



*Research article*

## **Chromium and nickel in the soils of industrial areas at Asopos river basin**

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**Abstract:** The purpose of this paper is to present and compare previous efforts aiming to investigate whether previous wastewater disposal practices in selected (four) metal finishing facilities, located at Asopos river basin (near Athens at East-Central Greece), and resulted in relevant soil contamination. The work is focused mainly on Cr and Ni, which are the primary elements of concern in the Asopos river Basin area. To assess the natural geochemical levels of Cr and Ni, 30 soil samples were collected from locations that were assumed free of contamination. In these 30 soil samples, Cr concentration varied from 60 to 418 mg/kg, and Ni concentrations varied between 91 and 1200 mg/kg. A second group of soil samples consisted of more than 100 samples from drill cores and surface soil samples, assumed affected by the disposal of effluents of the metal finishing facilities and/or the relevant drainage of runoff water. A third group of samples consisted of 10 more surface soil samples collected in summer 2015 (campaigns by Sybilla ltd in the framework of EU IED Directive Baseline Site Investigation Study for two metal finishing units). The above mentioned groups of data were evaluated and compared with a fourth group of data (collected from Inofyta industrial area in the framework of EU funded project LIFE-CHARM “Chromium in Asopos groundwater system: Remediation technologies and Measures”). The conclusion of this study is that there is no indication of downstream pollution migration from the land-based treated effluents disposal of the above mentioned metal finishing facilities. Cr and Ni concentrations in the lower soil layers were of the same order of magnitude to those of the reference soils. On the contrary Inofyta Industrial Area soil seems to be rather contaminated and requires special attention.

**Keywords:** Asopos River Basin pollution; soil contamination; hexavalent chromium; nickel; metal finishing effluents

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## 1. Introduction

Asopos River basin, in East-Central Greece is characterized by a recorded problem of hexavalent chromium contamination, exceeding in some cases the value of  $100 \mu\text{g L}^{-1}$  as measured in groundwater samples collected from the area [1]. Geogenic and anthropogenic components have contributed to the recorded high levels of chromium contamination in the Asopos River Basin. The geological character of surrounding area of Asopos River basin mainly is Neogene lake-shallow marine sediments, clastic formations of continental origin and parts of ophiolite complexes [2]. The detection of elements, such as Cr and Ni in soils and waters, has often a strong lithogenic origin correlated to the existence of ophiolite outcrops composed by ultramafic rocks [3], but also Fe-Ni deposits [4,5]. Cases where occurrence of hexavalent chromium is primarily of geogenic origin have also been documented for California [6-8], New Caledonia [9], Zimbabwe [10], Italy [11], etc. The geogenic mobilization of Cr(VI) from highly insoluble Cr(III) minerals, like chromite, takes place via a two-stage mechanism [10]. At first Cr(III) in the matrix of chromite is hydrolyzed to  $\text{Cr}(\text{OH})_3$ . The following stage is the oxidation of Cr(III) to Cr(VI) under the action of easily reducible Mn oxides (the mixed Mn(II)/Mn(III) oxide hausmannite ( $\text{Mn}_3\text{O}_4$ ) or the Mn(III) oxide manganite ( $\text{MnOOH}$ )). It is considered [10] that this natural process is probably continuous in concretionary subsoils subject to wetting-drying cycles.

Industrialization in the Asopos River Basin area started in the early 1960's and today more than 400 installations exist in the area. Metal finishing and manufacturing plants, often using Cr-based chemicals in their processes were major chromium polluters in the area. All facilities were obliged to treat their effluents in-house in appropriate wastewater treatment units, but until 2008 the treated effluent was allowed to be discharged underground via disposal in absorption type sinks. As a result of this the anthropogenic factor, the observed Cr contamination in Asopos River basin cannot be neglected. University of Athens research [12] suggests that the Asopos river sediments are enriched with Cr and Ni by a factor of almost 2.5 compared to the local background values.

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, and
- to compare the potential contaminated soil concentration values of the metal finishing facilities with
  - ❖ greater area background metal concentration values
  - ❖ Potentially polluted and newly investigated soil metal concentration values of the Inofyta Industrial Area (IIA).

The four investigated metal finishing industrial sites are Hellenic Aerospace Industry S.A. (designated as HAI), Europa Profile Aluminium S.A. (EU), Aluminco S.A. (AL) and Viometale S.A. (VI) [13-16]. The reason for selecting these metal finishing sites is:

- HAI, EU, AL are three of the larger installations in the area using Hexavalent Chromium
- In VI a discrete thin metal contamination layer on surface soils was found to the south of the area during a Prefecture Environmental Audit.
- Prefecture of Sterea Ellada (relevant Environmental Authority) considers HAI, EU, AL and VI as priority potential polluters.

