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Occurrence and distribution of selected heavy metals in the surface sediments of Thermaikos Gulf, N. Greece. Assessment using pollution indicators

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ABSTRACT

Forty sediment samples and fifteen water samples were collected from the Gulf of Thermaikos and the Bay of Thessaloniki in order to determine the concentration of Zn, Cu, Pb and Cr and measure various seawater parameters. The level of pollution attributed to heavy metals was evaluated using several pollution indicators in order to determine anthropogenically derived sediment contamination. Enrichment Factors, Contamination Factors, Modified Contamination Degree, and Geoaccumulation Indexes for the sediments were used to assess and visualize using GIS. Association with adverse effects to aquatic organisms was determined, using the classification of the sediments according to the Sediment Quality Guidelines (SQGs). The highest metal levels were concentrated along the shoreline of the Bay of Thessaloniki, reflecting long-term exposure to anthropogenic activities. Enrichment Factors reveal the anthropogenic sources for chromium and lead. This is supported by separate Contamination Factors, the mean Contamination Degree, and the Geoaccumulation Index. The majority of the sediment samples can be occasionally and frequently associated to toxic biological effects, according to the effect-range classification for Zn, Cu and Pb. Based on the analysis of the overlying seawater columns it appears that under the present physicochemical conditions, dissolution of the accumulated metals from the sediments is unlikely. Although the total metal content in the sediments has decreased with time, the long-term effect of the industrial and urban activities in the area is still reflected in sediments from the gulf.

1. Introduction

The presence of heavy metals in sediments poses a potential threat to the marine ecosystems. Accumulation of heavy metals in sediments, even when present in low concentrations in the overlying water column, is dependant on various factors such as the nature of the sediment particles, the properties of the adsorbed compounds and the prevailing physicochemical conditions. Sediments show a great capacity to accumulate and integrate heavy metals and organic pollutants even from low concentrations in the overlying water column [1–3]. Although most pollutants adsorbed on the sediments are not bioavailable, certain mechanisms may induce the release of pollutants back to the water column. These processes include direct consumption from the benthic fauna, sediment resuspension, desorption, redox reactions or (bio) degradation of the sorptive substance [4–7]. Sediments may act as potential sinks or sources of various contaminants in aquatic systems [8,9] under different environmental conditions. Metal contamination of surficial sediments could directly affect the seawater quality, resulting in potential consequences to the sensitive lowest levels of the food chain and ultimately to human health.

The distribution of metals within the aquatic environments is governed by complex processes of material exchange affected by various anthropogenic activities or natural processes including riverine or atmospheric inputs, coastal and seafloor erosion, biological activities, water drainage, discharge of urban and industrial wastewaters [10,11]. Sources of Zn, Cr and Pb in the environment are mainly from smelting and metallurgical processes, discharge of metal containing waste (tannery processes, industrial effluents), landfill leachates and secondary precipitation of polluted airborne matter [12]. Anthropogenic sources of copper are primarily related to textile production, marine anti-fouling agents, pipes and copper-based fungicides or pesticides [13].

Heavy metals are of critical ecological significance due to their toxicity, resistance to degradation and their consequent tendency to bioaccumulate [14]. Metal toxicity and availability to algae depend on: the concentration of metal ions, pH, redox potential, available inorganic and organic ligands (complexation agents) and the presence of a variety of other compounds that may act antagonistically and could inhibit or reduce the toxic effect of metals, salinity, temperature and microbial mass present [15]. Heavy metals exert their toxicity by competing with essential metals for active enzyme or membrane protein sites and by reacting with biologically active

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Table 1
Metal concentrations in average continental shale µg/g (except Fe which is expressed in %) and in less contaminated sediment.

Metal	Average continental shale[a]	Average of the less contaminated sample
Zn	95	74
Cu	45	19
Cr	90	7
Pb	20	10
Fe (%)	4.7	2.9

[a] [21].

groups, interfering with the photosynthetic processes and affecting the composition of a plankton community [16,17].

1.1. Estimation of pollutant indicators

The anthropogenic contribution of the selected trace elements in marine sediments can be estimated from the metal enrichment relative to unpolluted reference materials or widely accepted background (pre-industrial) levels. Different approaches to determine enrichment have been reported using different rationales to determine the background concentrations to use as a reference value [18–21]. The differences between methods produce different enrichment results, which complicate the interpretation of analytical data.

Various methods have been suggested for quantifying metal enrichment in surface sediments. The central notion is to produce a numerical result comparing the metal content of each sample with a background level, such as the average continental shale [22] or average continental crust abundances [23]. An alternate approach is to use the metal content found in deeper sediment samples as reference backgrounds. The advantage in this case is that their metal content is the product of a long-term sedimentation process and not as likely to be affected by random metal content variations [20]. Pollutant indicators were calculated based on the average shale content and the value of the least contaminated sample (Table 1).

