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Occurrence of Cr(VI) in drinking water of Greece and relation to the geological background

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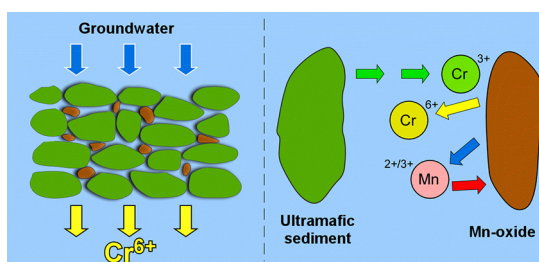
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HIGHLIGHTS

- Cr(VI) was determined in 600 tap waters of small-medium sized communities of Greece.
- Cr(VI) concentration in water samples accounts for 96% of total chromium in average.
- Typical Cr(VI) containing waters have a pH > 7.5 and Ca concentration < 50 mg/L.
- Contact with ultramafic rocks activates Cr(VI) formation by a catalytic mechanism.
- Highest Cr(VI) values observed in shallow porous aquifers downstream of ophiolites.

GRAPHICAL ABSTRACT



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ABSTRACT

This study provides a survey on potential Cr(VI) exposure attributed to drinking water in Greece. For this reason, a wide sampling and chemical analysis of tap waters from around 600 sites, supplied by groundwater resources, was conducted focusing on areas in which the geological substrate is predominated by ultramafic minerals. Results indicate that although violations of the current chromium regulation limit in tap water are very rare, 25% of cases showed Cr(VI) concentrations above 10 µg/L, whereas Cr(VI) was detectable in 70% of the samples (>2 µg/L). Mineralogy and conditions of groundwater reservoirs were correlated to suggest a possible Cr(VI) leaching mechanism. Higher Cr(VI) values are observed in aquifers in alluvial and neogene sediments of serpentinite and amphibolite, originating from the erosion of ophiolitic and metamorphic rocks. In contrast, Cr(VI) concentration in samples from ophiolitic and metamorphic rocks was always below 10 µg/L due to both low contact time and surface area, as verified by low conductivity and salt concentration values. These findings indicate that under specific conditions, pollution of water by Cr(VI) is favorable by a slow MnO₂-catalyzed oxidation of soluble Cr(III) to Cr(VI) in which manganese products [Mn(III)/Mn(II)] are probably re-oxidized by oxygen.

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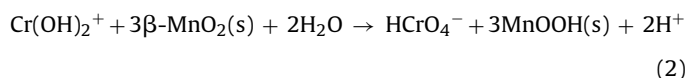
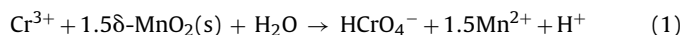
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1. Introduction

Chromium is a naturally occurring element, found in rocks, soil and groundwater, and commonly appears in environment in two oxidation states: Cr(III) and Cr(VI). The fact that Cr(VI) has been identified as toxic, causing various types of cancer and DNA damage [1,2], is the main reason for the increased focus on this metal. On the contrary, Cr(III) is considered an essential element for human and animal nutrition. Relevant studies indicate that exposure to Cr(VI) may result in asthma, and damage to the nasal epithelia and skin [3], while the effect of Cr(VI) on the thio redoxin system is likely to have widespread implications for cell survival and several aspects of redox signaling [4]. Despite such worrying indications, the World Health Organization [5] and the European Union [6] still follow the established Maximum Contaminant Level (MCL) of 50 µg/L in drinking water addressed for total Cr concentration. However, the severe toxicity of Cr(VI) has drawn the attention of both the scientific community and environmental organizations generating an increasing number of headlines and a general rise in public awareness. Under this pressure, the increased concern for Cr(VI) effects on human health is expected to contribute to the re-evaluation of chromium limits in the near future. In this direction, on July 1st, 2014, the U.S. State of California established a MCL of 10 µg/L for hexavalent chromium.

Chromium can enter waters from both anthropogenic and natural sources. Specifically, it can enter groundwaters in the form of industrial wastes from manufacturing processes for stainless steel, chrome plating, dyes, pigments and wood preservation. Regarding its natural origin, mineral leaching is considered the main cause of chromium occurrence in groundwater. The pollution of Asopos river, first revealed at 2006, was the most pronounced incident of Cr(VI) contamination in Greece. Systematic investigations in Asopos river and its basin reported Cr(VI) concentrations as high as 80 µg/L in surface and groundwaters used for public water supply [7]. According to other studies [8], a wide spatial variability of the total chromium content in groundwaters of the Asopos basin was found, reaching up to 180 µg/L. Intensive industrial activity utilizing large amounts of chromium in the area was initially accused as responsible for the increased Cr(VI) levels in waters. However, recent surveys [8–10] support the natural occurrence of chromium, verified by the presence of Cr-containing minerals (chromite, Fe-chromite, Cr-bearing goethite and silicates) in the Asopos basin. The contact of water with ultramafic rocks and soils such as serpentinite, dunites, and ophiolites was also proved the cause of high Cr(VI) concentrations in numerous cases in Mexico [11], California [12–14], Zimbabwe [15], Italy [16], Brazil [17], Japan and Indonesia [18].

