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An environmental quality approach of the sediments of Maliakos gulf (Central Greece) based on heavy metal levels

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Abstract

Heavy metal concentrations were determined in the <2μm fraction of surface sediments of Maliakos gulf (central Greece). In order to assess the pollution degree of the area, the *Igeo Index* of the sediments was calculated and the samples were classified in *Igeo Classes*. According to these classes Maliakos gulf is characterised as "practically unpolluted" area in heavy metals, with the exception of Cu, Pb and Co, due to anthropogenic activities and Ni due to terrestrial natural processes.

1 Introduction

Maliakos Gulf is a semienclosed area in central Greece (Figure 1) into which flows Sperchios river, carrying a large amount of fresh water and suspended load. Maliakos is a rather shalow gulf, with a maximum depth of 27 m in the inner part, while the depth of the outer part does not exceed the 60 m. A number of pollutants reach the gulf via the hydrographic network, the drainage channels as well as the overflow ones. These pollutants could be attributed to the economic activities taking place within the greater catchment area (agricultural, handicraft and industrial activities).

The aim of the present study is to investigate the fate and the distribution of heavy metals in the sediments of Maliakos gulf. These sediments are characterised as mud with a very low proportion of sand. The more important heavy metals, such as Zn, Cu, Ni, Co, Pb, Mn, Fe and Al, were determined in the surface sediments of the inner and the outer Maliakos gulf.

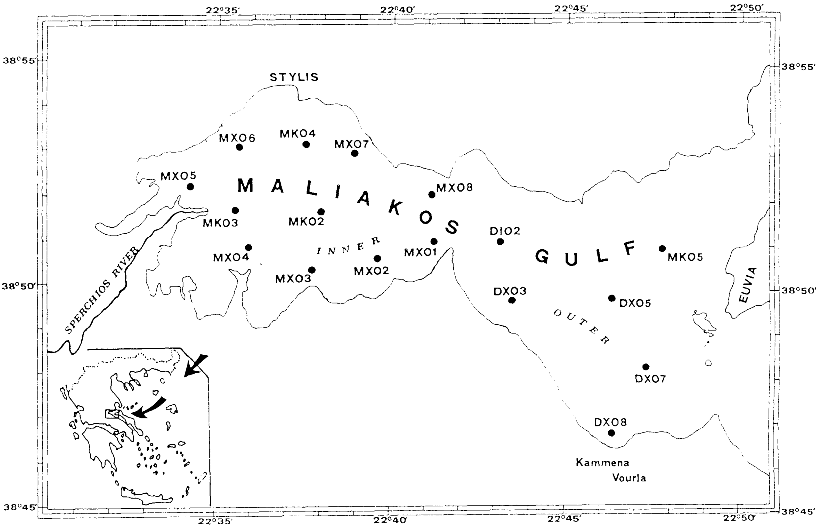

Figure 1. Geographical location of Maliakos gulf and the position of the sampling stations.

In addition, a methodological approach of the environmental quality of the sediments was made on the basis of geochemical data. For this purpose, heavy metal concentrations were determined on the <2μm clay fraction of the sediments and then the geoaccumulation index (*Igeo Index*) was calculated, as the ratio of the metal concentration to the geochemical background. Using this index it was possible to map the whole area of Maliakos gulf and discriminate various sub-areas according to their pollution intensity.

Dissolved and particulate heavy metals have been determined in the area of Maliakos gulf by Nacopoulou [1] and Nikitopoulos [2], and their levels were found comparable with those of other Greek areas.

