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Investigation of potential soil contamination with Cr and Ni in four metal finishing facilities at Asopos industrial area

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HIGHLIGHTS

- High Cr, Ni levels, both natural and anthropogenic, were measured in Asopos soils.
- Natural geochemical levels of Cr ranged between 60 and 418 mg/kg.
- Cr concentration up to 2000 mg/kg was measured at some inactive industrial sinks.
- Contamination seems to be limited to a thin soil layer close to the sinks bottom.

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ABSTRACT

The objective of this work was to investigate whether previous disposal practices in four metal finishing facilities, located at Asopos river basin (East-Central Greece), have caused any potential serious contamination of soils. The study focused mainly on Cr and Ni, which are the primary elements of concern in the area. To estimate the natural geochemical levels of Cr and Ni, thirty soil samples were collected from locations that were not suspected of any contamination. In this group of samples, Cr concentration varied between 60 and 418 mg/kg, and Ni concentrations varied from 91 to 1200 mg/kg. The second group of samples consisted of more than 100 drill cores and surface soil samples, potentially affected by the disposal of effluents and/or the drainage of runoff water from the industrial facilities. According to the findings of the study, the disposal of treated effluents in absorption type sinks resulted occasionally in the contamination of a thin layer of soil just at the bottom of the sinks, but there was no indication of downward migration, since Cr and Ni concentrations in the lower soil layers were similar to those of the reference soils.

1. Introduction

An extensive problem of chromium contamination has been recorded in the Asopos River basin, in East-Central Greece. Concentrations of hexavalent Cr, exceeding in some cases the value of 100 $\mu g\,L^{-1}$ were measured in groundwater samples collected from the area [1–3]. Asopos is a typical case where both geogenic and anthropogenic components have contributed to the recorded high levels of chromium contamination. The surrounding area of Asopos basin is composed by Neogene lake-shallow marine sediments, clastic formations of continental origin and parts of ophiolite complexes [4]. As often reported in the literature, the detection of elements, such as Cr and Ni in soils and waters, has often a strong lithogenic origin related to the presence of ophiolite outcrops composed by ultramafic rocks (peridotites, pyroxenites, serpentinites) [5,6], but also Fe–Ni deposits [7,8]. Cases where occurrence of hexavalent chromium is primarily of geogenic origin have also been documented for California [9–13], New Caledonia [14], Italy [15], Zimbabwe [16] etc. According to Cooper [16] the geogenic mobilization of Cr(VI) from highly insoluble Cr(III) minerals, like chromite, takes place via a two-stage mechanism. Firstly Cr(III) in the matrix of chromite is slowly hydrolyzed to $Cr(OH)_3$. The second stage is the oxidation of Cr(III) to Cr(VI) under the action of easily reducible Mn oxides, like the mixed Mn(II)/Mn(III) oxide hausmannite (Mn_3O_4) or the Mn(III) oxide manganite (MnOOH). Cooper considers that this natural process is probably continuous in concretionary subsoils subject to wetting–drying cycles.

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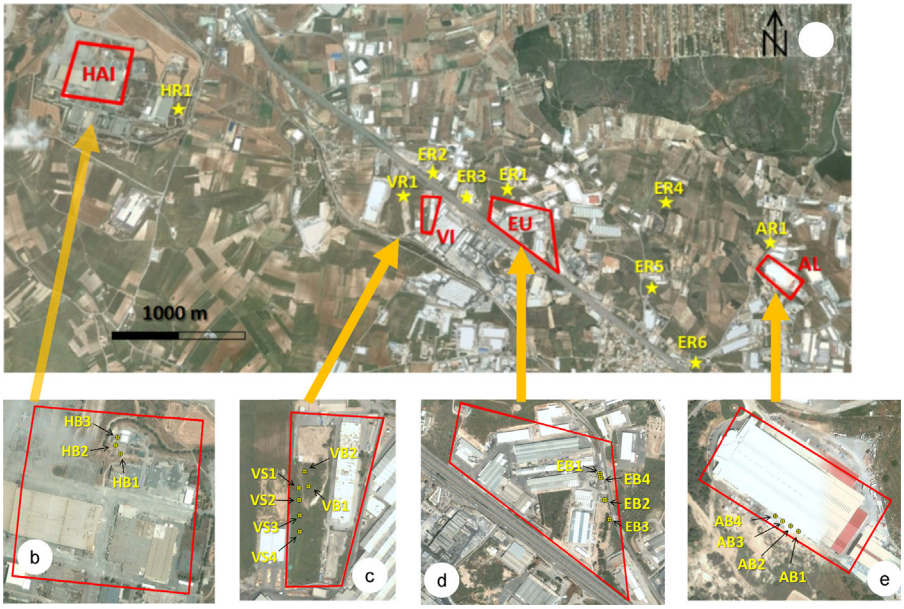

