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Application of chromium stable isotopes to the evaluation of Cr(VI) contamination in groundwater and rock leachates from central Euboea and the Assopos basin (Greece)

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ABSTRACT

Major and trace elements (a) in groundwater, ultramafic rocks from natural outcrops and soil samples from cultivated sites of Central Euboea and Assopos basin, and (b) in experimentally produced laboratory water leachates of rocks and soils were investigated by SEM/EDS, XRD and ICP/MS. In addition, stable chromium isotopes (expressed as δ^{53}Cr values) were measured in groundwater and leachates in order to identify potential sources for Cr-contamination.

The higher Cr(VI) concentrations in soil leachates compared to those in the rock pulp leachates potentially can be explained by the presence of larger amounts of Fe (Fe(II)) and Mn (Mn-oxides acting as oxidizing catalysts). Assuming that redox processes produce significant Cr isotope fractionation (groundwater δ^{53}Cr values range between 0.8 and 1.98‰), the compilation of the obtained analytical data suggests that the dominant cause of Cr isotope fractionation is post-mobilization reduction of Cr(VI). However, the lack of a very good negative relationship between Cr(VI) concentrations and δ^{53}Cr values may reflect that sorption, precipitation and biological processes (fractionation during uptake by plants) complicate the interpretation of the Cr isotope signatures.

The variation in δ^{53}Cr values (0.84 to 1.98‰ in groundwater from Euboea, and from 0.98 to 1.03‰ in samples from the Assopos basin) imply initial oxidative mobilization of Cr(VI) from the ultramafic host rocks, followed by reductive processes that lead to immobilization of portions of Cr(III). Using a Rayleigh distillation model and different fractionation factors of Cr(VI) reduction valid for aqueous Fe(II) and Fe(II)-bearing minerals, we calculate that more than ~53%, but maximum ~94%, of the originally mobile Cr(VI) pool was reduced to immobile Cr(III) in the waters investigated. This indicates that efficient processes in the aquifers may facilitate natural attenuation of the toxic Cr(VI) to less harmful Cr(III).

1. Introduction

Chromium contamination of soil and groundwater is a significant problem worldwide and is becoming a serious threat to our environments. In nature, chromium occurs as trivalent [Cr(III)] and hexavalent [Cr(VI)] species, with respective compounds (Hem, 1970). Health problems, such as lung cancer and dermatitis are caused by the highly toxic and very soluble oxidized Cr(VI), in chromate oxyanions such as CrO_4^{2-}, $HCrO_4^-$ and $Cr_2O_7^{2-}$ (ATSDR, 2000; Losi et al., 1994). In contrast, the reduced Cr(III) is an essential nutrient, required for normal glucose and lipid metabolism in human bodies, adsorbs strongly on solid surfaces and co-precipitates with Fe(III) hydroxides (Kotas and Stasicka, 2000). Due to the toxicity of Cr(VI), most countries of the European Union have currently regulated the limit to 50 $\mu g \cdot L^{-1}$ for total chromium [EC, 1998 Council Directive (98/83/EC)].

A number of studies have shown that chromium stable isotopes are effective in monitoring Cr in natural conditions to determine natural and/or anthropogenic sources (Basu and Johnson, 2012; Berna et al., 2010; Døssing et al., 2011; Ellis et al., 2002, 2004; Han et al., 2012; Izbicki et al., 2008; Jamieson-Hanes et al., 2012; Johnson, 2011; Kitchen et al., 2012; Novak et al., 2014). Recently, Cr stable isotopes have seen growing use in environmental applications that range form monitoring Cr at a contaminated site to paleo-environmental applications that examine oxygenation of our environment in the Precambrian (BIFs, paleosols) etc. (Crowe et al., 2013; Frei and Polat, 2013; Frei et al., 2009). The monitoring of Cr-contaminated groundwater using Cr stable isotope tracing has been demonstrated by Berna et al. (2010), Ellis et al. (2002), Halicz et al. (2008); Izbicki et al. (2008), Novak et al. (2014); Schoenberg et al. (2008), Sikora et al. (2008), Zink et al. (2010) and others.