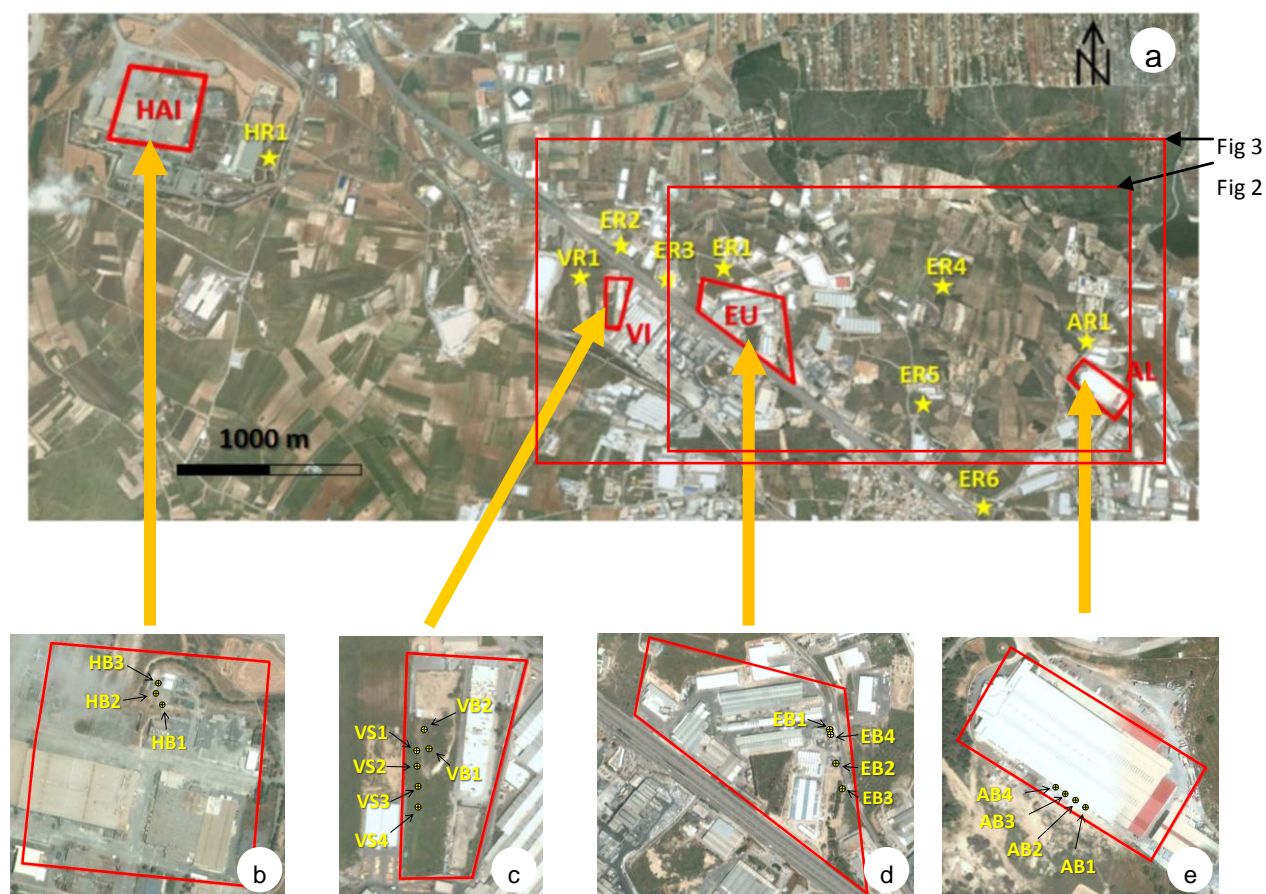
## 2. Materials and Methods

### 2.1. Study Sites, sampling strategy and data collected

The study area is focusing on the four above mentioned metal finishing industrial sites HAI, EU, AL VI and the Inofyta Industrial Area (IIA). Sampling strategy involved the collection of three groups of soil samples and for comparison reasons the data collected from Inofyta industrial area by the research team of the EU funded project LIFE-CHARM “Chromium in Asopos groundwater system: Remediation technologies and Measures” [17] (data available at <http://www.charm-life.gr/charm/index.php/en/documents>) were also evaluated, called as fourth group (LGR-4) sampling. The *first group* (GR-1) assumed free of anthropogenic influence was intended to represent natural geochemical background values close to the industrial sites. Selected sampling points (depicted as HR, ER, AR and VR in Figure 1) were in the vicinity of the metal finishing and industrial sites but not affected from any potential polluting factors. The *second group* (GR-2), collected in the period 2011–2012 (campaigns by Sybilla Ltd), and consisted of samples from areas suspected of pollution from ongoing activities or historical disposal practices. Samples are either samples from soil shallow layers, i.e. 0–80 cm, or soil core samples from boreholes, up to a depth of 15 meters. The greater Asopos river Basin area Industrial Sites, and location of investigated surface soil sampling points of investigated metal finishing units of GR-1 (HR1-VR1-ER1-ER2-ER3-ER4-ER5-ER6, AR1.) and GR-2 (HB1-HB2-HB3, VB2-VB2, EB1-EB2-EB3-EB4, AB1-AB2-AB3-AB4,HR1-VR1-ER1-ER2-ER3-ER4-ER5-ER6, AR1) group campaigns are presented in Figure 1. GR-1, GR-2, GR-3 and LGR-4 sampling locations and the total number of analyzed samples per industrial site are presented in Tables 1–4.

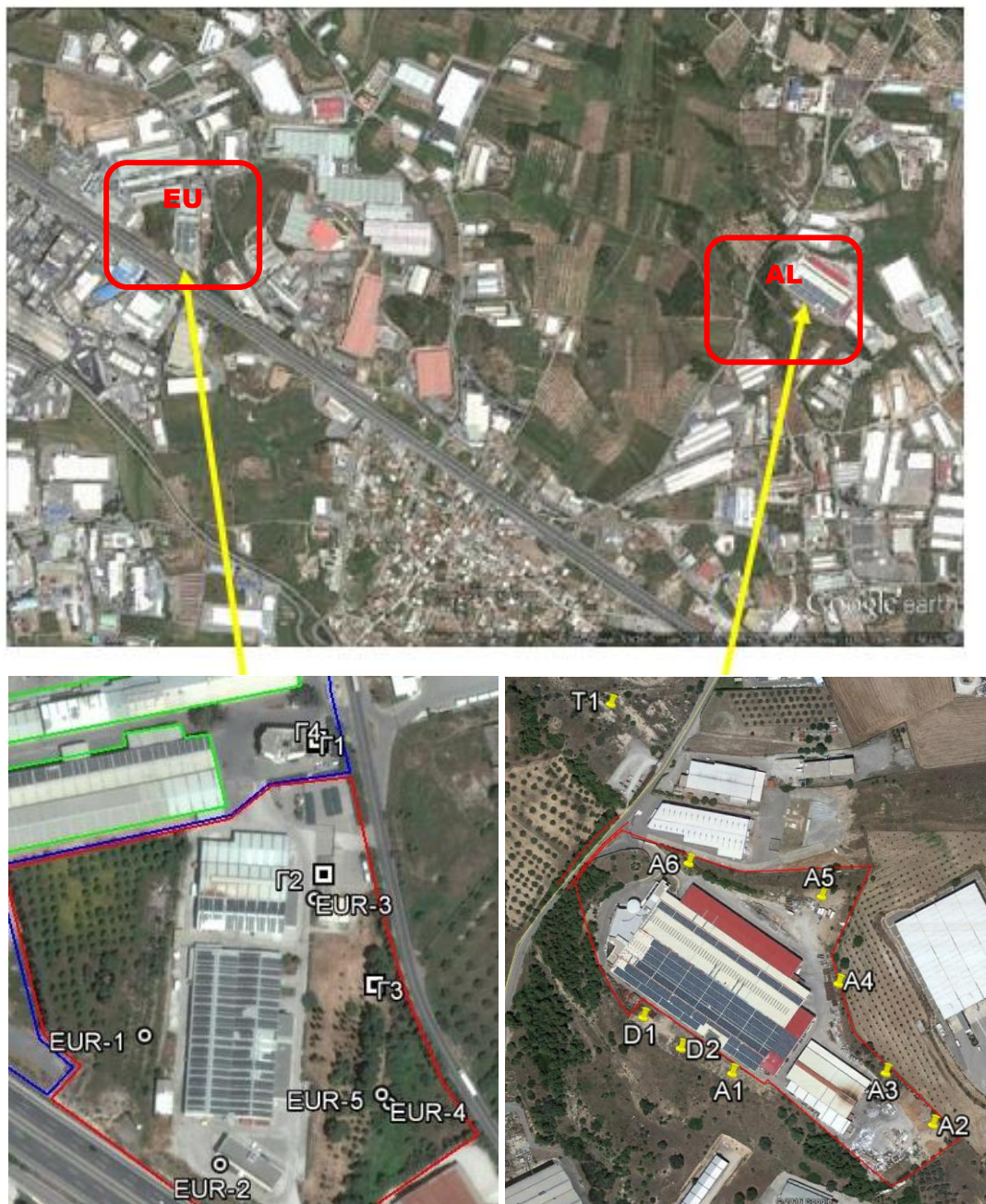
The *third group* (GR-3) consisted of more than 10 samples collected in summer 2015 (campaigns by Sybilla ltd in the framework of EU IED Directive [18]) Baseline Site Investigation Study [19,20]) from areas suspected of pollution from ongoing activities or previous disposal practices. Samples are either soils collected from the shallow layers, i.e. 0–80 cm, or core samples from boreholes, drilled down to a depth of about 15 meters. The location of boreholes is shown in Figure 2.