Due to the comparably low solubility of Cr(III) (<5 µg/L) within the common pH range of natural waters (6.5–8.5) [19], the hexavalent form is expected to dominate whenever increased levels of naturally leached chromium occur. However, the path of natural Cr(VI) formation in groundwater passes through the Cr(III) oxidation state which is present in soils derived from ultramafic and ophiolitic rocks [15,16]. These soils contain chromite grains (0.2–1 mm) usually accompanied with or covered by manganese oxides or hydroxides (i.e., MnO₂). Manganese oxides, often assisted by microbial reactions, are considered as direct oxidizing agents or as catalysts that promote chromium oxidation in aquatic systems [20,21]. Their contribution to the electron transfer reaction, which is unique among common soil minerals, is attributed to variations in the Mn oxidation state caused by unusual structural features [22]. The proposed oxidation reactions scheme involves: (i) the adsorption of Cr(III) onto MnO₂ surface sites, (ii) the oxidation of Cr(III) to Cr(VI) by surface Mn(IV), and (iii) the desorption of the reaction products Cr(VI) and Mn(II), suggesting the following theoretical stoichiometries:



Conclusively, recent evidence suggests that the presence of Cr(VI) in natural waters should be examined from a new perspective. For this reason, the monitoring of drinking water quality concerning Cr(VI) presence would be highly informative especially in Greece, a country with extensive ophiolitic substrates where natural Cr(VI) formation is very likely. The aim of this study was to examine the possible correlation of Cr(VI) appearance in the drinking water of Greece with the corresponding geological background by analyzing a statistically significant number of samples obtained from public water networks focusing on regions known for their supply dependency on groundwater resources and the intense ultramafic rocks presence. In this survey, several water parameters were measured in order to support the possible mechanism of Cr(VI) dissolution and verify any indices that predict its appearance. This study can also stand as the most extensive report to date on the levels of Cr(VI) in the drinking water of Greece indicating the potential risks to consumers health.

2. Geological background

The chromium deposits of Greece occur in mantle origin peridotites and ophiolite complexes. Formation of ophiolite complexes is the result of the convergence of two oceanic crusts where most of the oceanic crust is destroyed and the remainder rises to the surface. In Greece, ophiolite rocks record a Mesozoic history of subduction, accretion and obduction during the closure of the Tethys and Paleo-Tethys Sea. Fig. 1 shows the distribution of ophiolite and ultramafic rocks in the Greek territory. Ophiolite complexes form two distinct, parallel lanes with a general northwest-southeast orientation: the internal ophiolite complex (IRO) along the Axios zone, and the external ophiolite complex (ERO) along the sub-pelagonic and Pindos zones [23,24]. In western Greece, from Epiros to the Peloponnese, the main geological formations are limestone and dolomite. Crystalline and metamorphic rocks are mainly found in the central and eastern part of the country. Late neogene sediments and quaternary alluvial fans occur mainly in large basins as a result of the erosion and alternation of the mountain rock formations.

The major ophiolitic appearances in the external zone occur in Pindos [25], Vourino [26], Othris [27], Euboea [28], while minor ophiolitic occurrences are present in Kastoria [23], Koziakas [29,30], Vermio, East Thessaly, Oiti [24], and Argolida [31]. In the internal zone, ophiolites are found in Thessaloniki (Triadi), central Chalkidiki (Vavdos, Gerakini, etc.), Oraiokastro, and Gevgelis. Additionally, ophiolites are also present in Evros (Soufli and Dadia), Rodopi (Organi and Murtiskos), Samothrace, Lesvos [32], Rhodes, and Crete. Ophiolite complexes comprise ultramafic rocks, such as dunites, peridotites, pyroxenites and diabases, in the basal layers, whereas the upper layers of the complex consist of gabbros and pillow lavas.

The chromium content of these minerals varies widely. For example, the worldwide average chromium content in peridotites reaches 1800 mg/kg [33]. High chromium concentrations are found in minerals such as magnesio-chromite and chromite, members of the spinel group, and magnetite. On the contrary, olivine is very poor in chromium (<70 mg/kg) whereas the content of chromium in serpentine is 100 mg/kg [34]. Even lower chromium concentrations are found in sandstones (35 mg/kg), granites (22 mg/kg), and limestone (11 mg/kg) [16,33].

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