

Heavy metal distribution in the different sediment fractions in the Estuaries of Axios River in Northern Greece

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Introduction

A five-step sequential extraction technique was used to determine the chemical association of heavy metals, (Pb, Cd, Cu, Fe, Mn, Zn, Cr) with major sedimentary phases (exchangeable cations, easily reducible compounds, organic sulfidic phases, carbonates and residual components) in samples from the estuaries of Axios River in Northern Greece. (1,2). For the determination of the heavy metals which were associated (chelated or adsorbed) with humic and fulvic acids the sediments were treated with 0,1 N NaOH for 10 hours. An easy and fast extraction method using 0,5 N HCl has also been used for the evaluation of the pollution level of the examined area. This extraction removes mainly the "anthropogenic" trace element fraction from the sediment. The concentration of the metals in each phase was determined by AAS.

Results and Discussion

Analytical data concerning the metal distribution in the different fractions for the 3 seasonal samplings during the period of March 1987-October 1987 are given in table 1. The mean values are given by the ratio of the extracted amount to the amount of metals in percentages. In most cases, the sum of the sequential extractions of trace elements was satisfactorily close (10%) to the "total" metal concentrations.

The main conclusions which can be drawn from the chemical fractionation of sediments are the following:

The cation exchangeable fraction which represents the elements adsorbed on the sediments, was comparatively limited except for that of Cd. Hydrous Mn and Fe oxides in sediments are generally strong scavenging agents for heavy metal ions. The H₂O₂ treatment should remove mainly sulfides and organic matter and have only a minor effect on the silicate lattice. The residual solid contain mainly primary and secondary minerals which hold trace metals within their crystal structure.

The various fractions very generally from higher to lower metal concentrations in the following order:

Residual fraction organic fraction easily reducible fraction carbonates fraction cation exchangeable fraction.

The anthropogenic heavy metals in sediments follow the order: Fe Mn Pb Zn Cu Cr Cd.

From the obtained data it can be suggested that the surplus of metal contaminants introduced into the aquatic system from anthropogenic sources usually exists in relatively unstable chemical forms. (3)

The higher proportions of the examined elements are found to remain in the residual fraction. Most of the non-residual portion of them is bound to the ferromanganese oxides and to the organic matter.

Table 1 Heavy metal distribution in the different sediment fractions in St.1 (µg/g)(estuaries)

Fraction	Zn				Cr				Cu				Cd											
	2	3	4	2	3	4	2	3	4	2	3	4	2	3	4									
Cation exchangeable	1,50	1,40	2,60	0,07	0,30	0,16	0,22	0,97	0,44	0,14	0,19	0,08	14,4	17,20	17,4	0,70	3,31	0,98	0,27	3,73	1,95	1,5	2,47	2,72
Carbonates	34,7	16,90	20,6	17,65	4,97	2,20	1,58	0,24	2,0	3,67	0,25	0,11	38,1	44,7	46,1	55,3	42,5	15,1	23,16	24,53	14,74	2,0	0,21	0,10
Fe-Mn Hydrous oxides	45,5	52,86	63,40	61,2	14,8	16,5	21,26	17,07	11,37	2,33	4,04	4,48	147,7	146,8	163,5	150,4	64,3	37,3	50,25	53,6	35,81	8,4	7,1	6,7
Organic-sulfides	60,5	49,7	62,75	32,4	7,93	10,3	25,26	17,67	15,0	7,71	4,0	5,0	10,26	7,86	16,4	1,03	1,3	6,62	1,79	6,37	7,61	0,34	0,32	0,49
Residual																								
Total																								
Anthropogenic																								
Humic-fulvic acids																								

2 Spring 1987, 3 Summer 1987, 4 Autumn 1987

Literature

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Trace metals in the sediments of the Acheloos Estuary I. General Trends

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Acheloos is one of the major rivers of Greece with mean average flow estimated to 167 m³d⁻¹ (Scoullios 1982). Major changes in it affect the overall "structure" of its estuary and consequently the distributions of salinity, nutrients and trace metals in the entire NW section of the Patraikos Gulf and part of the Ionian Sea. It might also affect the productivity of the wellknown traditional fishfarms of the nearby Messolongi lagoon.