For comparison reasons data collected from Inofyta industrial area by the research team of the EU funded project LIFE-CHARM “Chromium in Asopos groundwater system: Remediation technologies and Measures” [17] (data available at <http://www.charm-life.gr/charm/index.php/en/documents>) were also evaluated. This Life Project, fourth group campaign (LGR-4) of samples was collected at the period 2011–2012. A sampling program was carried out during which seven (7) new groundwater wells with a depth of approximately 30–50 m were drilled at Inofyta industrial area (N1, N2, N3, N4, N5, N6, N7), between January and February 2012. During the construction, drill core samples were collected from each borehole and relevant chemical analyses followed. Boreholes sampling was followed by a surface soil sampling where a series of 12 surface soil samples were also collected during this action in order to investigate the presence of Cr. The location of relevant boreholes is shown in Figure 3.



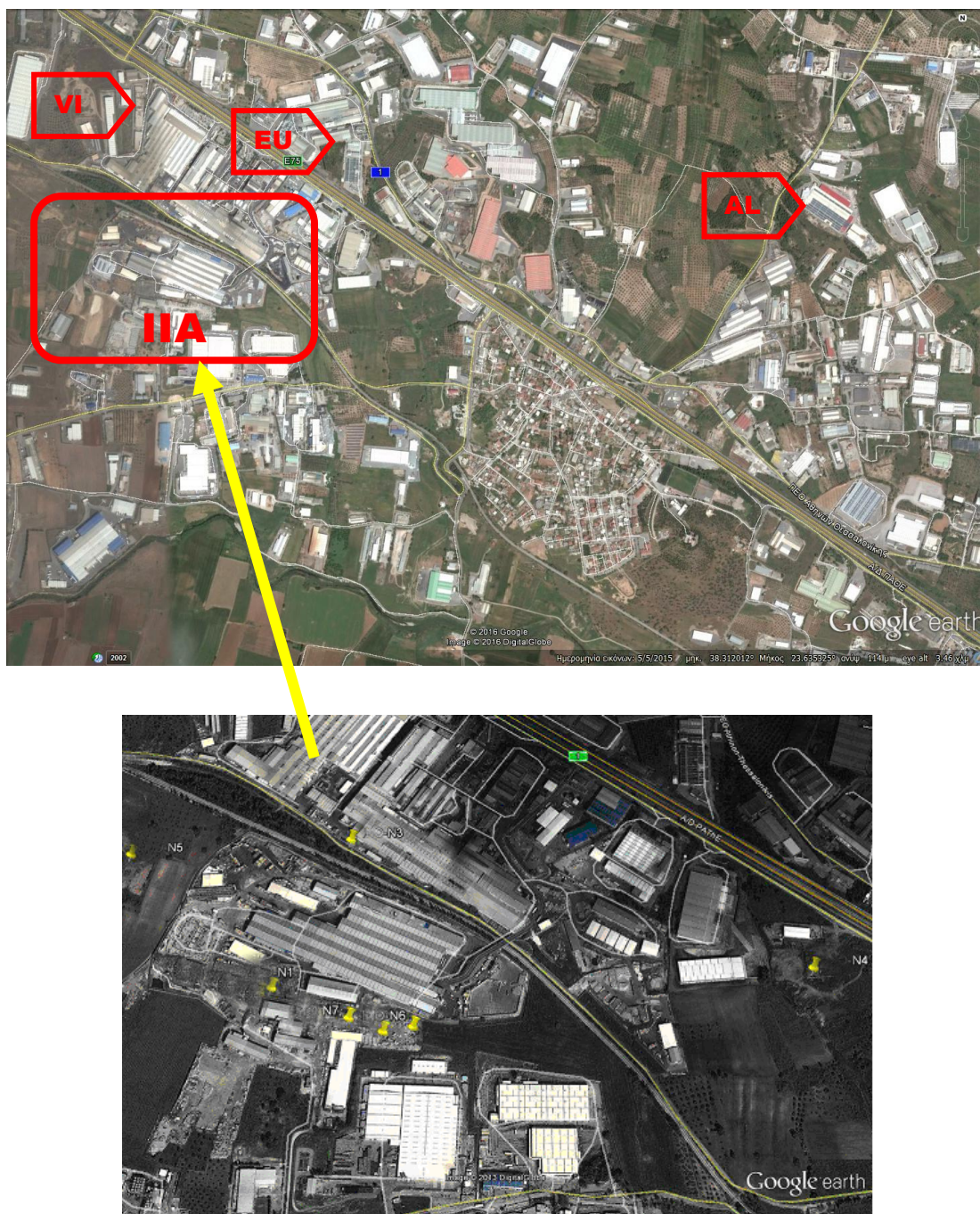
**Figure 1. First (GR-1) and Second (GR-2) Group Campaigns.** Investigated metal finishing installation sites (a-total sampling area, b- Hellenic Aerospace Industry S.A.-HAI area, d-Europa S.A.-EU area, e-Aluminco S.A.-AL area and c-Viometale S.A.-VI area) and boreholes (GR-2 sampling points HB1-HB2-HB3, VB2-VB2, EB1-EB2-EB3-EB4, AB1-AB2-AB3-AB4) and surface soil sampling points (GR-1 and GR-2 sampling points HR1-VR1-ER1-ER2-ER3-ER4-ER5-ER6, AR1) are depicted.





**Figure 2. Location of investigated surface soil sampling points for the Europa SA. (EU) and Aluminco SA (AL). Sybilla 2015. Third Group (GR-3) campaign.**





**Figure 3. Location of investigated industrial sites and surface soil sampling points. LIFE-CHARM 2012. Fourth Group (LGR-4) Campaign.**

## *2.2. Parameters analyzed and analytical methods used.*

Laboratories involved in the chemical analysis of the collected soil samples, the analytical methods used, and the parameters analyzed, are presented in Tables 1–4.

**Table 1. Number of samples, parameters analyzed and analytical methods used. GR-1 Campaign. Sampling locations assumed free of anthropogenic influence (Boreholes at HAI, EU, AL, VI and additional Surface Soil samples at EU).**

Site	No of sampling locations (no of samples)	Parameters analyzed	Methods	Labs (*)
HAI	1 (1)	Cr, Ni, Cu, Zn, Pb, Al Cr(VI)	Digestion with AR <sup>(a)</sup> Elution with water <sup>(b)</sup>	Andreou
Europa	6 (6)	Cr, Ni Cr(VI)	Digestion with AR <sup>(a)</sup> Elution with water <sup>(b)</sup>	Andreou
Aluminco	1 (1)	Cr, Ni, Fe, Al	Digestion with AR <sup>(a)</sup> XRF <sup>(d)</sup>	EuF/LabMet
Viometale	1 (1)	Cr(VI) Cr, Ni, Cu, Zn, etc. Cr(VI)	Alkaline digestion <sup>(c)</sup> XRF <sup>(d)</sup> , AR <sup>(a)</sup> Alkaline digestion <sup>(c)</sup>	LabMet LabMet

**Table 2. Number of samples, parameters analyzed and analytical methods used. GR-2 Campaign.**

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 <sup>(a)</sup> Elution with water <sup>(b)</sup>	Andreou
Europa	6 (13)	4 (49)	Cr, Ni Cr(VI)	Digestion with AR <sup>(a)</sup> Elution with water <sup>(b)</sup>	Andreou
Aluminco	1 (6)	4 (12)	Cr, Ni, Fe, Al	Digestion with AR <sup>(a)</sup> XRF <sup>(d)</sup>	EuF/LabMet
Viometale	1 (4)	6 (19)	Cr(VI) Cr, Ni, Cu, Zn, etc. Cr(VI)	Alkaline digestion <sup>(c)</sup> XRF <sup>(d)</sup> AR <sup>(a)</sup> Alkaline digestion <sup>(c)</sup>	LabMet LabMet

