INVESTIGATION OF POTENTIAL SOIL CONTAMINATION WITH Cr AND Ni IN FOUR METAL FINISHING FACILITIES AT ASOPOS INDUSTRIAL AREA

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EXTENDED ABSTRACT

The objective of this work was to investigate whether previous disposal practices in four (4) metal finishing facilities in the Asopos area have caused any serious contamination of soils. Several chemical elements related with the composition of process liquids were analysed, but the study focused mainly on Cr and Ni, which are the primary elements of concern in the area. The four investigated industrial sites are Hellenic Aerospace Industry (HAI), Europa Profile Aluminium, Aluminco and Viometale.

To estimate the natural geochemical levels of Cr and Ni, 26 soil samples were collected from locations which were not suspected for any contamination. In this group of samples, Cr was found to range between 60 and 418 mg/kg, with a mean value of 220 mg/kg, and Ni concentrations varied from 91 to 1200 mg/kg with mean value 620 mg/kg. The second group of samples consisted of more than 100 drillcore and surface soil samples, which were collected from locations potentially affected by the disposal of effluents and/or the drainage of runoff waters in the installations of the four industrial sites. In the case of HAI, the soil samples which were collected close to existing wastewater and sludge storage facilities were not found to be negatively affected. All measured Cr and Ni concentrations were within the range of values determined for the uncontaminated reference soils. At Europa the disposal of treated effluents in absorption type sinks had led to the accumulation of a thin layer of entrained sludge solids in the bottom of the sink. However, the soil beneath was not found to be contaminated. Similarly at Aluminco a thin layer of soil just at the bottom of the sinks seems to be affected due to the entrainment of suspended solids, but in the lower soil layers the concentrations of Cr and Ni had values which varied within the range of reference soils. Finally at Viometale the quality of soil near and beneath the sink used in the past for treated effluents disposal was found to be unaffected. However, contamination of surface soils with Cu and Ni was identified in a piece of land located to the south of the Viometale premises. It is estimated that these high surface soil metal concentrations do not have any significant impact to Asopos groundwater taking into consideration the low soil permeability at this site.

Keywords: soil investigation, chromium, nickel, soil contamination, background levels

1. INTRODUCTION

An extended problem of chromium contamination has been recorded in the Asopos River basin, in eastern Central Greece. Concentrations of Cr(VI) exceeding in some cases the value of 100 μg/l were measured in groundwater samples collected from the area (Giannoulopoulos & Gintoni, 2008; Vasilatos et al., 2008; Economou-Eliopoulos et al., 2011). Asopos is a typical case where both geogenic and anthropogenic components have probably contributed to the recorded high levels of chromium contamination. Asopos basin is composed by Neogene lake-shallow marine sediments and continental clastic formations, with many recorded outcrops of ultramafic rocks (Moraetis et al. 2012).
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 ultramafic rocks (peridotites and pyroxenites) of ophiolite complexes, as well as of Fe-Ni deposits (Moraetis et al. 2012; Antibachi et al., 2012). Cases where occurrence of hexavalent chromium is primarily of geogenic origin have been documented for California, New Caledonia, Italy, Zimbabwe etc. (Fantoni et al., 2002; Morison et al., 2009).

The contribution of an anthropogenic component to the observed Cr contamination in Asopos basin cannot be neglected, since the area is characterized by intense industrial activities. Industrialization started in the 1960’s and currently more than 400 industrial units are operating in the area. Industrial activities include metal finishing and metal manufacturing plants, which are often using Cr-based chemicals in their production chain. All the 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 adsorption type sinks. Since 2008, due to the concerns about the quality of groundwater in Asopos area, the underground disposal of processed wastewater was banned. The industries were obliged to modernize their wastewater treatment plants in order to obtain 100 % recycling of treated water in the process. The objective of this work was to investigate whether previous disposal practices in four (4) metal finishing facilities have caused any contamination to the adjacent soils. The four investigated industrial sites are Hellenic Aerospace Industry (HAI) S.A., Europa Profile Aluminium S.A., Aluminco S.A. and Viometale S.A. (Sybilla, 2009, 2011, 2012).

