LEVELS AND PARTITIONING OF CHROMIUM IN SURFACE SEDIMENTS ENRICHED WITH METALLURGICAL SLAG

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Abstract
The geochemical fractions of Cr were investigated in the surface sediments of the Evoikos Gulf, as well as in metallurgical slag originating from a Fe-Ni smelter which dispose it, daily, into the gulf. The surface sediments in the areas affected by the smelter were highly enriched in Cr that was allocated in the residual and relatively inert fraction. However, Cr leachability was increased from the slag to the surface sediments, implying the occurrence of labile Cr-bearing phases that could potentially be mobilized and released to the environment.

Keywords: Geochemistry, Metals, Pollution, Sediments, Aegean Sea

Introduction
Since 1960's metallurgical slag originating from a Fe-Ni smelter located in the Larymna Bay (Evoikos gulf, Greece) is daily discharged in a designated marine area of about 80 m depth [1] and contributes to heavy metal enrichment of the surface sediments. In this study, we determined the geochemical fractions of Cr in surface sediments from the Evoikos Gulf and in the slag discharged by the smelter in order to detect potential changes that occur in the deposition area. The sampling network of surface sediments in the Northern Evoikos Gulf is shown in Fig.1. Additionally, a slag sample was collected directly from the smelter right before its discharge. The geochemical fractions of Cr were investigated through sequential extractions according to the BCR protocol (EUR report 19502EN) and a weak-acid digestion with 0.5N HCl [2]. Total Cr contents were determined by ultrasonic assisted digestion with a mixture of concentrated acids, including HF. Analysis of Cr in all extracts was carried out by GF AAS.

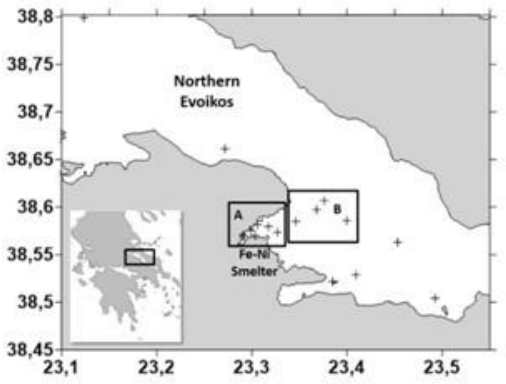

Fig. 1. Sampling stations in the Northern Evoikos Gulf: A) Larymna Bay, B) Slag deposition area, C) unaffected area.

Results
Chromium values were increased in the surface sediments affected by the Fe-Ni smelter while decreasing in the open and unaffected stations (Table1). Grain size distribution showed that Cr was allocated in the sand fraction (63 μm< f<1 mm) of the surface sediments that were enriched with metallurgical slag. The percentage of 0.5 N HCl extractable Cr of the pure slag was 16.4%, giving an estimation of the more labile Cr-bearing phases. Mineralogical analysis of the slag showed that chromite - $FeCr_2O_4$ was the major crystalline phase containing Cr, while other Fe-Cr spinels were also identified which explains the low leachability. For the surface sediments these percentages ranged from 3 to 49% for the silt/clay fraction and from 5 to 53% for the sand fraction for all samples analyzed, and maximum values were determined for the underwater slag deposit. The leachability of Cr increased from the slag to the sediments associated with the smelter, implying a potential transformation of Cr-bearing phases from the sources to the deposition area. Sequential extractions showed that Cr was primarily distributed in the residual fraction which accounted from 79 to 99% for the silt/clay fraction and from 91 to 99% for the sand fraction of all the samples analyzed. Therefore, the majority of Cr is inert under common environmental conditions. However, significant amounts of Cr were detected in fractions F1, F2 and F3 representing the amount of Cr that could potentially be released to the environment. Additionally, the percentage of the sum F1+F2+F3 to total Cr for the pure slag accounted for 4%, and increased to 6–21% in the surface sediments affected by the smelter. This difference is attributed to an increase in the oxidizable fraction F3 and to a slight increase in the F2 fraction. The positive correlation of Cr in the F2-reducible fraction with Mn and Fe in both silt/clay and sand fractions of the surface sediments associated with the smelter implies that Cr is possibly bound to Fe-Mn oxy-hydroxides.

Tab. 1. Chromium contents of sediments in various extracts (in mg/kg).

Samples	Fraction	Total Cr	HCl extr.Cr
Slag	f<1 mm	17577	2772
Area A	f<63 μm	1726-10299	142-3422
	f>63 um	72.8-1826	38.7-390
Area B	f<63 um	4017-8131	1433-3553
	f>63 um	18158-21933	5315-7102
Open Stations	f<63 μm	447-733	17.8-70.5

Samples	Fraction	BCR - sequential Extraction F1	F2	F3	F4
Slag	f<1 mm	113	223	410	14555
Area A	f<63 um	0.07-10.7	3.8-173	135-1140	1587-8978
	f>63 um	0.12-3.5	8.2-191	117-338	2251-18068
Area B	f<63 um	1.1-21.3	27.7-277	426-792	3227-7142
	f>63 um	5.4-144	383-747	153-1035	14731-20705
Open Stations	f<63 μm	0-0.11	0.23-1.8	11.5-57.8	411-718

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

Conclusions
The surface sediments near the Fe-Ni smelter and inside underwater slag deposit were highly enriched in Cr and the grain size distribution showed the contribution of the slag in the total Cr-content of the sediments. Although Cr was distributed mainly in the residual fraction, it was observed that the Cr-leachability increased in the surface sediments enriched with slag compared to pure slag, implying a transformation in more mobile Cr-bearing phases. Increase in fractions F2 and F3 of these sediments confirmed this assumption.

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References
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