2 Materials and Methods.

Sampling was undertaken on a cruise of the oceanographic vessel AEGAEO. Surface sediment samples were collected at stations shown in Figure 1. The position and the depth of the stations are presented below:

Station	Depth (m)	Coordinates LON	Coordinates LAT	Station	Depth (m)	Coordinates LON	Coordinates LAT
MX-01	17	38°51,3'	22°41,0'	MK-03	18	38°52,0'	22°35,5'
MX-02	13	38°51,0'	22°40,0'	MK-04	19	38°53,0'	22°37,5'
MX-03	14	38°50,7'	22°37,6'	MK-05	39	38°47,0'	22°46,5'
MX-04	18	38°51,3'	22°35,6'	DX-03	21	38°50,2'	22°43,5'
MX-05	12	38°52,5'	22°34,3'	DX-05	37	38°50,0'	22°46,0'
MX-06	15	38°53,1'	22°35,5'	DX-07	49	38°48,6'	22°47,6'
MX-07	15	38°53,0'	22°39,2'	DX-08	30	38°47,5'	22°46,2'
MX-08	17	38°52,3'	22°41,0'	DI-02	20	38°51,5'	22°43,1'
MK-02	22	38°52,0'	22°37,5'				

Sediment sampling was carried out using a McIntyre sampler. For the heavy metal determination, the <2μm sediment fraction was mechanically seperated by settling.

The <2 μm fraction was selected for:

-- comparability purposes of the results since in this way the impact of the grain size dissimilarity of the sediment samples is diminished,

-- the calculation of the geoaccumulation index, which is necessary for the estimation of the heavy metal pollution degree of the sediments [3].

For the determination of the metals Zn, Cu, Ni, Co, Pb, Mn, Fe and Al, sediment samples were digested with concentrated nitric acid, hydrofluoric acid, royal water (a 1:3 mixture of nitric and hydrochloric acid) and perchloric acid at 160°C, and finally diluted with metal free distilled water. Metal concentrations of solutions were measured by employing Atomic Absorption Spectrometry using a Varian SpectrAA 300 model, with flame for Zn, Cu, Ni, Co, Mn, Fe and Al, and with graphite furnace for the Pb. The final metal concentrations were corrected in relation to a standard sediment sample (SD-M-2/TM IAEA - MONACO, No 182).

For a better assessment of the results, a geoaccumulation index (*Igeo Index*) [4] was calculated. This index is a comparison guideline of the heavy metal concentrations in sediments and is calculated using the formula:

$$I\ geo = \log_2 \frac{Cn}{Bn * 1,5}$$

where: I geo = the geoaccumulation index, Cn = the metal concentration in the <2μm sediment fraction and Bn = is the geochemical background metal concenration in fossil argillaceous sediment ("average shale"); factor 1,5 is used because of possible variations of the background data due to lithogenic effects.

Based on the values of the geoaccumulation index, samples are ranked in classes (0 to 6) that show the degree of metal contamination of the sediments, according to the following:

Igeo Index	Igeo Class	Pollution degree
<0	0	practically unpolluted area
0-1	1	unpolluted to moderately polluted
1-2	2	moderately polluted
2-3	3	moderately to strongly polluted
3-4	4	strongly polluted
4-5	5	strong to very strong pollution
>5	6	very strong pollution

3 Results and Discussion

Heavy metal concentrations of the <2μm sediment fraction and the *Igeo classes* are presented in Table 1. The percentage of this grain size fraction to the total sediment is shown in the same table as well. In this sediment fraction a fluctuation from 26.6% to 38.4% is observed, with the exception of DX-07 sample with a percentage of 7.0%. By reducing the metal concentration to the percentage of the <2μm fraction of the sediment, the % metal concentration of this fraction is calculated in relation to the total metal concentration as it is determined in the <63μm sediment fraction (unpublished data). The range of the percentage of each metal concentrated in the <2μm grain size fraction, reduced to the total sediment, for the whole area of Maliakos gulf, is shown below:

Zn	24 - 47%	**Fe**	23 - 48%
Cu	23 - 49%	**Mn**	16 - 35%
Ni	21 - 51%	**Al**	22 - 46%
Co	27 - 65%		

Table 1. Heavy metal concentrations of the <2μm fraction of sediments in Maliakos gulf and the corresponding *Igeo classes*.

