Cadium, Chromium, Lead and Manganese content in sediment of the Gruz Bay

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The determination of the metal content in sediment of a particular environment is essential for the assessment of its pollution levels. Vertical distribution of metals in sediment, if appropriately determined, may provide historical background of pollution.

The Gruz Bay is situated in the eastern part of the southern Adriatic (near the town of Dubrovnik) (Fig. 1). The area has its special features due to its geomorphological, hydrographic, chemical and biological properties which distinguish it from the similar bays on the eastern Adriatic coast.

This peculiarity is due to a variety of factors of which river Rijeka Dubrovacka freshwater input and strong influence of the open sea are most important. The major contributors to this area are industrial waste waters and smaller amounts of domestic sewage and precipitation run-off. Sediment of the Gruz Bay is formed of two layers. The upper layer (mud) contains very high quantitites of organic matter, its thickness ranging from 0.5 to 5 m. The other layer is formed of clay with fragments of lime-stone. Sediment samples were collected from seven stations (depth range 5-40 m). Five-cm fragments of 54 to 300 μm fraction were analyzed for metal content and percentage of organic substance.

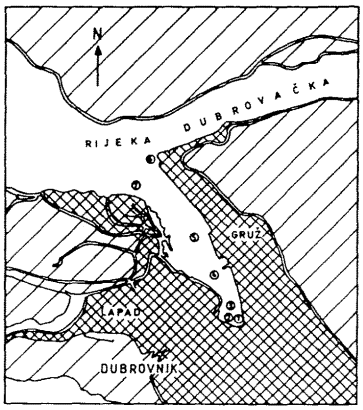

Fig. 1. Study area with station positions

Electrochemical atomic absorption spectrometry was used for Cd, Pb, Cr and Mn determination on Perkin-Elmer atomic absorption spectrophotometer, Model 1100B, with a HGA-700, graphite furnace and AS-70 autosampler system.

Organic matter content was very high, ranging from 8 to 28%, in all parts of the bay. The highest level was recorded from the bottom of the bay in the vicinity of municipal and industrial sewage outfalls. This level was reduced going towards the centre of the bay.

Spatial distribution of cadmium (0.02-3.43 μg g^{-1} DW) and lead (6.98-357.42 μg g^{-1} DW) significantly varied. Like for the organic matter, the highest quantities were recorded from the inner part of the bay, at stations 1, 2 and 3 (Fig. 2). This is quite normal since that area is strongly affected by municipal and industrial waste loads. At the same time manganese content (6.98-357.42 μg g^{-1} DW) is higher towards the bay outlet which is indicative of the fact that pollution loads there largely derive from the river Rijeka Dubrovacka inputs (Fig. 2). Chromium content (95.14-273.99 μg g^{-1} DW) is highest in the central part of the bay (Fig. 2). Even though this may be due to the vicinity of the town port, presumably chromium here is of terrigeneous origin.

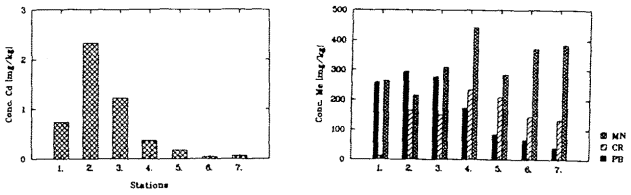

Fig. 2. Mean metal concentrations

Since the effects of organic matter on metal contents has been proved, the relationship between organic matter content and individual metals has been determined.

Table 1. Relationship between metal concentration and organic matter content expressed by linear equation: **metal conc. = a + b x org.matter(%)** (**r** is the correlation coefficient, **P** significance of correlation).

Metal	a	b	r	P
Cadmium (Cd)	-0.592	0.090	0.536	0.005
Lead (Pb)	55.604	7.930	0.417	0.034
Chromium (Cr)	218.148	-3.508	-0.325	0.105
Manganese (Mn)	452.371	-8.055	-0.494	0.010

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The significance of outlying P-PO_4 values in eutrophication studies

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The existence of "extreme", "doughtful" or "anomalous" values in collected data of nutrients from the natural environment have been characterized as "outliers" or outlying values (BARNETT and LEWIS, 1987). Outliers are often seen as reducing and distorting the information provided by the data and in this case they might be removed (EVERITT,1981). On the other hand, outliers might characterize extreme conditions of an ecosystem associated with pollution problems and thus, their presence should be taken into account in any statistical analysis concerning eutrophication assessment and coastal management.