**Table 3. Number of samples, parameters analyzed and analytical methods used. GR-3 Campaign.**

Site	No of sampling locations (no of samples)		Parameters analyzed	Methods	Labs(*)
	Un-contaminated	Suspected for contamination			
Europa	2	3	Cr, Ni, Fe, Al Cr(VI)	Digestion with AR <sup>(a)</sup> Alkaline digestion <sup>(c)</sup>	LabMet
Aluminco	1	5	Cr, Ni, Fe, Al Cr(VI)	Digestion with AR <sup>(a)</sup> Alkaline digestion <sup>(c)</sup>	LabMet

**Table 4. Number of samples, parameters analyzed and analytical methods used at the EU funded Life Project Group LGR-4 Campaign. (Boreholes and Surface Soil samples).**

Site	No of sampling locations (no of samples)		Parameters analyzed	Methods	Labs(*)
	Un-contaminated	Suspected for contamination			
Boreholes	-	38	Cr, Ni, Fe, Al Cr(VI)	XRF <sup>(d)</sup> AR <sup>(a)</sup>	LabMet
Surface Soil	-	12	Cr, Ni, Fe, Al Cr(VI)	XRF <sup>(d)</sup> AR <sup>(a)</sup>	LabMet

(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)

(\*) Laboratories: (a) Andreou, K. Andreou. Ltd, Athens, (b) EuF: Eurofins Umwelt Ost GmbH, Jena, Germany,

(c) LabMet: Laboratory of Metallurgy, NTUA, Athens.

For the majority of samples, namely those collected from HAI, Europa and Aluminco, the elemental analysis was carried out following the digestion of samples with aqua regia (AR). The samples collected from Viometale were analyzed by X-ray fluorescence (XRF) spectrometry, (mainly due to time constraints - XRF analysis is much more rapid, as there is no need for any pretreatment steps, such as acid leaching or fusion). The LIFE-CHARM samples were also analyzed by XRF.

### 3. Results

#### 3.1. Cr and Ni soil background concentrations

Analysis by XRF determines the total content of elements in the solid samples, which does not coincide with the amount extracted by aqua regia. As discussed in a previous paper [21], using GR-1 and GR-2 campaigns results and a dataset of 40 surface soil samples collected throughout the whole Greek territory in the framework of the Geochemical Atlas of Europe [22], the concentration of chromium determined by the method of aqua regia digestion, Cr (AR), is about 4 times less compared to the total content of Cr determined by XRF, Cr (XRF). This can be attributed to the fact



that the highest percentage of chromium in Greek soils is incorporated into insoluble minerals, e.g. substituted aluminosilicates or spinel minerals like chromite, which are not affected by the AR digestion. On the contrary, the total amount of Ni in soils is soluble in AR. As a consequence, the concentration of Ni determined by the AR digestion method, Ni(AR), is very close to the total content, as determined by XRF, Ni (XRF).

For the assessment of Cr and Ni background concentration values in Asopos River Basin area soils, we quote data collected from various references consisting of various soil samples analyzed from locations which were assumed free of contamination from industrial activities. Total Cr, Ni and Cr (VI) concentrations are presented in the following Table 5.

**Table 5. Analyses of Asopos reference soils (n = 30 samples) compared to Cr and Ni values determined in soils of adjacent areas and in all Greece [3,21,24].**

Area (Number of samples)	Cr (mg/kg)		Ni (mg/kg)		Cr(VI) (mg/kg)	Source
	Range	Mean	Range	Mean	Range	
Asopos (n = 30)	60–410	220	91–1200	620	>0.1–9.3 (a)	[21]
Oropos (n = 33)	17–600	212			--	[3]
Thebes (n = 51)	134–856	277	621–2639	1591	--	[23]
Atalante (n = 64)	48–4200	453	44–2730	533	--	[24]
All Greece (n = 41)	2–466	102	2–1812	171	--	[22]

(a) Cr(VI) detected in 3 among the 30 analyzed reference soils (5.5, 6.0 and 9.3 mg/kg).

Chromium concentration values determined by aqua regia (AR) method are similar to the concentration levels determined at Oropos [3] and at Thebes [24], adjacent to the study area, with similar geological formations. As far as Cr (VI) is concerned, this species was detected only in three (3) among the 26 analyzed samples of Asopos Area, with concentrations 5.5, 6.0 and 9.3 mg/kg respectively. Ni concentrations determined by aqua regia (AR) method in the Asopos river Basin Area, were significantly higher.

Since Greece has not yet developed national soil quality guidelines for Cr and Ni, relevant guidelines from three European countries, namely Italy, Germany and Belgium (Wallonia), were used and are presented in Table 6 [25]. These values represent the upper allowed concentration levels of Cr and Ni in soils for residential and industrial land use. Cr(VI) threshold concentrations limits exist only in the regulations of Wallonia.

As seen in Table 5, the mean concentration of total Cr in Asopos soils (220 mg/kg), slightly exceeds the Italian threshold limit value for residential areas, but satisfies all other limit values. On the contrary, the mean concentration of Ni (620 mg/kg) exceeds the German limit for industrial areas. In Thebes's soils, most samples of Ni were exceeding the threshold limits. An analysis of Table 6, ends up to the conclusion that the use of these soil quality guidelines when applied in metalliferous

areas, like those encountered in many regions of Greece is questionable (since the geochemical background for at least Cr and Ni elements is often higher).

**Table 6. National Soil quality guidelines in three European Countries (IT = Italy, DE = Germany, BE (W) = Belgium (Wallonia)).**

	Soil limit values (mg/kg)					
	Residential areas*			Industrial areas*		
	IT	DE	BE(W)	IT	DE	BE(W)
Cr	150	400	520	800	1000	700
Ni	120	140	300	500	900	500
Cr(VI)	--	--	4.2	--	--	--

(\*) Cr, Ni digestion of samples with aqua regia (AR).