Station	Depth (m)	Zn		Cu		Ni		Co		Pb		Mn		Fe		Al		Fraction <2μm % of the total
		$\mu g g^{-1}$	Igeo class	$\mu g g^{-1}$	Igeo class	$\mu g g^{-1}$	Igeo class	$\mu g g^{-1}$	Igeo class	$\mu g g^{-1}$	Igeo class	$\mu g g^{-1}$	Igeo class	%	Igeo class	%	Igeo class	
INNER MALIAKOS GULF																		
MX-01	17	87	0	42	0	215	2	28	1	24	0	858	0	4,58	0	5,85	0	38,4
MX-02	13	97	0	41	0	221	2	27	0	18	0	728	0	5,12	0	6,18	0	32,1
MX-03	14	105	0	47	0	229	2	30	1	37	1	846	0	5,84	0	7,22	0	36,2
MX-04	18	93	0	41	0	191	1	24	0	16	0	685	0	4,74	0	5,87	0	34,4
MX-05	12	105	0	67	1	172	1	28	1	30	1	721	0	5,88	0	7,27	0	33,8
MX-06	15	95	0	43	0	185	1	26	0	26	0	1013	0	5,20	0	6,54	0	33,5
MX-07	15	88	0	39	0	210	2	27	0	20	0	708	0	4,67	0	5,62	0	32,9
MX-08	17	92	0	43	0	240	2	29	1	27	0	771	0	5,03	0	6,00	0	28,0
MK-02	22	89	0	40	0	170	1	24	0	14	0	914	0	4,48	0	5,80	0	33,6
MK-03	18	90	0	43	0	173	1	23	0	24	0	924	0	4,97	0	6,04	0	38,1
MK-04	19	99	0	39	0	169	1	24	0	24	0	776	0	4,51	0	5,63	0	28,4
OUTER MALIAKOS GULF																		
MK-05	39	75	0	30	0	258	2	27	0	21	0	611	0	3,99	0	4,39	0	31,1
DX-03	21	77	0	34	0	265	2	29	1	21	0	641	0	4,42	0	4,72	0	29,7
DX-05	37	89	0	38	0	320	2	33	1	26	0	759	0	4,69	0	5,23	0	30,1
DX-07	49	92	0	32	0	277	2	30	1	17	0	943	0	4,01	0	4,45	0	7,0
DX-08	30	83	0	35	0	331	2	30	1	36	1	619	0	4,49	0	4,88	0	30,6
DI-02	20	80	0	37	0	231	2	27	0	20	0	787	0	4,44	0	5,14	0	26,6

These fluctuations show clearly that the <2μm grain size fraction of the sediments plays an important role as a carrier of heavy metals in the marine ecosystem.

Zinc concentrations range from 75 to 105 μg g^{-1}. According to Table 1, all the samples are classified to *Igeo class* 0, which means that both parts, the inner and the outer, of the Maliakos gulf are characterised as "practically unpolluted" area.

Copper concentrations range from 30 to 67 μg g^{-1}. As it is shown in Table 1, all sediment samples are classified according to *Igeo Index* in the *Igeo class* 0, with the exception of sample MX-05 which is ranked in *class* 1. As a result, the whole area of Maliakos gulf is characterised as "practically unpolluted", except the western part of the inner gulf which is characterised as "unpolluted to moderately polluted". The increased Cu concentration in this specific station is attributed to the industrial discharges deriving from a nearby cable industry.

Nickel concentrations in the inner part of Maliakos gulf range from 169 to 240 μg g^{-1}, while in the outer part of the gulf are increased ranging from 231 to 331 μg g^{-1}. According to the *Igeo Index*, the samples are grouped in two categories; that of the outer part as well as the south-eastern part of the inner Maliakos gulf, which are characterised as "moderately polluted" areas (*Igeo class* 2), and that of the rest of the inner gulf which is characterised as "unpolluted to mederately polluted" area (*Igeo class* 1).

Map in Figure 2 illustrates the geographical distribution of the Ni *Igeo classes* of sediments in Maliakos gulf. It seems that this geographical Ni distribution is related to the alluvial fun formation that constitutes also the cape of Chiliomili and is supplied with suspended load by the ephemeral streams.

The increased Ni concentrations cannot be attributed to human activities, since there isn't any installation known in this particular area which could supply the marine environment with discharges enriched in Ni. On the contrary, they could be attributed to natural causes, and particularly to the existence of ophiolite formations in the southern area of Kammena Vourla and whithin the catchment area. The weathering products of the ophiolites reach the marine coastal area enriching the sediments in Ni.

