Chromium and Nickel distribution in sediments of a coastal area impacted from metallurgical activities: the case of the Larymna Bay

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Abstract

In the present study, the distribution of Cr and Ni was investigated in the surface sediments from the Larymna Bay (Northern Evoikos Gulf) and in metallurgical slag samples discharged in the marine environment. The results were compared to concentrations of Cr and Ni in parent rocks that outcrop extensively in the catchment area of N. Evoikos in order to distinguish natural and anthropogenic sources of these two elements. Elevated concentrations of Cr and Ni as well as high values of magnetic susceptibility were determined in all samples. Low leachability was determined for Cr since chromite is the major crystalline phase of Cr in the samples analyzed whereas higher leachability was observed for Ni.

Keywords: chromium, nickel, parent rocks, slag, sediments, Evoikos.

1. Introduction

Natural weathering, surface runoff, atmospheric transport and direct discharges of waste materials of urban or industrial origin contribute to the enrichment of the marine environment in heavy metals. Marine sediments act as primary repositories of the transferred particles. However, in areas where local minerals contain high natural metal concentrations, the investigation of element geochemistry in marine sediments is not always straightforward (Angelidis & Aloupi, 2000).

Northern Evoikos Gulf is surrounded by a variety of sedimentary, magmatic and metamorphic rocks containing naturally high concentrations of Cr and Ni (Voutsinou-Taliadouri & Varnavas, 1993). Moreover, the daily discharge of a slag originating from a Fe-Ni smelter located in Larymna Bay, contributes significantly to sedimentation processes in the Northern Evoikos Gulf by forming an underwater bottom layer of 20 km^2 (Simboura et al., 2007). Previous studies have documented the elevated concentrations of heavy metals, including Cr, in Northern Evoikos Gulf (Voutsinou-Taliadouri & Varnavas, 1993). In the present study, the distribution of Cr and Ni was investigated in parent rocks, slag and marine sediments of Northern Evoikos/Larymna Bay, in order to study Cr and Ni geochemistry and to assess the relative influence and contribution of natural and anthropogenic enrichment of the marine environment. For comparison reasons, the study of these two elements was also extended in the less polluted Southern Evoikos Gulf.

2. Materials and methods

Sampling of parent rocks from the catchment area of Northern Evoikos took place in May 2013. Parent rocks included ophiolites, Ni -laterites and soil. These Ni-laterites are used as a feedstock in the Fe-Ni smelter located in the Larymna Bay.

Sampling of surface sediments in the Northern Evoikos Gulf took place in October 2014 in the Larymna Bay, where the ferro-nickel plant is located (Stations NEV-1 to NEV-6). NEV-8 sediment was collected from the underwater slag deposition area. Station NEV-7 located far from the Larymna bay in the Northern Evoikos Gulf. Additionally, a slag sample was collected directly from the factory right before its discharge. Surface sediments were also collected from the Southern Evoikos in October 2014 (Stations CEV-2 to CEV-11). All sediments were immediately transferred to the laboratory and placed in deep freeze.

Moreover two sediment cores were collected in order to investigate background levels for Cr and Ni; one from station NEV-12 in the Northern Evoikos and one from station CEV-10 in the Southern Evoikos.

Concerning the analysis of surface sediments from the Larymna Bay, all analytical procedures were performed for both fractions <63μm and >63μm since slag particles were visible in the fraction f>63μm. Analysis of sediments from the Southern Evoikos was performed in the <63μm fraction only.

Magnetic parameters, low-field magnetic susceptibility (χlf) and frequency dependent susceptibility (χld%) were measured on a mass specific basis by a Bartington susceptibility sensor (Botsou et al., 2011; Scoullos et al., 2014).

The labile fraction of Cr and Ni was determined in the parent rocks, the slag and the freeze-dried sediments after a weak-acid digestion with 0.5N HCl (Agemian & Chau, 1977). Total Cr and Ni contents were determined by ultrasonic assisted digestion with a mixture of concentrated acids including HF. Additionally, sequential extractions according to the BCR protocol were carried out in the parent rocks, the slag and the surface sediments of from the Northern Evoikos in order to determine the different geochemical fractions of Cr and Ni (EUR report 19502EN). Cr and Ni analysis was carried out by FAAS and GFAAS (Varian SpectrAA-100) in all extracts.