The ongoing works and the announced new gigantic projects for deviation of the major part of the Acheloos waters to Thessaly, in order to irrigate farming lands, construct hydroelectric power plants and finally discharge to the Aegean Sea, raise a series of serious environmental questions and urgently calls for in depth study and understanding of the present function and distribution of the Acheloos estuary system, since its structure might be altered drastically in the course of the coming years.

Acheloos acts as a major source of inorganic nitrogen for the Patraikos Gulf (Scoullios et al 1985) due partly to the washout of fertilizers and runoff. However, in general it is not among the polluted rivers since it does not pass through heavily industrialised areas.

In the present work which is part of a project carried out since 1982 we present the overall distribution patterns of various metals and we attempt to establish simplified trends and identify correlations between trace metals and major constituents of the sediments.

A series of minicores (1m in length) have been collected from 14 stations from the estuary of the Acheloos river using a Mackereth (1969) pneumatic corer and Perspex tubes. The sediments were analysed for carbonates, organic carbon and a series of trace metals extracted (a) by 0.5N HCl and (b) by conc. HNO₃ from fractions with grain sizes smaller and greater than 61µm.

Acheloos is silled with a mouth bar. Its relatively narrow mixing zone having significant salinity gradients (‰.38 - 1‰) has a total width of a few kilometers upstream as well as outside the mouth. An accumulation of carbonates in the bottom sediments was observed throughout this zone. However, this was not the case for a distinct small strip of the river bed located at the shallowest part of the bar where carbonate concentration in the fine sediment is extremely low and the aluminum one is particularly high.

The carbonate concentration in the sediments decreases in the upstream "riverine" stations as well as in the offshore "marine" ones. Aluminum shows, in general, the reverse trend.

From the results became clear that most of the metals show their peak concentrations (see Table I) in two sites. The most prominent one is located outside the river mouth, in fact in the area where salinity usually exceeds 25 ‰, and the dynamic energy of the particles decreases abruptly following a steep increase of the depth of the sea bottom.

TABLE I: MINIMUM AND MAXIMUM CONCENTRATIONS OF TRACE METALS IN THE ACHELOS RIVER ESTUARY.

Metal	extracted with HCl(ppm)		extracted with HNO ₃ (ppm)	
	min	max	min	max
Al	400	3000	4500	39600
Cd	0.10	0.25	0.10	0.25
Cr	2.30	10.0	23.6	130
Cu	3.70	29.5	7.00	38.4
Fe	800	6600	2400	22700
Mn	300	740	400	890
Ni	17.1	50.2	26.4	180
Pb	2.5	14.4	3.7	15.1
Zn	7.2	34.9	24.8	82.9

The other zone of relatively high metal concentration is located upstream, right before the river mouth bar. There, the metals seem to be deposited mainly as a result of the abrupt increase of the pH. In fact the pattern of each metal is differentiated according to its major species present and its response to desorption, coagulation and precipitation processes.

Trying to establish simplified correlations for the interpretation of a large series of data we have identified, in a first approximation, two groups of trace metals: The first, and most numerous one (Cu, Pb, Cr, Zn, Fe, Ni) shows a negative correlation with carbonates and a positive one with Al, at least in the surface sediments. Scoullios and Oldfield (1986) have identified the ability of fine "clay" particles to act as major metal carriers in the system. The correlation is extended to the entire sediment column for few metals such as copper. It is noteworthy that throughout a long series of samplings of suspended particles from the Acheloos estuary we have established excellent correlations between aluminum and various metals (e.g. iron) in the suspended matter which is reflected also in the sediments.

The second group has metal concentrations following the trend of carbonates. Mainly manganese follows this pattern and in a lesser extent cadmium. These two elements are also the ones more effectively extracted by HCl (having the highest M_{HCl}/M_{HNO₃} ratios). Several metals slightly deviate from the above described trends and their distribution seems to be largely influenced by the organic carbon content of the sediments. Using "surface enrichment factors":

$$K_{en} = \frac{(C_w/Al_w - C_r/Al_r)}{(C_w/Al_w)} \quad \text{where } C_w = \text{the measured surface concentration} \\ C_r = \text{the reference concentration at a given depth of the sediment column}$$

Al_w and Al_r the relevant Al concentrations, it appears that lead, zinc and nickel are the elements which have been affected more obviously by anthropogenic inputs.

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