In the present investigation outliers in nutrient (P-PO_4) data sets were identified and their spatial and temporal distribution was examined. Sampling was carried out monthly from 9 stations of Saronikos Gulf, Aegean Sea during 1981 (Fig.1, A). The net of these stations covered an area characterized by strong nutrient gradients (KARYDIS *et al.*, 1983) due to the influence of the sewage outfall. Outliers in the P-PO_4 data sets were detected by the method of "Box and Whisker Plot" described by TUKEY (1977) and OTT (1988). Data points lying outside 1.5 times the interquartile range of the upper quartile were recorded as outliers.

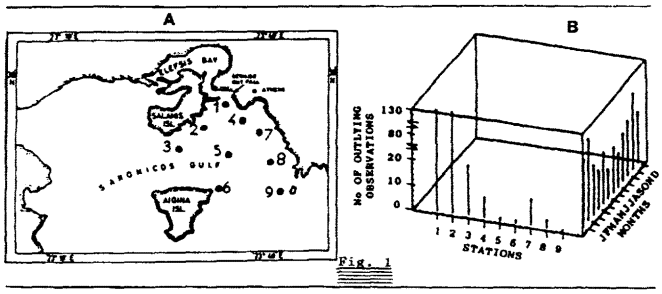

Fig. 1

Table 1. Distribution characteristics of the raw P-PO_4 data sets.

Data set	N	x	s	range
A. Before the exclusion of outliers	942	0.34	0.67	0.01-13.72
B. After the exclusion of outliers	697	0.12	0.08	0.01- 0.33
C. Outlier's set	245	0.96	1.10	0.34-13.72

The results on the distribution characteristics of the parent data sets of P-PO_4 are given in Table 1. It is seen that the original number of the raw data (N=942) was reduced (N=697) after the exclusion of outliers (N=245). The raw data and the outliers were further classified per station in an attempt to evaluate the contribution of each station in the entire set of values before and after the exclusion of outliers. The results showed (Table 2) a well defined gradient in the distribution of the number of outliers and their mean values which seems to be related with the vicinity of the corresponding stations to the sewage outfall. For example, the highest scores of outling values (129) and their mean (1.29 μg-at $P.l^{-1}$) were recorded at station S1 which was located near the sewage outfall and has been characterised as strongly eutrophic (IGNATIADES *et al.*, in press) and they diminished gradually along with the distance of each station from it. Also, at station S1, the outlying values comprised the 75% of the total recorded observations from this station whereas this percentage diminished again along with the distance of each station from the sewage outfall. A graphical presentation of the distribution of outliers at the 9 stations is given in Fig. 1B, along with their seasonal distribution. It is seen that seasonality might also play an important role in contributing outlying values in the P-PO_4 annual data.

Table 2. Summary statistics of the raw and outlying values of P-PO_4 data sets per station.(N=total No of observ.,x=means, s=stand.dev.)

	Raw data (r)			Outliers (o)			% Outliers over Raw data	
	N(r)	x(r)	s(o)	N(o)	x(o)	s(o)	N(%)	x(%)
S1	173	1.00	1.29	129	1.29	1.38	75	77
S2	174	0.35	0.30	74	0.60	0.31	43	58
S3	174	0.18	0.20	19	0.54	0.41	11	33
S4	72	0.17	0.41	8	0.81	1.02	11	21
S5	71	0.12	0.09	1	0.41	-	1	29
S6	72	0.10	0.07	1	0.40	-	1	25
S7	68	0.16	0.19	10	0.55	0.21	15	29
S8	69	0.12	0.14	3	0.68	0.22	4	18
S9	69	0.09	0.04	0	-	-	0	27

The results of this work indicate the possibility of using outliers as an index of eutrophication and applying statistical tests among outlying data as a means for detecting differences concerning nutrient loadings in the marine environment.

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