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Characterization and mobility of geogenic chromium in soils and river bed sediments of Asopos basin

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HIGHLIGHTS

- Surface agricultural soils and river sediments were geochemically characterized.
- Soil and sediments were classified into 3 classes with respect to the origin of Cr.
- Geogenic chromium is present in Asopos soils and river bed sediments.
- The mobility of Cr is controlled by ferric oxides surface complexation.

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ABSTRACT

A field and laboratory study was conducted to assess the origin and mobility of CrVI in Asopos basin in Greece. Sampling was designed in such way as to capture the spatial variability of chromium occurring in sediments and soils in different lithological units in the area. Physicochemical and geochemical characterization of surface agricultural soils obtained from river terraces and river bed sediments was conducted in order to determine the natural background of chromium. Lithologies with strong calcareous, siliceous and ultramafic components were identified using principal component analysis. Laboratory mobility studies quantified the rates of chromium sorption and release from soils and their capacity to adsorb chromium. Heavy metal analysis and local geology study support the hypothesis that the main source of chromium is of geogenic origin. Chromium distribution in Asopos river bed was influenced from the eroded products derived from extensive areas with ultramafic rocks the last 5 Ma. The mobility studies showed that leaching process was very fast and sorption capacity was significant and capable to retain chromium in case of waste release in the river. Finally the mobility of chromium release is limited due to existing attenuation capacity controlled by ferric oxides coatings on the soil and sediments.

1. Introduction

A growing worldwide concern on human health risks of chromium has stimulated research on its fate and transport in groundwater [1]. In the environment, Cr is found mainly in two oxidation states, the trivalent Cr(III) and the hexavalent Cr(VI). Hexavalent Cr is mobile and highly toxic for humans, whereas Cr(III) is immobile, has low toxicity and is considered to be an essential trace element in human metabolism. The differences of the two oxidation states of chromium make the assessment of potential human health risks, difficult [2]. The European Commission (Directive 98/83/EC) established 50 μg/L as the maximum permissible limit of total chromium in drinking water, similar to the one established by the World Health Organization. The Italian regulation defined a maximum allowable concentration of 2 mg/L (on a dry basis) for Cr(VI) in soils for private use, and a maximum acceptable concentration of 150 mg/L for total Cr [3].

The processes of chromium release from soils and adsorption to soils has been the subject of significant body of research and the understanding of the mechanisms affecting chromium fate in aquifers (oxidation, reduction, adsorption and desorption) is of paramount importance [4]. The kinetics of the chromium redox reactions complicate chromium transport because each chromium species presents a different sorptive behavior depending on the prevailing physicochemical conditions (e.g. pH, organic matter content) [5]. Transport of chromate is mainly controlled by adsorption

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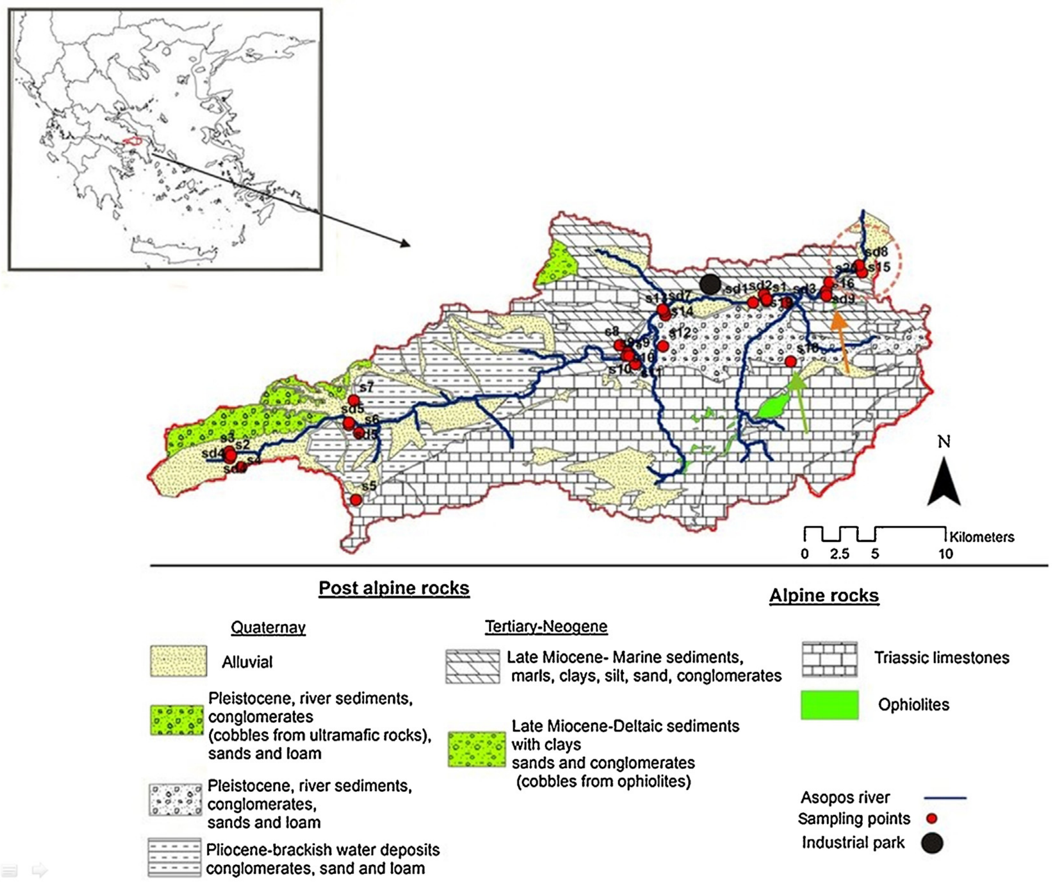

