

Adsorption of Cadmium and Lead Ions on Calcite in Estuarine Waters and Seawater

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According to classification of Whitfield and Turner (1987), toxic cadmium shows deep-sea profiles characteristic of the recycled elements. It is held in the organic matrix via sulfur bonds. Price and Morel (1990) reported cadmium substitution for zinc in the marine diatom *Thalassiosira weissflogii* and have attempted to explain cadmium surface depletion relative to deep waters.

Regarding inorganic particles, we have shown that cadmium had very poor affinity for SiO_2 , Al_2O_3 (Bilinski et al., 1976), for MnO_2 (Bilinski et al., 1977), for bentonite and kaolinite (Bilinski et al., 1990a). Cadmium could be adsorbed on synthesized northpite (Vancina et al., 1986) and on calcite (Bilinski et al., 1990b).

In the present work the primary interest is on the simultaneous interaction of cadmium and lead ions with calcite, which mineral is present in surface sediments in the Krka River Estuary.

Cadmium and lead ions were added to natural water samples in low concentrations (8×10^{-8} M) to have solutions undersaturated with respect to $\text{CaCO}_3(\text{s})$ and $\text{PbCO}_3(\text{s})$. Adsorption isotherms of simultaneously and individually adsorbed cadmium and lead ions show that the two ions do not compete for the same surface sites. This fact can be explained comparing ionic radii and crystallographic space groups of corresponding metal carbonates. So, Ca^{2+} and Cd^{2+} have similar and Pb^{2+} has greater ionic radius ($r(\text{Ca}^{2+}) = 0.99 \text{ \AA}$; $r(\text{Cd}^{2+}) = 0.97 \text{ \AA}$; $r(\text{Pb}^{2+}) = 1.20 \text{ \AA}$). Calcium and cadmium carbonates crystallize in R3C space group, and show similar parameters of the unit cell (ASTM, 8-456 and 5-586) while lead carbonate crystallizes in Pmcn group (ASTM, 5-417). Behaviour of cadmium can be directly compared with one observed for zinc by Zachara et al. (1988). Zinc carbonate also shows R3C space group (ASTM, 8-449). Analogously to zinc ion, cadmium can exchange with calcium ion, present at the surface layer of calcite. As Ca^{2+} and CO_3^{2-} species have been identified as the only major surface ions on calcite (Thompson et al., 1989), it can be concluded that lead ion adsorbs via surface CO_3^{2-} group.

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Fate of Trace Elements (Co, Sb, Zn) Entering Saronikos Gulf, Greece

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INTRODUCTION

Saronikos Gulf receiving the industrial and domestic wastes of the greater Athens area is among the most polluted gulfs of Greece. In order to study the fates and pathways of trace elements in Saronikos Gulf, several sampling cruises were organised and a big number of seawater and sediment core samples were collected from several stations (See Fig. 1). The trace element content of the samples was determined by Instrumental Neutron Activation Analysis. The results obtained for three selected trace metals namely cobalt, antimony and zinc, are presented and discussed.

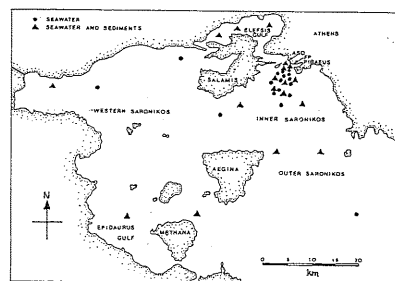


Figure 1. Sampling Stations

DISCUSSION

The main pollution sources of the trace elements studied are the Athens Sewage Outfall (ASO) and a big Fertiliser Plant (FP) at the entrance of Piraeus Harbour where the highest concentrations of Co, Sb and Zn in seawater and sediments were observed (See Tab. 1 and 2).

The settling of particles and flocs in the area of the outfall is very effective in removing the bulk of these trace elements from the water column, since their concentrations decrease with distance from the sources to reach those of unpolluted coastal regions at a distance of 5-7 Km. The rapid sedimentation was confirmed by the analysis of particulate matter which revealed that with the exception of the area close to the point sources where 15-25% of total Co, Sb and Zn were found to be associated with particulate matter, the bulk of the elements in seawater were in dissolved forms which constituted 95-99% of their total concentrations in the rest of the stations.

The concentrations of Co and Sb in seawater and sediments of Inner Saronikos were almost equal to those of the Open Saronikos, while the respective Zn levels were higher in the Inner Gulf. In the water column the higher concentrations were observed in summer samples. The following can be considered as typical concentrations for the waters of open Saronikos: Co: $0.090 \pm 0.014 \mu\text{g/l}$, Sb: $0.23 \pm 0.11 \mu\text{g/l}$ and Zn: $4.8 \pm 3.0 \mu\text{g/l}$. For the open Saronikos sediments the respective values are: Co: $9.2 \pm 0.41 \mu\text{g/g}$, Sb: $0.43 \pm 0.13 \mu\text{g/g}$ and Zn: $83 \pm 5.8 \mu\text{g/g}$.

A distinction among the point sources was possible by means of sediment treatment with 0.5N HCl, which extracts the "anthropogenic" fraction of trace elements (Agemian and Chau, 1976). It was found that 40-60% of total Zn and Co were in extractable form in the sewage outfall cores, while in sediments affected by the fertiliser plant solid wastes (gypsum, pyrites, phosphorites etc) this fraction was much lower, ranging from 6-18%.

A correlation study among several trace elements and organic carbon in the "anthropogenic" fraction of the sediments revealed that the easily dissolved iron forms and the organic matter on recent particle coatings affect the distribution of Co, Sb and Zn in the Saronikos sediments. Furthermore, concerning the distribution patterns of trace elements in polluted and not polluted samples, it was documented that Zn and Co in Saronikos Gulf behave in a similar manner with other trace elements of anthropogenic origin like Ag, Cr, V (Kalogeropoulos et al., 1989), while Sb together with As consist a distinct group mainly as a result of their distribution in the polluted samples (Grimanis et al., 1984; 1988).

TABLE 1. Cobalt, antimony and zinc in seawater ($\mu\text{g/l}$). Average values are given in parentheses.

AREA	COBALT	ANTIMONY	ZINC	AREA	COBALT	ANTIMONY	ZINC
ASO, FP	0.12-0.60 (0.22)	0.60-1.40 (1.0)	9.0-41 (19)	Fertiliser Plant	35-87 (54)	14-100 (60)	840-2100 (1520)
Inner Saronikos	0.03-0.18 (0.10)	0.16-0.55 (0.29)	0.5-19 (10)	Sewage Outfall	13-24 (18)	6.6-32 (16)	220-620 (430)
Outer Saronikos	0.03-0.16 (0.09)	0.11-0.31 (0.23)	0.5-14 (4.8)	Inner Saronikos	8.6-9.6 (8.0)	0.48-0.72 (0.57)	81-110 (91)
				Outer Saronikos	7.8-10 (9.2)	0.31-0.60 (0.43)	60-100 (83)

TABLE 2. Cobalt, antimony and zinc in silt-clay fraction of sediments ($\mu\text{g/g}$). Average values are given in parentheses.

AREA	COBALT	ANTIMONY	ZINC
ASO, FP	0.12-0.60 (0.22)	0.60-1.40 (1.0)	9.0-41 (19)
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