2. MATERIALS AND METHODS
The location of investigated industrial sites is presented in Figure 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 site. So, sampling locations (depicted with letters HR, ER, AR and VR in Figure 1a) were selected to be in the vicinity of the industrial site but unaffected from any known or suspected polluting activity. The second group consisted of samples collected from areas suspected for 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 approximately 15 meters. The number of sampling locations and the total number of analyzed samples per industrial site are presented in Table 1.

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

<table>
<thead>
<tr>
<th>Site</th>
<th>No of sampling locations (no of samples)</th>
<th>Parameters analyzed</th>
<th>Methods</th>
<th>Labs(*)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Uncontaminated</td>
<td>Suspected for contamination</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HAI</td>
<td>1 (7)</td>
<td>3 (33)</td>
<td>Cr, Ni, Cu, Zn, Pb, Al</td>
<td>Digestion with AR(^{(a)})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cr(VI)</td>
<td>Elution with water(^{(b)})</td>
</tr>
<tr>
<td>Europa</td>
<td>6 (9)</td>
<td>4 (49)</td>
<td>Cr, Ni</td>
<td>Digestion with AR(^{(a)})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cr(VI)</td>
<td>Elution with water(^{(b)})</td>
</tr>
<tr>
<td>Aluminco</td>
<td>1 (6)</td>
<td>4 (12)</td>
<td>Cr, Ni, Fe, Al</td>
<td>Digestion with AR(^{(a)}) [XRF(^{(d)})]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cr(VI)</td>
<td>Alkaline digestion(^{(c)})</td>
</tr>
<tr>
<td>Viometale</td>
<td>1 (4)</td>
<td>6 (19)</td>
<td>Cr, Ni, Cu, Zn, etc.</td>
<td>XRF(^{(d)}) [AR(^{(b)})]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cr(VI)</td>
<td>Alkaline digestion(^{(c)})</td>
</tr>
</tbody>
</table>

\(^{(a)}\) 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
The parameters which were analyzed, the analytical methods and the laboratories involved are also presented in Table 1. 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, because there is no need for any time consuming pretreatment step, such as acid leaching or fusion. Analysis by XRF determines the total content of elements in the solid samples, which may be different from the amount extracted in aqua regia. Part of Viometale and Aluminco samples were analyzed by both methods for comparison reasons. This aspect is discussed in section 3.1.

Figure 1. Location of investigated industrial sites and sampling points

3. RESULTS AND DISCUSSION

3.1 Comparison of Cr and Ni content in soils based on XRF and Aqua Regia digestion methods

The total content of chromium, as determined by XRF, is much higher compared to that determined after AR digestion. Plots (a) and (b) in Figure 2 present the relationship between the amount of Cr extracted from soils with aqua regia and the total concentration of the element as determined by XRF. Plot (a) corresponds to a dataset of 40 surface soil samples collected throughout the whole Greek territory in the framework of the establishment of the Geochemical Atlas of Europe (Salminen, 2005). Plot (b) corresponds to a subset of the soils collected from Asopos area for the needs of current study. As shown in the figure, the concentration 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. This behavior indicates that the highest percentage of chromium in the examined Greek soils is incorporated into insoluble minerals, e.g. substituted aluminisilicates or spinel minerals like chromite, which are not affected by the AR digestion. A similar behavior of Cr in soils was also observed in previous studies (Medved et al. 1998, Chen and Ma, 2001). The concentration of Ni in the process of AR digestion, Ni (AR), is approximately equal to or slightly lower than the total content, as determined by XRF, Ni (XRF), or after
complete dissolution of the solid with HF, Ni (HF). As seen in Figures 2(c) and 2(d), Ni concentrations determined by the AR method, Ni (AR), correspond to 84-95% of the total content, as determined by XRF or after complete dissolution in the presence of HF.