Fig. 1. Geology map of the study area with the main lithological units. Red circles depict soil and river sediment sampling sites and black circle depicts the industrial park at the Oinophyta area. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

on the surfaces of iron oxides such as hematite [6]. Generally, assessment of contaminant mobility is a necessary tool in order to establish either risk-based or mobility-based, site-specific cleanup levels for remediation [7].

Chromium existence in soils and water can be a result of anthropogenic activities i.e. industrial activities and phosphorus fertilizers [8], or of natural processes as the weathering of ultramafic rocks [9,3,10,11,12]. Serpentine soils are the soils derived from ultramafic rocks or serpentinites [13]. Chromium and nickel in soils are primarily derived from the weathering of minerals contained in the ultramafic rocks like chromite, olivines, pyroxenes, etc. [14]. Although serpentinites and serpentine soils cover about 1% of the earth's exposed surface, they are common along the Circum-Pacific margin and the Mediterranean [13]. A two-stage mechanism of chromite weathering was proposed by Cooper [9]: a slow hydrolysis of Cr(III) to $Cr(OH)_3$, followed by a slow oxidation step to Cr(VI) by Mn oxides. During this process, Cr derived from pyroxene, olivine and chromites weathering, is integrated into minerals, i.e. iron oxides or smectite [10]. An appreciable amount of chromium is associated with iron oxides, clay minerals [11] and spinels as magnetite, chromite and other spinels containing Al, Mg, Fe, Cr [13]. The difference in the geochemical characterization of the Cr host minerals is the Cr solubility in acids like HNO_3. According to Morrison et al. [14], Cr in chromite and other Cr-rich spinels are mainly recalcitrant in acid etching, whereas Cr in pyroxenes, olivines, serpentine, chlorite-chromium mixtures or in clays contain a higher proportion of acid-soluble forms.

Asopos River received waste discharges from metallurgies and industries related to textile, dyes, and food production. The waste release has been ceased at least 5 years ago after the rising of public awareness. The western part of Asopos watershed (Thiva valley) is covered with topsoil enriched in Cr and Ni as a result of transport of the weathered parent rock fragments from the higher elevations of the basin [15]. According to Moraetis et al. [16], weathered ultramafic rock fragments in the Neogene and Alluvial deposits have resulted in producing geogenic origin hexavalent chromium in the groundwater at least in the eastern part of the watershed close to Oropos area (dashed orange line Fig. 1). Despite the last two studies there is no complete characterization of the Asopos watershed and specifically of the river bed sediments where probably both chromium of geogenic and anthropogenic origin may exist. Thus, having already strong evidences of geogenic chromium origin we consider that chromium geochemical characterization along the Asopos river sediments would reveal the critical factors influencing the presence of chromium in the watershed and groundwater.

The objectives of this study are twofold: (1) to assess the geochemical characterization and classification of soils and river sediments with respect to the origin of Cr along Asopos river, and (2) to assess the processes affecting the mobility of hexavalent chromium in soils and sediments along Asopos river.

2. Materials and methods

2.1. Site description

Asopos river basin is located in the Region of Sterea Ellada, about 100 km north from Athens and has a surface area of approximately 703 km^2. Asopos is considered representative of a Mediterranean intermittent river [17]. It has a total length of 54 kilometers and runs through the areas of Thebes, Avlona, Tanagra, Schimatari,