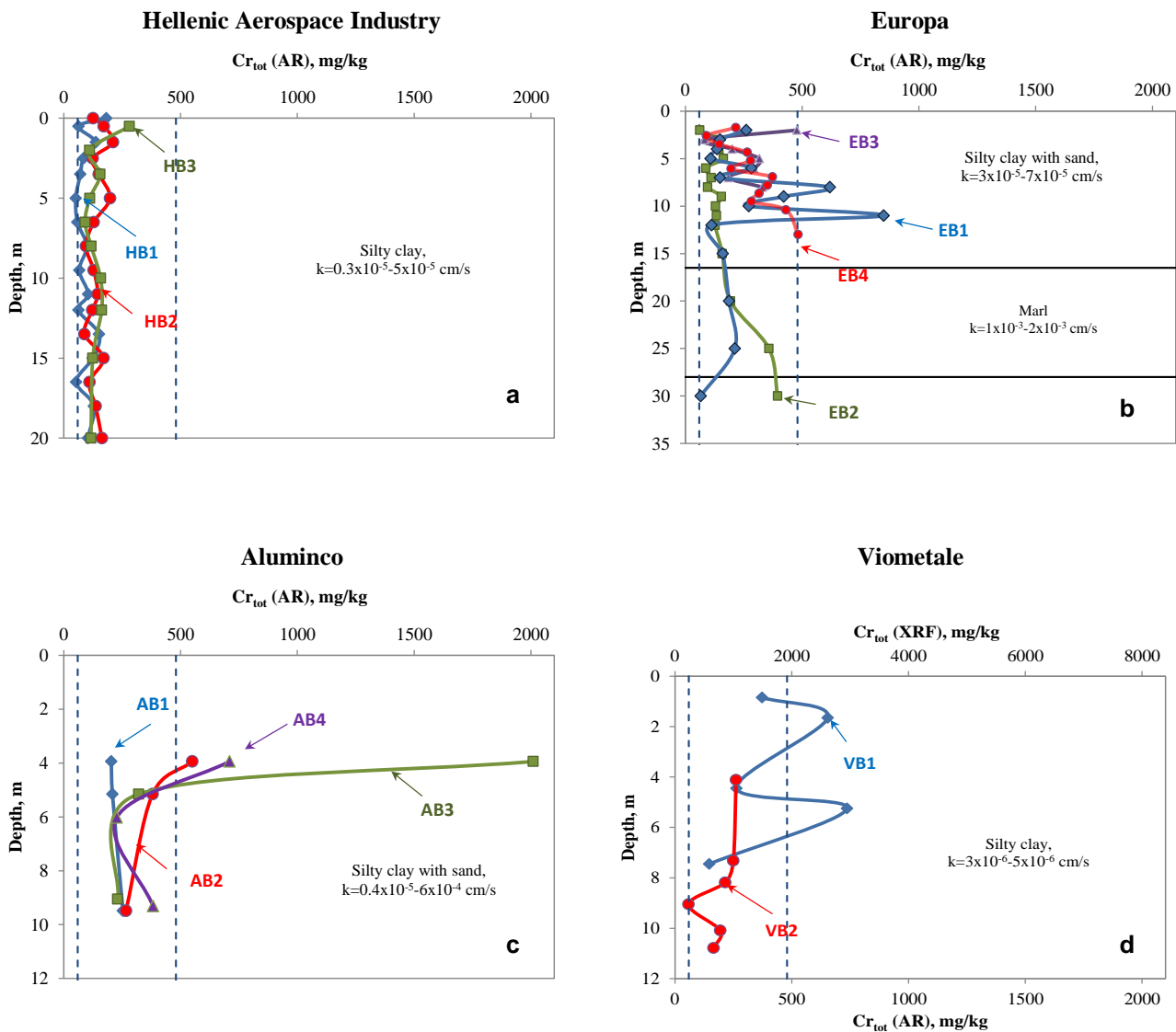
### 3.2. Cr and Ni concentration values in soils potentially contaminated

#### 3.2.1. Cr and Ni concentration values in soils at Hellenic Aerospace Industry

Figure 1b presents three boreholes that were drilled at HAI grounds, close to potentially polluting HAI sites, i.e. ponds that were used for the treatment of hazardous industrial wastewater, storage of physicochemically treated wastewater and for the storage and drying of industrial sludge. Total Cr concentration profiles are presented in Figure 4a. Total Chromium, Aqua regia (AR) Cr(AR), concentration values varied from 51 to 281 mg/kg with a mean value of 124 mg/kg. Total Ni aqua regia (AR) Ni (AR), concentration values varied from 132 to 618 mg/kg with a mean value of 262 mg/kg (Figure 5a). All these Cr(AR) and Ni(AR) soil concentration values are of the same order of magnitude with soil concentration values assumed free of anthropogenic contamination. Hexavalent Cr content was not detected in any of the soil samples examined.

#### 3.2.2. Cr and Ni concentration values in soils at Europa Profile Aluminium

For assessing the potential soil investigation in Europa grounds four boreholes were drilled at locations shown in Figure 1d. Borehole #1 (EB1) was drilled beneath the sink, where physicochemically treated wastewater from the electrostatic coating process was disposed for over two decades. For assessing the potentially contaminated soil directly beneath the sink, one inclined borehole was drilled with a 45° angle (EB4). A schematic drawing of the two above mentioned boreholes is given in Figure 6.



**Figure 4. Total Cr (AR) (and Cr(XRF) at Viometale) concentration values and profiles in boreholes drilled in the metal finishing industrial sites of the (HAI) Hellenic Aerospace Industry, Europa, Aluminco and Viometale. Second Campaign GR-2 Group. Dashed lines indicate the range of concentration values measured in the reference soils. (k: soil hydraulic permeability)**

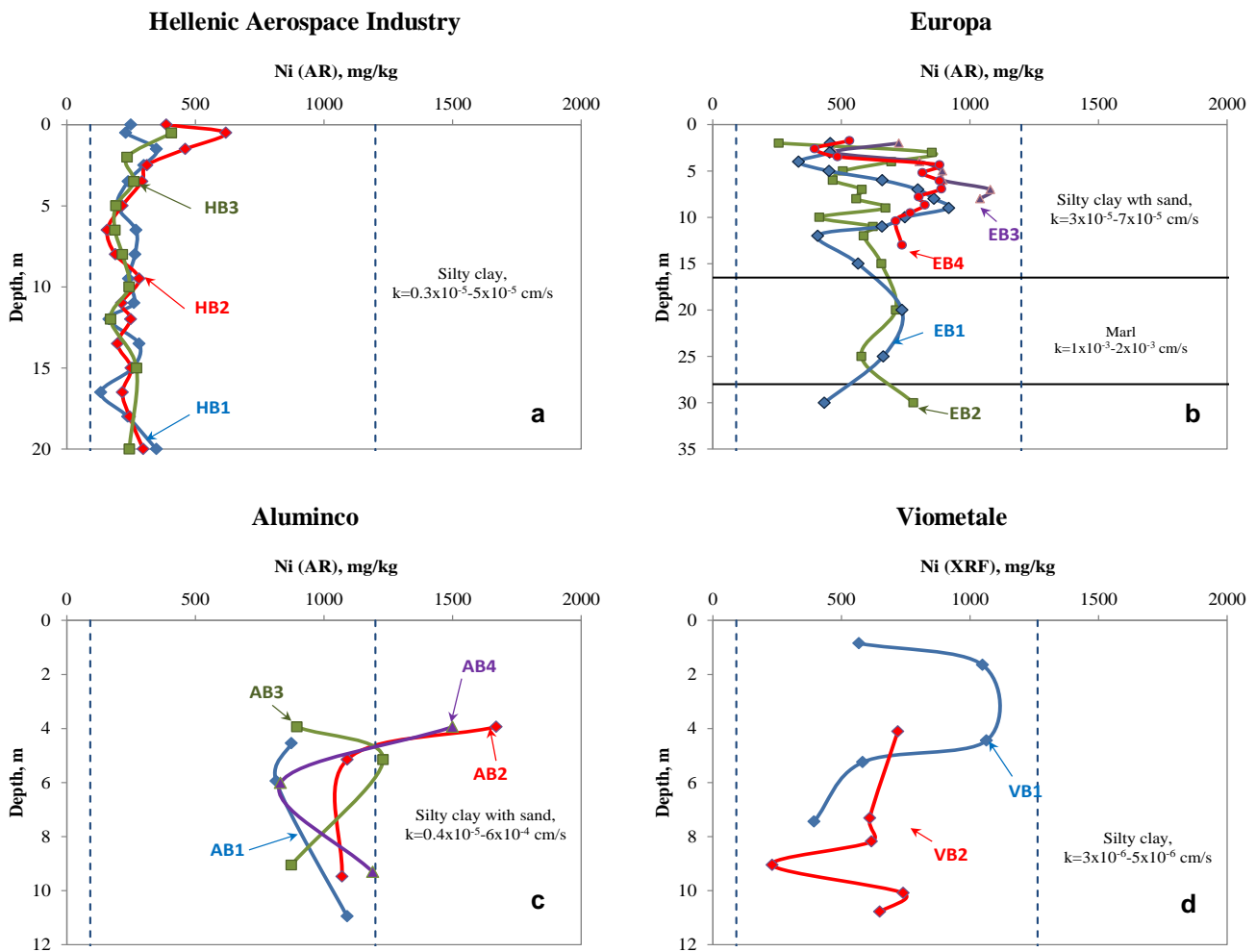


Figure 5. Ni concentration values and profiles in boreholes drilled in the sites of the metal finishing installations of (HAI) Hellenic Aerospace Industry, Europa, Aluminco and Viometale. Second Campaign GR-2 Group. Dashed lines indicate the range of concentration values measured in the reference soils. (k: soil hydraulic permeability)