3.2 Background concentrations of Cr and Ni content in Asopos area soils
Twenty six (26) soil samples were analyzed from locations which were not suspected for any contamination. Cr, Ni and Cr(VI) concentrations are presented in Table 2. Cr and Ni concentrations represent the values determined with the aqua regia (AR) method. Cr(AR) levels ranged between 60 and 418 mg/kg with a mean value of 220 mg/kg. These values are similar to the concentration levels determined by Moraitis et al. (2011) at Oropos, and by Antibachi et al (2012) at Thebes. Both sites are adjacent to the study area, with similar geological formations. At Oropos, which is located at the outlet of Asopos basin to South Evoikos gulf, approximately 8 km to the west of the study area, Cr levels varied between 17 and 600 mg/kg with a mean value of 212 mg/kg. At Thebes, which is situated 24 km to the north east of the study area, the range of Cr levels was 134-856 and the mean concentration of Cr was found to be 277 mg/kg. The Ni concentrations in the examined Asopos soils varied from 91 to 1200 mg/kg with mean value 620 mg/kg. In Thebes soils, measured Ni concentrations were significantly higher, ranging between 621 and 2639 mg/kg and with a mean value of 1591 mg/kg. As far as Cr(VI) is concerned, this species was detected only in three among the 26 analyzed samples of Asopos, with concentrations 5.5, 6.0 and 9.3 mg/kg.

![Graphs showing correlation between Cr and Ni concentrations determined by aqua regia and XRF methods.](image)

**Figure 2.** Chromium and nickel extracted by aqua regia from soil samples (Cr(AR) and Ni(AR)), compared to total concentration of elements as determined by XRF or following complete dissolution using HF. Plots (a) and (c) correspond to a dataset of 40 soil samples collected allover Greece (Geochemical Atlas of Europe, Salminen, 2005). Plots (b) and (d) correspond to a subset of soil samples collected from Asopos area in the framework of current study.

For comparison reasons, soil quality guidelines for Cr and Ni from three European countries, namely Italy, German and Belgium (Wallonia), are also shown in Table 2.
Given values represent the upper permitted levels of Cr and Ni in soils for residential and industrial use of land. Limit value for Cr(VI) exists only in the regulations of Wallonia and corresponds to 4.2 mg/kg for residential areas. As seen in the Table the mean concentration of Cr in Asopos soils, 220 mg/kg, slightly exceeds the Italian limit for residential areas, but satisfies all other limits. On the contrary, the mean concentration of Ni, 620 mg/kg, exceeds all the limit values with the exception of German limit for industrial areas. Even more characteristic is the case of Ni in Thebes soils, where almost all the samples were found to exceed the limits. It is evident that the use of soil quality guidelines established in other countries cannot be applied in metalliferous areas, like those encountered in many regions of Greece, since the geochemical background for some elements is often higher.

Table 2. Summary of analyses of Asopos reference soils (n=26 samples) compared to Cr and Ni values determined in soils of adjacent areas. Comparison with soil quality guidelines in European Countries (Carlson, 2007)

<table>
<thead>
<tr>
<th>Measured concentrations (mg/kg)</th>
<th>Soil limit values (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Asopos soils</strong>&lt;sup&gt;a&lt;/sup&gt; (n=26)</td>
<td><strong>Oropos soils</strong>&lt;sup&gt;b&lt;/sup&gt; (n=33)</td>
</tr>
<tr>
<td>Range</td>
<td>Mean</td>
</tr>
<tr>
<td>Cr (AR)</td>
<td>60-418</td>
</tr>
<tr>
<td>Ni (AR)</td>
<td>91-1200</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>&gt;0.1-9.3</td>
</tr>
</tbody>
</table>

<sup>a</sup> Current study, <sup>b</sup> Moraitis et al., 2011, <sup>c</sup> Antibachi et al., 2012