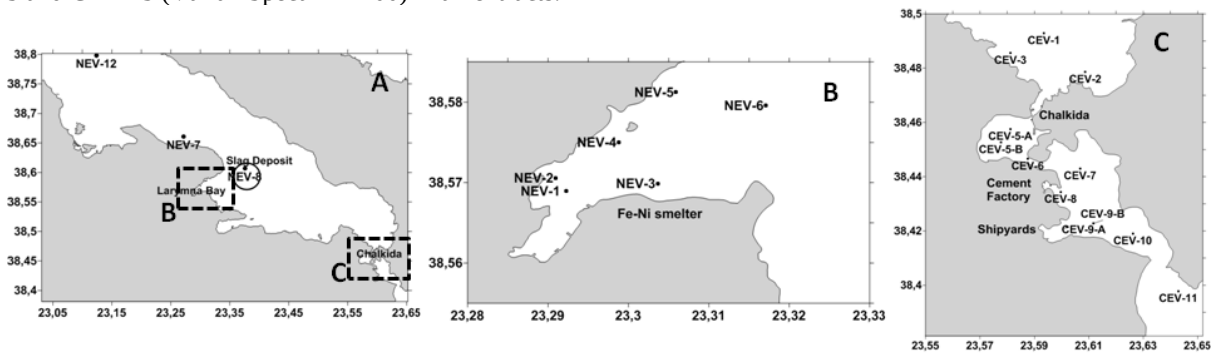

Fig.1: Surface Sediment sampling stations in **A)** Northern Evoikos Gulf, **B)** Larymna Bay and **C)** Southern Evoikos Gulf.

3. Results

Concerning the granulometric composition of the sediments, in the Larymna Bay most samples consist of sand, whereas the silt/clay fraction ranges from 9% to 48%. Station NEV-4 consists primarily of sand. Black grains of slag were detected during sieving in stations NEV-1, NEV-2, NEV-3 and NEV-6. The grains were visible in the fraction >63μm. On the other hand, the silt/clay fraction was dominant in sediments from Southern Evoikos ranging from 59 to 100% of the total sediment mass, with the exception of one station (CEV-2) where the silt/clay fraction was 16.2%.

Table 1: Total Cr and Ni concentrations in (mg/kg) and percentage of HCl-extractable Cr and Ni in the analyzed samples.

	Fraction	Total Cr	% HCl extr. Cr	Total Ni	% HCl extr. Ni	χlf 10^{-6} m^3/kg
Parent Rocks		2176-21929	0.22-6.5	1845-6611	6.7-50.1	1.85 -25.8
Slag		17577	16.4	1623	75.6	4.08
Marine Sediments						
Slag deposit (NEV-8)	f<63	4017	35.8	2447	65.4	1.52
	f>63	19878	32.0	670	84.9	2.36
Larymna Bay	f<63	1726-10299	8.2-33.2	1180-3207	7.0-23.0	2.57-11.64
	f>63	72.8-18262	7.1-53.16	82.8-1362	29.7-58.6	0.302-5.48
NEV-7	f<63	529	3.3	526	12.9	0.265
	f>63	38.4	34.5	65.6	55.4	0.061
Southern Evoikos	f<63	74.5 - 422	4.7 - 18.7	101 - 426	15.6 - 27.4	0.390 - 0.829

Chromium concentrations in the samples analyzed are presented in **Table 1**. Elevated concentrations of Cr are determined in all samples of N. Evoikos Gulf. The maximum value was determined in station NEV-8 in the slag underwater deposit. It was generally observed that in the stations where slag particles were detected (i.e. NEV-1, NEV-3, NEV-6, NEV-8), Cr concentrations were higher in the sand fraction indicating the contribution of the coarse slag particles to the Cr-content of the sediment. Lower Cr concentrations where observed in the Southern Evoikos where the maximum value of Cr was detected in stations CEV-2 and CEV-9, the stations near the town of Chalkida and the Shipyards respectively.