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Chromium has four stable isotopes; ^{54}Cr, ^{53}Cr, ^{52}Cr, and ^{50}Cr, with natural abundances of 2.37%, 9.5%, 83.8%, and 4.35%, respectively (Moynier et al., 2011; Rotaru et al., 1992). Redox processes have been shown to produce significant Cr isotope fractionation during the transition from Cr(VI) to Cr(III) (Schauble et al., 2004). During reduction, the lighter isotopes are preferentially reduced, resulting in an enrichment of ^{53}Cr relative to ^{52}Cr values in the remaining Cr(VI) pools. This enrichment is measured as the change in the ratio of $^{53}Cr/^{52}Cr$, and is expressed as $\delta^{53}Cr$ values in units per mil (‰) relative to a standard (Ellis et al., 2002). The enrichment or depletion of ^{53}Cr relative to ^{52}Cr can be quantified by measuring the $^{53}Cr/^{52}Cr$ values in aqueous solutions (Basu and Johnson, 2012; Berger and Frei, 2013; Berna et al., 2010; Farkas et al., 2013; Halicz et al., 2008; Han et al., 2012; Izbicki et al., 2008; Jamieson-Hanes et al., 2012; Kitchen et al., 2012; Schoenberg et al., 2008; Sikora et al., 2008; Zink et al., 2010; Wanner and Sonnenthal, 2013). The reduction of Cr(VI) species to Cr(III) species in aqueous systems, by abiotic (e.g. Fe(II)-minerals) and/or biological (microorganisms, organic acids) reduced species is accompanied by an isotope fractionation preferring the light isotopes in the reductant (Basu and Johnson, 2012; Sander and Koschinsky, 2000). The reduction of toxic and mobile Cr(VI) to Cr(III) is a remediation technology commonly proposed, and can naturally be enhanced by organic matter, Fe(II)-minerals and reduced species of sulfur (Kozuh et al., 1994). Thus, measurement of the $^{53}Cr/^{52}Cr$ values in groundwater has been proposed as a method to track Cr(VI) migration processes and evaluate the performance of remediation activities (Blowes, 2002; Ellis et al., 2002; Jamieson-Hanes et al., 2012).

Since the fractionation of Cr isotopes is considered to be little affected by dilution or adsorption processes (Ellis et al., 2004), local anomalies in the isotope signature of natural water can be used as a tracer for the reduction of Cr(VI). Thus, they can potentially give clues to the efficiency of natural attenuation processes transforming the dissolved and toxic hexavalent Cr(VI) to less harmful Cr(III) at specific sites (Berna et al., 2010; Ellis et al., 2002; Izbicki et al., 2008; Johnson, 2011; Raddatz et al., 2011).

The research interest has focused on the Assopos basin because it is an industrial zone (hundreds of industrial plants, such as using chromium plating, leather tanning, and applying wood staining) and the running Assopos river was proclaimed as a "processed industrial waste receiver" since 1969. Besides, untreated or poorly treated industrial waste may have been dumped illegally in now covered fills. The Assopos (Avlona) and Central Euboea basins (Messapia), dominated geologically by the widespread occurrence of ophiolites, were selected for the present study, because there is no clear-cut answer to the question regarding the influence of industry versus natural processes to the soil and groundwater contamination (Economou-Eliopoulos et al., 2011, 2012). The herein presented integrated approach is based on a compilation of geochemical/hydrochemical data of (a) ultramafic rocks, soils and groundwater samples, (b) experimentally produced laboratory water leachates of these rocks and soils and (c) stable chromium isotope data (expressed as $\delta^{53}Cr$ values) of selected natural and experimentally produced leachate water samples, originally aimed at identifying potential sources for Cr-contamination in these basins.

2. Geological and hydrological outline

2.1. Central Euboea

The area of central Euboea is covered by alluvial and Neogene sediments. It is characterized by strong geomorphological contrast and is built up mainly of Pleistocene to Holocene sediments hosting the most productive aquifers in this area (Fig. 1, sampling area). In addition, two different types of aquifers are hosted by strongly tectonized ultramafic rocks, which are widespread in central Euboea, and by the deeper karstified Triassic–Jurassic limestones.