* Cr(VI) detected in 3 among the 26 analyzed reference soils (5.5, 6.0 and 9.3 mg/kg)

3.3. Cr and Ni concentrations in soils suspected for contamination

**Hellenic Aerospace Industry.** Three boreholes were drilled at HAI grounds (see Figure 1b) close to potentially polluting installations, i.e. ponds which were used for the storage and drying of industrial sludge, as well as for the storage of treated wastewater. The profiles of Cr are shown in Figure 3a. Chromium, Cr(AR), concentration varied between 51 and 281 mg/kg with a mean value of 124 mg/kg. For Ni(AR) the range of concentrations was 132-618 mg/kg and the mean value 262 mg/kg. All the values are within the range of concentrations measured in the uncontaminated reference soils. Hexavalent Cr was not detected in any of the 33 samples examined.

**Europa Profile Aluminium.** Soil investigation in Europa grounds involved the drilling of four boreholes, whose location is shown in Figure 1d. The first borehole EB1 was drilled in contact with the sink, where processed wastewater of the electrostatic coating process was disposed of for over 20 years, in accordance with the pertaining at that period environmental permit. In order to investigate the pollution directly beneath sink, one inclined borehole was drilled with 45° slope (EB4). Schematic representation of the two boreholes is given in Figure 4. Borehole EB2 was drilled 60 meters downstream of the sink and borehole EB3 was drilled at a location where a small stream enters Europa ground. The Cr content of boreholes (Fig. 3b) is generally within the background values identified within the study. The only exception is for 2 samples of EB1 from 8 and 11m depths, which presented Cr content 619 and 849 mg/kg. The inclined EB4 borehole, which was drilled
close to EB1, presented a similar Cr profile but the concentrations at 8 and 11 m depths remained within the range of background levels. It is noted that the bottom of the sink is close to the depth of 4 m. A greenish solid, forming locally a thin film of no more than a few centimeters, was collected from this depth. The solid was found to be a Cr rich sludge, i.e. containing approximately 80,000 mg/kg of Cr in the trivalent state, similar to the sludge produced in the wastewater treatment plant of the electrostatic coating unit. Obviously, the treated effluents, which were disposed in the sink for approximately 20 years, entrained a small amount of suspended sludge solids, which were filtered and retained inside the sink. Despite sludge accumulation at this thin layer, the soil beneath the sink was not found to be contaminated. The samples collected at 4, 5 and 6 meters under the sink by EB1 and EB4 boreholes had a low Cr content, ranging between 100 and 280 mg/kg. As far as Ni is concerned, its content varied between 257 and 1080 mg/kg and did not exceed the range of Ni concentrations in reference soils. Finally, hexavalent chromium was detected in 15 of the 49 samples, with maximum concentration 10.1 mg/kg, a value which is close to the one measured in reference soils.

Aluminco. Aluminco applied the underground disposal of treated industrial effluents until May 2008. Discharge was carried out in two parallel sinks. Four boreholes were drilled, two per sink, and their location is shown in Figure 1e. All boreholes were inclined with slopes 60-75°. The objective was to collect samples just below the sinks, which had a depth of 4 meters and from lower depths until approximately 10 meters. Cr profiles are shown in Figure 3c. As seen in the figure, the soil samples collected with boreholes AB4 and AB3 from the depth of 4 m have high concentrations of Cr, 710 mg/kg and 2010 mg/kg, respectively. This depth is just below the depth of the sinks. It seems that the disposal of treated effluents has affected a soil layer of limited depth, since the samples of lower depths at 5, 6, and 9 meters had all concentrations ranging between 200 and 380 mg/kg. Hexavalent chromium was analyzed with the alkaline digestion method and was found to vary between 0.2 and 4 mg/kg. For Ni measured concentrations ranged between 830 and 1650 mg/kg. The two highest concentrations 1500 and 1650 mg/kg exceed the range of values measured in Asopos reference soils, however similar levels of Ni have been measured in uncontaminated soils near Thebes and thus a geochemical origin cannot be excluded (see Table 2, Antibachi et al., 2012).
Figure 3. Cr (tot) profiles in 12 boreholes drilled in the 4 industrial sites. Dashed lines indicate the range of concentrations measured in reference soils.

