological factors that influence Cr(VI) concentration in groundwaters, mainly in porous aquifers that cover the majority of the world's water demands.

Anthemountas basin in northern Greece was chosen as a suitable study area as it contains various aquifer types (Kazakis et al., 2013) and significant variations of Cr(VI) concentrations (Kaprara et al., 2015). Additionally, the water demands of the basin and its surrounding area are covered entirely by its groundwater. Anthropogenic sources of Cr(VI) in the basin are absent.

2. Study area

Anthemountas River basin is located in northern Greece in the eastern part of the Thermaikos Gulf (Fig. 1) and it covers an area of 374 km^2. The mean altitude and slope inclinations of the study area are 259 m and 20%, respectively, and the main River is Anthemountas which flows from east to west. The study area is characterized by a Mediterranean-type climate, with an average annual temperature of 15.1 °C and average annual precipitation of 451.3 mm. About 70–80% of the annual precipitation occurs during the wet period (October to May), while summers are usually dry (June to September).

The mountainous area surrounding the basin comprises Mesozoic igneous and metamorphic rocks, ultramafic rocks such as dunites, peridodites and gabbros, and metamorphic rocks such as schists, gneiss and recrystalline carbonate rocks. The recrystalline carbonate rocks are located in the south-central part of the basin and cover an area of 16 km^2 that hosts the karstic aquifer. The ultramafic rocks are serpentinized, form a narrow strip of northwest–southeast orientation and contain Cr–Mn-rich pyroxene, amphibole and clinochlore as their main mineral phases (Christofides et al., 1994). Chromium concentration of the area's ultramafic rocks reaches up to 2000 mg/kg (Sapoutzis, 1979). The ultramafic rocks of Anthemountas area are part of the ultramafic rock belt of the western Chalkidiki peninsula and are characterized by extensive cryptocrystalline magnesite deposits (Dabitzias, 1980). Neogene and Quaternary sediments are located in the basin with variable thicknesses, ranging from 150 m in the eastern part to over 1000 m in the western coastal area of the basin. Conglomerates, sandstones, marls and red-clay series constitute the Neogene sediments of the study area, while terrace systems (gravels, sands, pebbles and clays) in the east and alluvial deposits (sands, gravels and sands with clay) in the west form the basin's Quaternary sediments.

The water demands of the local population are met by the basin's porous aquifers exploited through a large number of boreholes. However, a few boreholes also exist in fissured rocks including the ophiolitic complex aquifer. The fissured ophiolitic complex aquifer is characterized by fractured porosity. In the eastern part of the Anthemountas basin (sub-basin of Galatista), the thickness of the unconfined porous aquifer does not exceed 100 m. In the western part of the basin the thickness of the porous, freshwater aquifers is about 300 m. The porous aquifer can be categorized into the upper, unconfined shallow aquifer with a mean thickness of 80 m, and the deep confined aquifer below 150 m (Fig. 2).

According to a previous study (Kazakis et al., 2013) the hydraulic characteristics of the upper aquifer are: i) hydraulic conductivity values between 0.3 m/d and 43 m/d, ii) storativity (S) from 10^{-2} to 3×10^{-1}, iii) specific capacity between 15 and 270 m^2/d, and iv) effective porosity from 18 to 26%, whereas the characteristics of the deep confined aquifer are: i) hydraulic conductivity values between 0.1 m/d and 8 m/d, ii) storativity (S) up to 10^{-3}, iii) specific capacity between 2 and 100 m^2/d, and iv) effective porosity from 15 to 20%. Calculation of the hydraulic parameters was based on the results of ten pumping test analyses, applying the Theis, Cooper–Jacob and recovery methods (Kazakis, 2013).

Recharge of the porous aquifers occurs via infiltration of precipitation, percolation from the Anthemountas River and torrents, and lateral inflows from the karstic aquifer in the south and the fissured rock aquifer in the north. Piezometric maps reveal the subsurface hydraulic connection between the aforementioned aquifers and the porous aquifers (Kazakis et al., 2013). According to list of local industries provided by the Municipalities and the National Statistical Service of Greece, no industrial sources of hexavalent chromium exist in the study area. A field inventory of the pollution sources in the basin confirmed the absence of such industrial activities, thus increasing the probability of the natural origin of hexavalent chromium in the groundwater. The magnesite mines of Vavdos are located near the south-east edge of the Anthemountas basin (Dabitzias, 1980). Chromite minerals and Cr-rich silicates have been recorded in the wastes of this mine (Grieco et al., 2011). Although these wastes constitute an anthropogenic source of chromium according to previous studies (Kazakis, 2013, 2014) they are located outside the recharge zone of the studied aquifers.