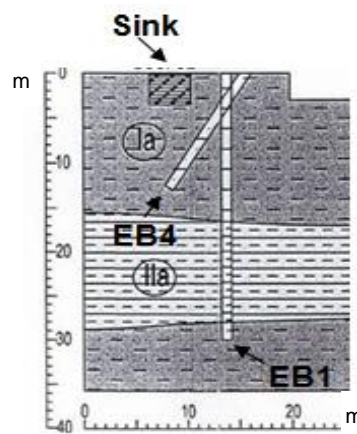
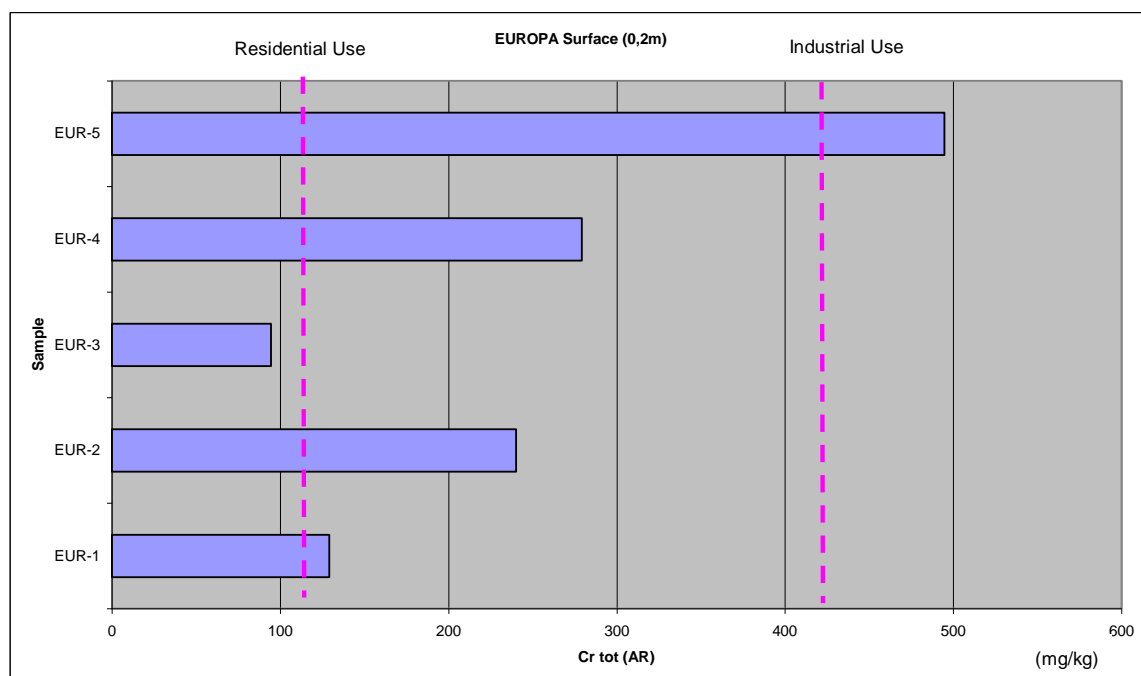


Figure 6. Boreholes at the metal finishing Europa (EB1 and EB4) beneath the sink of the installation (Ia: silty clay and IIa: marl).



Borehole EB3 was drilled at a location where a small stream enters the metal finishing Europa installation area whereas borehole EB2 was drilled 60 meters downstream of the treated wastewaters sink. Total Cr concentration values of Europa boreholes are within the background values of the area as presented within this article, except for two soil samples of EB1 (depths of 8 and 11 m), where Cr soil concentration values are 619 and 849 mg/kg respectively. Borehole EB4 (inclined borehole) close to EB1, presents a similar total Cr profile but the Cr soil concentration values at depths of 8 and 11 m lie within the background levels range. It must be noticed that at the bottom of the sink (depth of 4 m) a thin greenish solid layer no more than a few centimeters thickness was found. This layer was a Cr-rich sludge, i.e. Cr concentration value of about 80100 mg/kg of trivalent Cr. It is argued that the treated effluents containing some small amount of suspended sludge solids, had been filtered and retained inside the sink. It must be noticed though that the soil beneath the sink is relatively contamination free. Soil samples at 4, 5 and 6 meters under the sink (boreholes EB1 and EB4) have low Cr concentration values, ranging from 100 to 280 mg/kg. Ni soil concentration values varied between 257 and 1080 mg/kg and were close to Ni concentration values in reference soils (Figure 5b). Hexavalent chromium was found in 15 of the 49 samples, at a maximum soil concentration value of 10.1 mg/kg, close to reference soil samples.

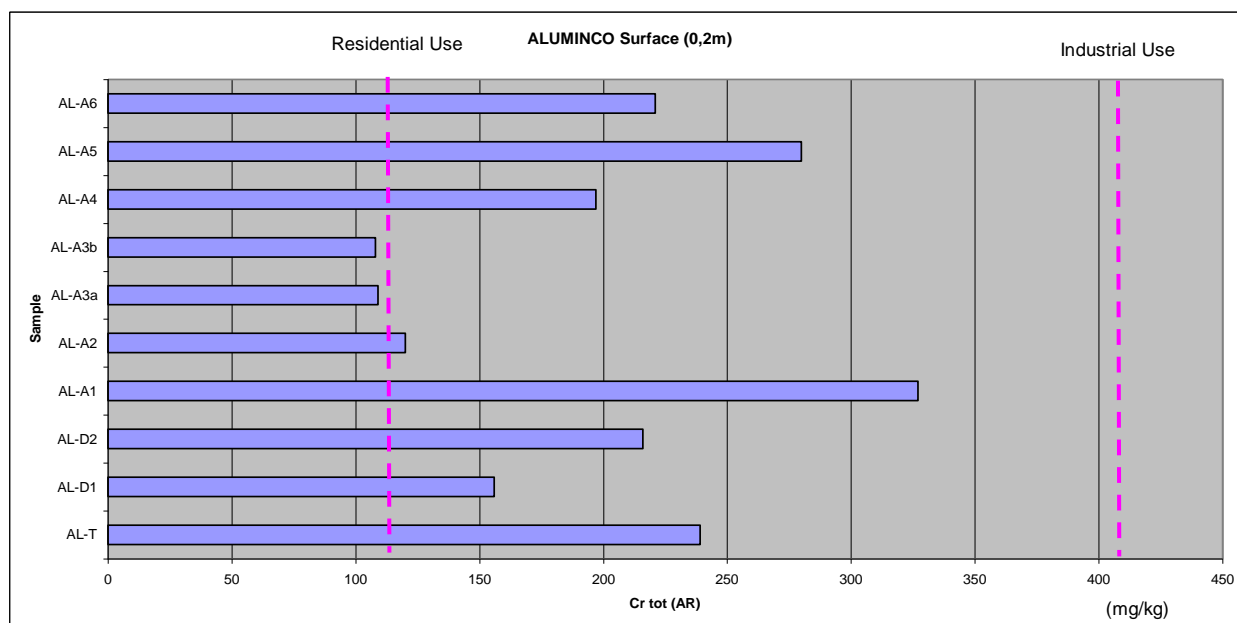
Five surface soil samples were analyzed during the Fourth Group GR-4 campaign at Europa Profile Aluminium grounds, within the facility borders. Chromium concentration values are shown in Figure 7. Chromium, Cr (AR), concentration varied between 95 and 495 mg/kg with a mean value of 247 mg/kg. All these values but one are within the range of concentrations measured in the uncontaminated reference soils. Hexavalent Cr (IV) soil concentration values were below detection limit in any of these samples examined.