Viometale. Soil investigation in Viometale included drilling of two boreholes near and beneath a sink, denoted as VB1 and VB2 in Figure 1c, as well as the collection of surface and low depth (0.8m) samples presented with codes VS1, VS2, VS3 and VS4 in Figure 1c. Samples VS1 to VS4 are located in a piece of land situated to the southwest of Viometale industrial installations and receiving runoff waters from the nearby fields, as well as from the outlet of a duct, draining storm water from areas situated to the north of the national road. The profiles of Cr from boreholes VB1 and VB2 are shown in Figure 3d. It is noted that Viometale does not make use of Cr-based chemicals, but the element was measured for comparison reasons. The elements of concern related with the industrial operations are Ni, Cu and Zn. It is also reminded that elemental analysis of Viometale samples was carried out applying the XRF technique. Measured Cr(XRF) concentrations were found to vary between 234 and 2950 mg/kg, which is equivalent to a range of 58-738 mg/kg of Cr soluble in AR, if we take into consideration that Cr(XRF) measurements are approximately 4 times higher compared to Cr(AR) values, as discussed in section 3.1. Concentrations of Ni were found to vary between 230 and 1064 mg/kg, remaining within the range of reference soils. For the other two elements, Cu and Zn, the concentrations measured in VB1 and VB2 samples were 19-50 mg/kg for Cu and 41-62 mg/kg for Zn. Similar ranges of Cu and Zn concentrations were measured in the nearby reference borehole VR1 (see Figure 1a). The analysis of surface and low depth samples at locations SV1, SV2, SV3 and SV4, indicated that this piece of land has been contaminated with Cu and Ni. Contamination seems to be located mainly at the upper 40 cm of soil, with measured Cu and Ni concentrations up to 10760 and 10340 mg/kg respectively. The permeability of soils at Viometale site was found to be low, in the order of 3-5x10^{-6} cm/s, it is thus estimated that the high levels of Cu and Ni at surface soils do not have any significant impact on the quality of groundwater, commonly abstracted from deep aquifer layers (>120m). Remediation of the site is currently planned by Viometale.

4. CONCLUSIONS

The objective of current work was to investigate potential soil contamination in 4 industrial sites at Asopos area. To estimate the natural geochemical levels of Cr and Ni, 26 soil samples were collected from locations which were not suspected for any contamination. In this group of samples, Cr was found to range between 60 and 418 mg/kg and Ni between 91 and 1200 mg/kg. The second group of samples consisted of more than 100 drillcore and surface soil samples, which were collected from locations potentially affected by the disposal of effluents and/or the drainage of runoff waters in the installations of the four industrial sites. In the case of HAI, the soil samples which were collected close to existing wastewater and sludge storage facilities were not found to be negatively affected. At Europa the disposal of treated effluents in absorption type sinks
had led to the accumulation of a thin layer of entrained sludge solids in the bottom of the sink. However, the soil beneath was not found to be contaminated. Similarly at Aluminco a thin layer of soil just at the bottom of the sinks seems to be affected due to the entrainment of suspended solids, but in the lower soil layers the concentrations of Cr and Ni had values which varied within the range of reference soils. Finally at Viometale the quality of soil near and beneath the sink used in the past for treated effluents disposal was found to be unaffected. However, contamination of surface soils with Cu and Ni was identified in a piece of land located to the south of the Viometale premises. It is estimated that the high surface soil metal concentrations do not have any significant impact to the quality of Asopos groundwater due to the low permeability of soils at this area.

REFERENCES