

METAL PARTITIONING IN PIRAEUS PORT SEDIMENTS

F.Sakellariadou^{1*}, L.Haralambides¹, M.Dassenakis²

¹ Department of Maritime Studies, University of Piraeus, Greece - fsakelar@unipi.gr

² Department of Chemistry, University of Athens, Greece - edasenak@cc.uoa.gr

Abstract

The metal partitioning among the geochemical phases of sediment samples from the Piraeus port was studied. It shows a total metal enrichment close to the ship repair and maintenance site of the port. Copper and Zn show significant bioavailability. Significant proportions of Pb, Fe and Zn are bound to ferromanganese oxides. Lead, Fe, Zn and especially Cu are highly associated with the organic and sulphide fraction. The major percentages of Pb, Fe and Zn are found to the residual fraction as they are bound in the lattice structure of aluminosilicate minerals.

Keywords : sediment, metals, zinc, lead.

Introduction

Piraeus port is considered as the third most frequent passenger port in the world and the leading container hub in the Eastern Mediterranean. Its main port areas are a central passenger port, a container terminal, a commercial port, and a ship repair and maintenance site. Previous studies of Piraeus port have shown high values of dissolved metals (Fe, Zn, Pb, Cu, Ni, Mn) indicating the relatively poor seawater quality in the area studied [1].

In the present paper metal partitioning among the various geochemical phases of the sediments is examined by sequential chemical extraction which, although a time consuming technique, can provide detailed information concerning the source, mode of occurrence, biological and physico-chemical availability, mobilization and uptake of metals in sediments [2].

Methodology

Twenty-five surface sediment samples from various locations of the Piraeus port (Fig.1) were collected during three annual cruises (1997,1998, 1999). The total metal content (Pb, Fe, Cu, Zn) was measured after treatment of the samples by a mixture of concentrated HNO₃, HClO₄, HF at high temperature [3]. The partitioning of the metals was examined following the Tessier *et al* (1979) procedure [4] with some modifications [5]. Pb, Fe, Cu and Zn were examined within five fractions, the following: exchangeable (E), (1M NH₄OAc, pH 8.2) ; carbonate associated (C), (1M NaOAc, pH 5) ; reducible (Red), (0.04M NH₂OH.HCl, pH 2) ; organic matter-sulphide bound (Ox+Sul), (HNO₃, 30% H₂O₂, NH₄OAc) and residual (Res).

All metal concentrations were measured by Atomic Absorption Spectrophotometry. The relative standard deviation of the measurements, which was obtained from the analysis of five discrete subsamples of selected samples was <5%.

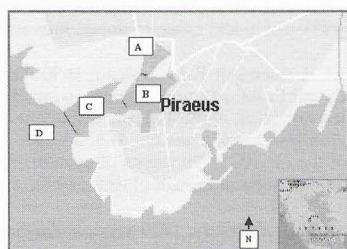


Figure 1 : The Piraeus port with the studied areas.

Results and Discussion

From the results of Table 1 the following conclusions are drawn:

- The total metal content shows an enrichment in area C that can be attributed to the presence of the ship repair and maintenance site of the port.
- Cu and Zn show significant percentages in the exchangeable fraction, indicating that they can be easily released.
- All metals show very small percentages present in the carbonate bound fraction, which represents sedimentary carbonates, mainly calcium carbonate.
- Pb, Fe and Zn show significant percentages in the reducible fraction, which represents metals bound to ferromanganese oxides.
- Pb, Fe, Zn and especially Cu show significant percentages in the organic/sulphide fraction indicating their association with the organic matter and/or sulphide minerals.
- The major percentages of Pb, Fe and Zn and a significant percentage of Cu are found to the residual fraction as they are bound in the lattice structure of aluminosilicate minerals.
- In area D, some extreme values (Fe >200,000 µg/g, Zn >6,000 µg/g) , not included in the Table 1, were found in restricted areas in the vicinity of industrialized sites (cement and fertilizer manufacturing).

Table 1. Metal content in total sediment and percentages in fractions.

Area A	Pb	Fe	Cu	Zn
Total (µg/g)	56-374	12619-18055	87-270	720-925
E (%)	<1	<1	12-33	6-20
C (%)	0-7	<1	1-4	0-4
Red (%)	18-44	9-15	1-4	12-22
Ox+Sul (%)	5-20	17-24	38-58	3-10
Res (%)	35-70	64-74	24-44	45-74
Area B				
Total (µg/g)	217-464	14175-20541	173-305	700-1090
E (%)	0-1	<1	17-25	9-16
C (%)	1-3	<1	1-3	1-4
Red (%)	13-48	9-15	0-3	10-20
Ox+Sul (%)	4-17	17-34	43-59	4-10
Res (%)	33-81	56-70	19-34	53-75
Area C				
Total (µg/g)	449-749	24869-64429	291-867	1059-2403
E (%)	0-1	<1	15-23	10-14
C (%)	1-5	<1	1-5	2-4
Red (%)	24-39	8-12	0-3	13-20
Ox+Sul (%)	11-20	8-26	49-65	6-10
Res (%)	39-63	62-84	15-25	56-66
Area d				
Total (µg/g)	279-390	11600-20250	160-408	1200-1605
E (%)	<1	0-1	15-25	6-18
C (%)	1-3	<1	1-2	1-4
Red (%)	18-42	14-18	0-3	11-31
Ox+Sul (%)	9-42	19-40	50-72	5-14
Res %	25-72	46-64	12-22	39-73

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