**Figure 7. Total Cr concentration values in Sybilla 2015 Fourth Group GR-4 Campaign surface samples. Europa Profile Aluminium (Locations in Figure 2). Dashed lines indicate German Soil Threshold concentration values for different land uses.**

### 3.2.3. Cr and Ni concentration values in soils at Aluminco

The metal finishing unit Aluminco disposed its physicochemically treated industrial wastewater in two parallel sinks, at a depth of 4 m, from 2003 until May 2008. For the assessment of potentially contaminated soil four boreholes, inclined with slopes  $60^{\circ}$ – $75^{\circ}$ , were drilled (two boreholes per sink), as shown in Figure 1e. There exists a thin layer of polluted soil just at the bottom of the sinks that seems to be affected due to the entrainment of suspended solids. Soil samples were collected below the sinks, from depths 4 m to about 10 m. Soil concentration values of total Cr profiles are shown in Figure 4c. At depth of 4 m, boreholes AB4 and AB3 soil samples have high total Cr (AR) concentration values between 710 mg/kg and 2010 mg/kg, while borehole AB2 Cr soil concentration value was slightly above the reference range. It appears that the treated effluents disposal has an impact on a limited depth soil layer below the sink since the samples of depths at 5, 6 and 9 meters had soil Cr concentration values from 200 to 380 mg/kg. Soil concentration values of Hexavalent chromium (analyzed with the alkaline digestion method) was found to be from 0.2 to 4 mg/kg. Soil concentration values of Ni, ranged from 830 to 1650 mg/kg, as presented in Figure 5c. The two Ni highest soil concentration values 1500 and 1650 mg/kg exceed the range of soil concentration values measured in Asopos river Basin reference soils, while similar levels of Ni soil concentration values were measured in soils assumed free of contamination near Thebes and thus a geogenic origin cannot be excluded [23].



**Figure 8. Cr concentration values in Sybilla 2015 Fourth Group Campaign surface samples. Aluminco (Locations in Figure 2). Dashed lines indicate German Soil Threshold concentration values for different land uses.**

Ten surface soil samples were analyzed during Fourth Group (GR-4) campaign at Aluminco grounds, and their locations are presented in Figure 2, within the facility borders. Chromium soil concentration values are shown in Figure 8. Chromium, Cr (AR), concentration varied between 108 and 327 mg/kg with a mean value of 197 mg/kg. All these values are within the range of

concentrations measured in the uncontaminated reference soils. Hexavalent Cr (IV) soil concentration values were below detection limit in any of these samples examined.

#### 3.2.4. Cr and Ni concentration values in Viometale soils

As mentioned before in Viometale site a discrete thin metal contamination layer on surface soils was found to the south of the area during a Prefecture Environmental Audit. Two boreholes were drilled in metal finishing unit Viometale grounds for assessing potentially contaminated soils. These boreholes, denoted as VB1 and VB2, were drilled near and beneath a sink and shown in Figure 1c. Figure 1c, depicts the surface (and low depth (0–0.8m)) soil samples noted as VS1, VS2, VS3 and VS4 samples. Samples VS1 to VS4 are assumed to be representative of incoming pollution located at a land point receiving runoff water from nearby fields, and the outlet of a duct, draining storm water situated to the north of the national road. Boreholes VB1 and VB2 soil Cr concentration values and profiles are depicted in Figure 4d. Since the metal finishing unit at Viometale does not use any trivalent or hexavalent Cr-based chemicals, Cr soil concentrations were measured for comparison reasons, while pollutant of concern (POC) related to these industrial operations is mainly Ni. Measured Cr(XRF) soil concentration values varied from 234 to 2950 mg/kg, equivalent to soil concentration values 58–738 mg/kg of Cr (AR), since Cr(XRF) soil concentration values are approximately 4 times higher to Cr(AR) values. Soil concentrations of Ni remained within the range of reference soils, as shown in Figure 5d and varied from 230 to 1064 mg/kg. Soil surface and low depth samples at points VS1, VS2, VS3 and VS4, end up to the conclusion that there exists high Ni soil contamination mainly in the upper 40 cm soil layer, measured Ni soil concentration values up to 10340 mg/kg.

#### 3.2.5. Inofyta Industrial Area (IIA)

As depicted in Figure 9, Inofyta Industrial Area (IIA) investigation campaign consisted of samples collected at the period 2011–2012 (LGR-4 campaigns by EU funded project LIFE-CHARM) [17], where

- drill core samples were collected from seven boreholes (N1, N2, N3, N4, N5, N6, N7)
- a series of 12 surface soil samples were also collected

and relevant chemical analyses followed in order to investigate the presence of Cr.