Elevated concentrations of Ni were also determined in all samples (**Table 1**). For example, in the underwater slag deposit area Ni concentrations were 2447 mg/kg and 670 mg/kg in the silt/clay and sand fraction respectively. The maximum concentrations of Ni were determined in station NEV-3 located outside the smelter while the lower concentrations were observed in station NEV-4. Distribution of Ni between the two fractions exhibited different behavior compared to Cr. Higher Ni concentrations are determined in the silt/clay fraction in all stations despite the presence of slag particles in the sand fraction. Lower concentrations of total Ni were observed in the Southern Evoikos Gulf (101 - 426 mg/kg Ni) where, similarly to Cr, the maximum Ni concentrations were determined in the stations CEV-2 and CEV-9.

Total Cr correlated well with total Ni using Spearman correlations for both the silt/clay (r= 0.952, p=0.01) and the sand fraction (r= 0.833, p=0.05) in Larymna Bay and for the silt/clay fraction in Southern Evoikos (r=0.707, p=0.01).

Table 2: Cr and Ni concentrations after BCR sequential extractions

(mg/kg)	Cr				Ni			
Fraction	**F1**	**F2**	**F3**	**F4**	**F1**	**F2**	**F3**	**F4**
Parent Rocks (Ni-Laterite)	5.0	16.7	65.4	17470	86.2	250	352	6680
Slag	103	215	357	15964	81.7	286	178	1159
Marine Sediments								
Larymna Bay	0.07-10.7	3.8-173	135-1139	1587-8975	5.3-58.7	8.1-142.8	28.0-127.3	1130-2901
Slag Deposit (NEV-8)	9.0	276	504	3227	216	554	552	1125
NEV-7	0.08	0.23	11.5	517	0.77	2.0	8.3	515

F1= Acid Soluble, F2=Reducible, F3=Oxidizable, F4=Residual

The extraction with 0.5N HCl gives an estimation of the more labile forms of an element. As shown in **Table 1**, the leachability of Cr in parent rocks ranges from 0.22 to 6.5% for Cr and from 6.65 to 50.1% for Ni. These percentages for both elements increase for both elements in the slag, in the slag deposit area, and in the marine sediments from the Larymna Bay. The highest percentages were observed for both elements in station NEV-8 where the underwater slag deposit is located. Low leachability was determined in the sediments of the Southern Evoikos Gulf, implying that Cr and Ni are of geological origin.

Sequential extractions performed for the parent rocks, the slag and the surface sediments from the Larymna Bay showed that the maximum concentrations of Cr are detected in the residual fraction in all samples (**Table 2**). However, significant amounts are detected in more labile fractions that might be mobilized and released to environment under changes of environmental conditions. For example, in the slag deposit area the sum of fractions f1+f2+f3 accounts for 789 mg/kg on Cr. Concerning Ni, in the parent rocks and in most of the surface sediments from the Larymna Bay, maximum concentrations are determined in the residual fraction. However, Ni contents increase in the f1, f2, f3 fractions of the pure slag and the underwater slag deposit, implying that Ni is more labile than Cr in these samples. For example in the silt/clay fraction of the slag deposit sample the percentages of Ni account for f1=8.8%, f2=22.7%, f3=22.5% f4=46.0% of the total Ni determined.

Mineralogical analysis performed by XRD and SEM in the parent rocks (i.e. Ni-laterites) and in the slag showed that chromite - $FeCr_2O_4$ is the major crystalline phase containing Cr, while the presence of other Fe-Cr spinels were also identified (Andrioti et al, 2014; Andrioti, 2015). Due to the low solubility of chromite present in the parent rocks and slag, the leachability of Cr after 0.5N HCl extraction and BCR sequential extraction is low in these samples. Thus, it is observed that the leachability of Cr increases in the following sequence: parent rocks < slag < marine sediments, indicating probably a transformation of Cr-bearing phases from the sources to the deposition area. On the other hand, the leachability of Ni is higher compared to Cr both in the parent rocks and the slag. This might be attributed to different and more soluble Ni-bearing mineral phases. The mineralogical phases of Ni both in the parent rocks and the slag are currently under investigation.