Fig. 1. Location of investigated industrial sites and sampling points.

The contribution of the anthropogenic factor to the observed Cr contamination in Asopos basin cannot be neglected as the area is characterized by intense industrial activities. Botchou et al. [17] have concluded that Asopos river sediments are enriched with Cr and Ni by a factor of almost 2.5 compared to the local background values. This enrichment factor provides a measure of the anthropogenic contribution in the observed contamination problems. Industrialization in Asopos region started in the 1960s and currently more than 400 industrial units are operating in the area. Industrial activities include metal finishing and manufacturing plants, which are often using Cr-based chemicals in their production chain. All facilities are obliged to treat their effluents in-house in appropriate wastewater treatment units, but until recently the treated effluent was allowed to be discharged underground via disposal in absorption type sinks. Since 2008, due to the concerns about the quality of groundwater in Asopos area, the underground disposal of processed wastewater was banned by law. Industries were forced to modernize their wastewater treatment plants in order to obtain 100% recycling of treated water.

The objective of this work was to investigate whether previous disposal practices in four (4) metal finishing facilities have led to potential contamination to the adjacent soils. The four investigated industrial sites are Hellenic Aerospace Industry S.A. (HAI), Europa Profile Aluminium S.A. (EU), Aluminco S.A. (AL) and Viometale S.A. (VI) [18].

2. Materials and methods

The location of the investigated industrial sites is presented in Fig. 1a. Sampling strategy at each industrial site involved the collection of two groups of soil samples. The first group was intended to represent the natural geochemical background close to the industrial sites. So, sampling locations (depicted with letters HR, ER, AR and VR in Fig. 1a) were selected to be in the vicinity of the industrial site but unaffected from any known or suspected polluting factors. The second group consisted of samples collected from areas suspected of pollution from ongoing activities or previous disposal

Table 1
Number of samples, parameters analyzed and analytical methods used.

Site	No of sampling locations (no of samples)		Parameters analyzed	Methods	Labs*
	Un-contaminated	Suspected for contamination			
HAI	1 (7)	3 (42)	Cr, Ni, Cu, Zn, Pb, Al Cr(VI)	Digestion with AR[a] Elution with water[b]	Andreou
Europa	6 (13)	4 (49)	Cr, Ni Cr(VI)	Digestion with AR[a] Elution with water[b]	Andreou
Aluminco	1 (6)	4 (12)	Cr, Ni, Fe, Al Cr(VI)	Digestion with AR[a] [XRF[d]] Alkaline digestion[c]	EuF/LabMet LabMet
Viometale	1 (4)	6 (19)	Cr, Ni, Cu, Zn, etc. Cr(VI)	XRF[d] [AR[a]] Alkaline digestion[c]	LabMet

* Laboratories: (a) Andreou: K. Andreou, Ltd, Athens, (b) EuF: Eurofins Umwelt Ost GmbH, Jena, Germany, (c) LabMet: Laboratory of Metallurgy, NTUA, Athens.
[a] Digestion with aqua regia followed by determination of metals in solution by AAS or ICP-MS (EN 13657).
[b] Elution with water, determination of soluble Cr(VI) (DIN 38405-24: 05.87, AWWA-3500-Cr/B).
[c] Alkaline digestion, determination of extracted Cr(VI) (USEPA, SW-846 Methods 3060A and 7196).
[d] Determination of total elements concentration by X-ray fluorescence spectrometry (EN 15309).