The ophiolitic masses consist mainly of serpentinised peridotites (harzburgites and lherzolites) with some minor mafic rocks. The ophiolitic rocks are overthrusted onto Upper Cretaceous limestones and flysch sediments. The main aquifer which is probed by the wells is hosted by ophiolitic rocks and is categorized as a fissured rock aquifer. Alluvial deposits are the host rocks to the aquifer which is probed by many shallow wells for agricultural activities. These wells reach depths between 11 and 180 m (Megremi, 2010).

2.2. Assopos basin (Avlona)

The Neogene Assopos basin (Fig. 1, sampling area 2) is mainly composed by Tertiary and Quaternary sediments of more than 400 m thickness, and expands over approximately 700 km^2. Alternations of marls and marly limestones occur in the lowest parts of the basin sequences, and continental sediments consisting of conglomerates with small intercalations of marls, marly limestones, schists, sandstones, clays and flysch are dominant in the upper parts. A sharp tectonic contact between the sediment types, due to the intense neotectonic deformation, is a characteristic feature of the entire area (Chatoupis and Fountoulis, 2004). Peridotites and a Ni-laterite occurrence, overthrusted on the Triassic–Jurassic carbonates, have been described from the Aynola area by (Valeton et al., 1987). The morphotectonic structure and evolution of this basin are the result of E–W to WNW–ESE trending fault systems (Chatoupis and Fountoulis, 2004; Papanikolaou et al., 1988). Quaternary sediments cover large parts of the Assopos valley and host two types of aquifers: a) aquifers within Neogene conglomerates, sandstones and marly limestone to a depth approximately 150 m, and b) karst type aquifers within the Triassic–Jurassic limestones at deeper levels of the basin fill (Giannoulopoulos, 2008).

3. Samples and methods of investigation

For the purpose of the present study, 10 groundwater samples, 15 soil samples and 21 rock samples were collected from the extended area of the municipality of Messapia in central Euboea and from the neighboring area of Avlona located in the Assopos basin (Fig. 1).

Soil and rock samples were collected from cultivated sites and from natural outcrops of ultramafic rocks on Central Euboea. Soils were air dried, crumbled mechanically and those containing large stones or clods were first sieved through a 10 mm mesh and then through a 5 mm mesh. Subsequently, after passing the samples through a 2 mm mesh, the fraction <2 mm was pulverized and used for analysis. Rock samples were crushed by jaw crusher, then pulverized using a triturator and an agate mortar and pestle, and subsequently sieved through a <2 mm mesh. This fraction was used for the leaching experiments. Major and trace elements were analyzed by inductively coupled plasma mass spectroscopy (ICP-MS) after multi-acid digestion (HNO_3–$HClO_4$–HF–HCl) at the ACME Analytical Laboratories in Canada. The detection limits for those elements are presented along with the analytical results in Table 1.

Groundwater samples were collected from domestic and irrigation wells spread over the study area in October 2012. Physical and chemical parameters (pH, redox, total dissolved solids, conductivity and total dissolved solids) of the water samples were measured in the field using a portable Consort 561 Multiparameter Analyzer. The collected samples were divided into two aliquots and each one was stored in polyethylene containers at 4 °C in a portable refrigerator. One of the sample aliquots was acidified by addition of concentrated HNO_3 and stored at 4 °C as well. Because acidification potentially can affect the solubility of Cr(VI) and because biotic activity could change the valence state of chromium in the samples, concentrations of total Cr and Cr(VI) were determined in the non-acidified aliquot of the water samples, within 24 h after collection. The analyses of total chromium were performed by GFAAS (Perkin Elmer 1100B system), with an estimated detection limit of ~2 μg/L. The chemical analyses for Cr(VI) were performed by the 1,5-diphenylcarbohydrazide colorimetric method, using a HACH DR/4000 spectrophotometer. The estimated detection limit of the method was