Regarding the magnetic susceptibility-χlf, high values were observed in parent rocks, pure slag and surface sediments from the Larymna Bay including the underwater slag deposit. In surface sediments, χlf values were increased in silt/clay fraction, whereas the lower values in the sand fraction are attributed to the presence of carbonates, which is a diamagnetic component and decreases the magnetic signal. Spatial distribution showed that the strong signals are observed in stations NEV-1, NEV-2, NEV-3 and NEV-6, where slag grains are present. The maximum value was determined in station NEV-3. Comparison of the sediments' and slag's χlf values implies that there are other components apart from the slag contributing to magnetic susceptibility. These components might be of geological origin, since strong signals were observed for the parent minerals as well. Weaker signals were observed in the surface sediments from the Southern Evoikos Gulf, since χlf ranges from 0.390 to 0.829 10^{-6} m^3/kg. Magnetic susceptibility - χlf correlated well with total Cr both in sand (r= 0.952, p= 0.01) and in silt/clay fraction (r=0.833, p=0.05) in the Larymna Bay and in Southern Evoikos (r=0.717, p=0.05). This positive correlation ascribes to the presence of Fe-Cr spinels and chromite that were identified by mineralogical analysis. Although chromite is among the “less common” magnetic minerals, is one of the more resistant minerals in nature and together with other Fe-Cr spinels could represent a significant proportion of relict magnetic assemblage (Scoullos et al., 2014).

Finally, Enrichment Factors (EFs) were calculated for the silt/clay fraction according to the formula $EF= (element/Al)_{sample}/ (element/Al)_{reference\ value.}$ For the Northern Evoikos Gulf, a 200 cm sediment core (NEV-12; Fig. 1A) was analyzed in order to establish the reference values for Cr and Ni (Reference Values: Cr= 240 mg/kg, Ni= 510 mg/kg).

Enrichment Factors in the Larymna Bay ranged from 1.9 to 49.1 for Cr and from 1.0 to 6.1 for Ni. The maximum values were observed for both elements in stations associated with the smelter (NEV-1, NEV-3, NEV-6, NEV-8) implying that surface sediments are strongly affected by the smelter’s activity and the slag’s disposal. In the case of the Southern Evoikos Gulf, EFs were calculated using as reference values the lower parts of a sediment core obtained from Station CEV-10 (Fig. 1c; Reference values: Cr= 252 mg/kg, Ni= 355 mg/kg). Enrichment Factors in the Southern Evoikos were lower compared to

the Larymna Bay and ranged from 0.21 to 3.16 for Cr and from 0.20 to 1.55 for Ni. The maximum values in the S. Evoikos for both elements were observed in stations CEV-2 and CEV-9.

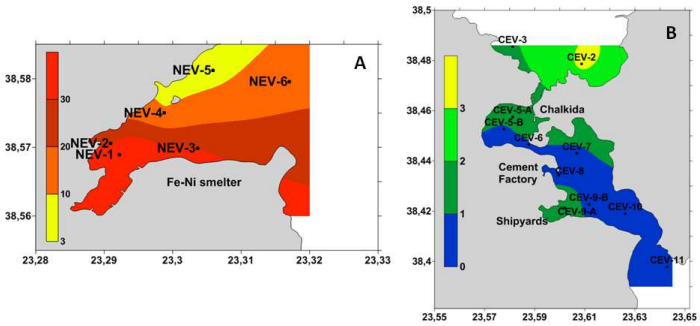

Fig. 2: Spatial Distributions of Enrichment Factor - EF for Cr in **A)** Larymna Bay, and **B)** Southern Evoikos.

4. Conclusions/Discussion

This study of Cr and Ni distribution in the Larymna Bay showed that the area is strongly affected by the plant's activity and highly enriched in both Cr and Ni. Compared to the Larymna Bay, Southern Evoikos is less enriched in Cr and Ni.

Chromite is the prevailing crystalline phase of Cr both in the parent rocks that outcrop in the catchment area of N. Evoikos and in the slag deposited in the marine environment. However, the higher leachability of Cr both in the slag deposition area and in surface sediments indicates the increasing contribution of the more soluble, Cr-bearing phases. Sequential extractions performed in parent rocks, slag and marine sediments from the Larymna Bay in the current study confirm this assumption. Furthermore, preliminary results indicate that minerals containing Ni are more soluble than those containing Cr. This explains the higher leachability of Ni in all samples analyzed.

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