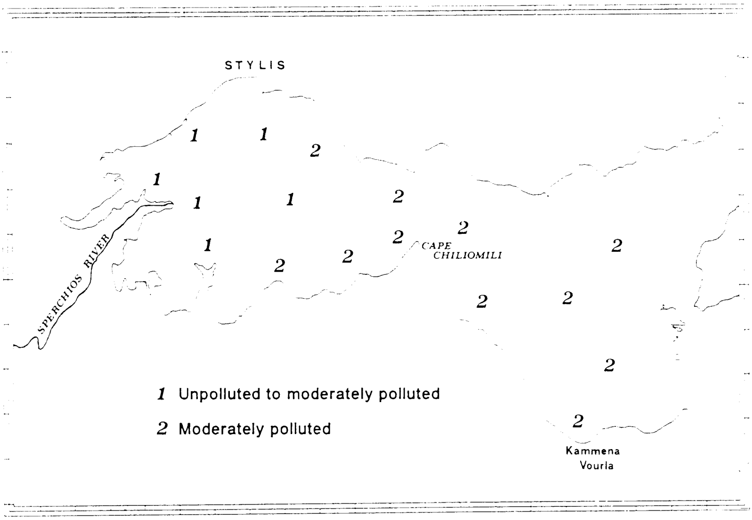

Figure 2. Geographical distribution of the Ni *Igeo classes* of sediments.

Cobalt concentrations range from 23 to 33 µg g^{-1}, and thus according to the *Igeo class* of the sediment samples, the south-western part of the inner Maliakos gulf as well as its outer part are characterised as "unpolluted to mederately polluted" area. The rest of the inner gulf is characterised as "practically unpolluted" area, with the exception of MX-05 station in the western part of the inner gulf which is characterised as "unpolluted to moderately polluted" due to anthropogenic sources of pollution.

As it is shown in Table 1, **lead** concentrations range from 14 to 37 µg g^{-1}. According to the *Igeo Index* of the sediment samples, the whole area of Maliakos gulf could be characterised as a "practically unpolluted" area, with the exception of three specific stations, MX-03, MX-05 and DX-08. These stations are classified in *Igeo class* 1, characterising the corresponding areas as "unpolluted to moderately polluted". Station MX-05 is affected by anthropogenic activities, as it was mentioned above for Cu and Co, while the pollution in Pb of the two other stations could also be the probable result of the human impact in the areas.

Manganese concentrations range from 611 to 1013 µg g^{-1}, **iron** concentrations range from 3,99% to 5,88% and **aluminium** from 4,39% to 7,27% (1% corresponding to 10000 µg g^{-1}). All these metal concentrations are similar to natural levels, and according to the *Igeo Index* of the sediments, samples are classified in *Igeo class* 0. Thus the whole area of Maliakos gulf is characterised as "practically unpolluted" in Mn, Fe and Al.

4 Conclusions

Heavy metals were determined in surface sediments as indices of the pollution degree of Maliakos gulf. Metal concentrations in the <2 μm sediment fraction were found to be of natural levels in the inner as well as in the outer part of the gulf, with the exception of the increased Ni concentrations in the outer gulf which are attributed to natural causes. By calculating the *Igeo Index* of the samples, it became also obvious that, in comparison with the metal concentrations of sediments before the impact of human activities in the environment, Maliakos gulf is characterised as "practically unpolluted" area. Nevertheless, there are some exceptions of "moderate pollution" in Cu, Pb and Co due to anthropogenic discharges into the marine environment. As far as Ni is concerned, Maliakos gulf could be characterised as "moderately polluted" area because of terrestrial natural processes.

It is known that Maliakos gulf receives a great amount of industrial and agricultural pollutants. However, these pollutants do not contribute substantially to the pollution levels of the sediments, as it was shown by the *Igeo classes*, due to the high sedimentation rates within the whole area of Maliakos gulf [5].

5 References

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