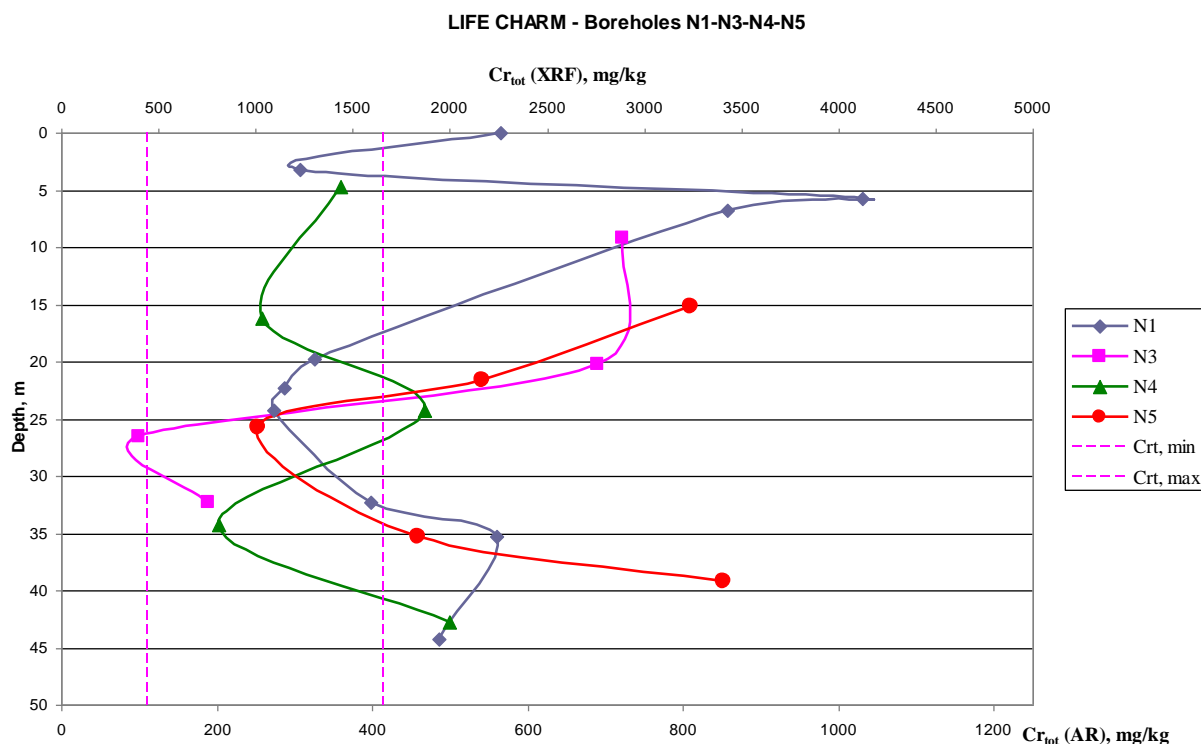
The relevant soil Cr (XRF)/Cr (AR) concentration values are presented at Figures 9 and 10. The elevated Cr concentrations demonstrate that the industrial site studied is contaminated. Chromium, Cr (AR), concentration values varied between 51 and 281 mg/kg with a mean value of 430 mg/kg which exceeds slightly the maximum background concentration. 26 of these values are within the range of concentrations measured in the uncontaminated reference soils while 12 exceed the range of background concentrations. Hexavalent Cr (IV) soil concentration values were below detection limit in of 37 (out of 38) samples examined. Potential sources of this contamination are either buried hazardous wastes or wastewater directly discharged into groundwater.

### 3.2.6. Summary

Soil samples collected close to the existing wastewater physicochemical treatment unit and the sludge storage facilities at the Hellenic Aerospace Industry S.A. (HAI) do not seem to indicate soil contamination.

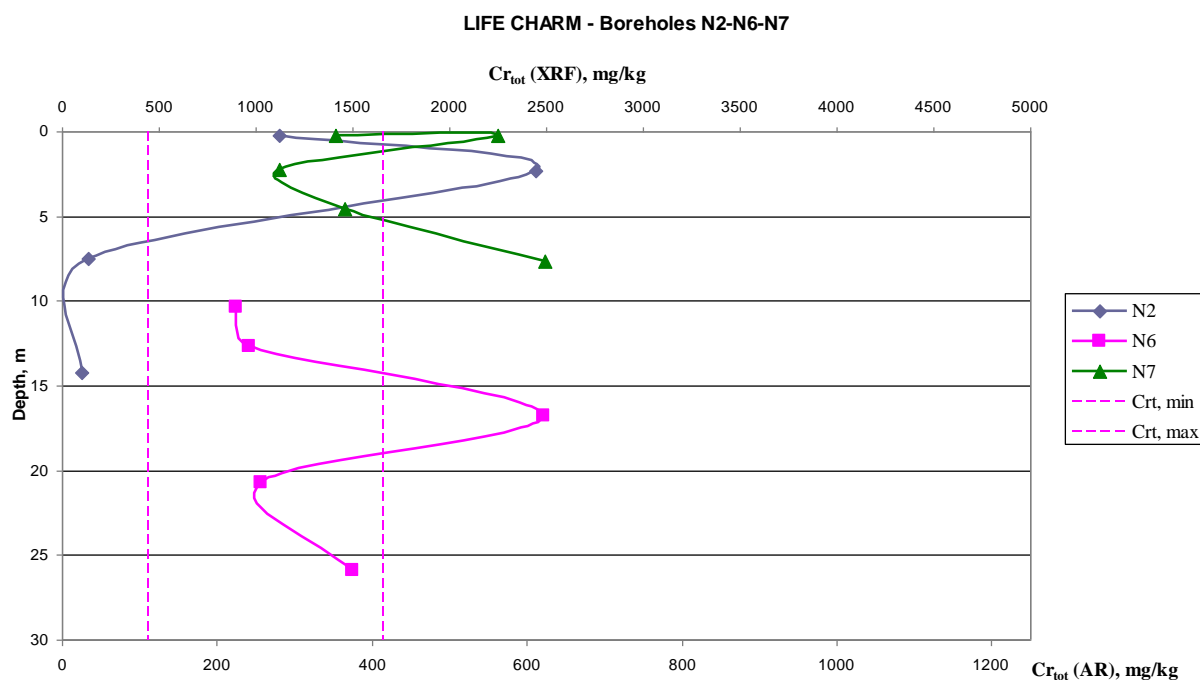
At the second metal finishing unit under investigation, Europa (EU), disposal of physicochemically treated effluents in absorption type sinks led to a thin layer of sludge solids in the bottom of the sink. However, the soil beneath the disposal sink was found to be rather contamination free, and the relevant contamination seems to be localized and not dispersed further.

Measured soil concentration values at Aluminco (AL) end up to the conclusion that there exists a thin layer of polluted soil just at the bottom of the sinks that seems to be affected due to the entrainment of suspended solids. At lower soil layers the soil concentration values of Cr and Ni varied within the range of reference soils concentration values. So the above mentioned contamination (polluted soil just at the bottom of the sinks), does not seem to have an impact on soil contamination beneath it.



**Figure 9. Cr profiles in LIFE-CHARM Campaign boreholes N1, N3, N4, N5 drilled in the Inofyta industrial area.**





**Figure 10. Cr profiles in LIFE-CHARM Campaign boreholes N2, N6, N7 drilled in the Inofyta industrial area.**

Finally, at the last unit analyzed for soil pollution, Viometale (VI), Ni contamination of surface soils was found to the south of the area. However, the soil near and beneath the sink used in the past for physicochemically treated effluents disposal, seems to be contamination free. So the above mentioned contamination (thin discrete layer on the surface soil), does not seem to have an impact on soil contamination beneath it.

Comparison of soil pollution measurement of the four above mentioned metal finishing units (HAI, EU, AL, VI) with a group of data collected in the framework of EU funded project LIFE-CHARM indicate that the Inofyta Industrial Area (IIA) soil seems to be contaminated. Mean Cr soil concentration values of the boreholes samples slightly exceed the maximum background concentration of the greater area while around 33% of the IIA Cr soil concentration values are well above the maximum background concentration by a number of two.

#### 4. Conclusions

Comparison of obtained results allows to ascertain that previous disposal practices at the mentioned four (4) metal finishing facilities HAI, EU, AL and VI have not led to significant potential contamination to the adjacent soils and definitely these installation do not pose a general soil contamination threat to the study area. There was no indication of downstream migration from the land-based treated effluents disposal of the above mentioned facilities. Soil concentration values adjacent to these facilities were rather free of contamination.

The Cr and Ni soil concentration values in the lower soil layers of the above mentioned metal finishing facilities are of the same order of magnitude with greater area background metal concentration values and significantly lower of documented and newly investigated contaminated soil metal concentration values of the Inofyta Industrial Area (IIA).

At Inofyta Industrial Area (IIA) the detected soil contamination (measured high Cr soil concentration values) requires special attention for future environmental protection planning actions.

### Conflict of interest

The authors declare there is no conflict of interest.

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