For the calculation of pollutant indicators the following factors have been suggested.

1.1.1. Enrichment Factor (EF)

This method estimates the anthropogenic impact on sediments calculating the EF, which uses a normalization element (Al or Fe) in order to alleviate the variations produced by heterogeneous sediments. The reference element is selected so as to have minimum variability of occurrence or is present in such large concentrations in the studied environment, that neither potential small concentration variations nor other synergistic or antagonistic effects towards the examined elements are significant [20]. Since the sediments from Thermaikos Gulf are rich in iron content, this element was selected to normalize the data as normalization factor.

The EF is calculated using the following equation [20]:

$$\mathrm{EF} = \frac{M_\mathrm{x} \times \mathrm{Fe}_\mathrm{b}}{M_\mathrm{b} \times \mathrm{Fe}_\mathrm{x}}$$

where M_x and M_b are concentrations of examined metal in sample and background reference respectively; Fe_x and Fe_b are concentrations of Fe in sample and background reference respectively.

1.1.2. Degree of Contamination C_d

Introduced by Hakanson [6], this was originally a method to calculate an overall pollution factor, based on seven metals and one organic contaminant. Individual Contamination Factors are calculated based on the following formula:

$$C_\mathrm{f}^i = \frac{M_\mathrm{x}}{M_\mathrm{b}}$$

where M_x is the mean concentration of the target metal in at least five sub-samples and M_b is the concentration of the metal in the selected reference background.

The overall degree of contamination is given by:

$$C_\mathrm{d} = \sum_{i=1}^{8} C_\mathrm{f}^i$$

Since it is not always feasible to analyze all of the components used for this index, a variation of this method was proposed by Abrahim and Parker [20] providing the modified degree of contamination ($\mathrm{m}C_\mathrm{d}$):

$$\mathrm{m}C_\mathrm{d} = \frac{\sum_{i=1}^{n} C_\mathrm{f}^i}{n}$$

which enables the extraction of a final degree of contamination based on the available contaminant determinations.

The classification of the sediments according to the modified degree of contamination is the following:

$\mathrm{m}C_\mathrm{d} < 1.5$	zero to very low degree of contamination
$1.5 < \mathrm{m}C_\mathrm{d} < 2$	low degree of contamination
$2 < \mathrm{m}C_\mathrm{d} < 4$	moderate degree of contamination
$4 < \mathrm{m}C_\mathrm{d} < 8$	high degree of contamination
$8 < \mathrm{m}C_\mathrm{d} < 16$	very high degree of contamination
$16 < \mathrm{m}C_\mathrm{d} < 32$	extremely high degree of contamination
$\mathrm{m}C_\mathrm{d} \geq 32$	ultra high degree of contamination

1.1.3. Geoaccumulation Index (I_{geo})

In order to characterize the level of pollution in each sample point, I_geo values were calculated using the following mathematical formula [24]:

$$I_\mathrm{geo} = \log_2\left(\frac{C_n}{1.5 \times B_n}\right)$$

C_n: measured concentration of the element; B_n: geochemical background concentration of the element for the average continental shale [21]. The 1.5 factor is introduced to include possible variations of the background values due to lithogenic effects.Sediment quality based on the I_geo values [20,24]:

I_geo	Pollution status
>5	*Extremely polluted*
4–5	*Strongly to extremely strongly polluted*
3–4	*Strongly polluted*
2–3	*Moderately to strongly polluted*
1–2	*Moderately polluted*
0–1	*Unpolluted to moderately polluted*
<0	*Unpolluted*

This classification is a methodological approach based on the geochemical data that makes possible to map the study area and discriminate various sub-areas according to their pollution degree. In addition it is possible to obtain a proper comparison between various marine areas in terms of their heavy metal quality.

1.1.4. Sediment Quality Guidelines

Sediments can act as both a source and a sink for potential toxic compounds. In order to predict adverse biological effects in contaminated sediments, numerous Sediment Quality Guidelines (SQGs) have been developed over the past decade [25,26], in order to protect aquatic organisms living in or near the sediments from the toxic effects associated with sediment-bound contaminants. They include sediment quality criteria, sediment quality objectives and sediment quality standards. These guidelines are useful for the evaluation of spatial variations of sediment contamination, the classification of the contamination state of the sediments, the design of

Fig. 1. The Gulf of Thermaikos and the Bay of Thessaloniki (N. Part) with the selected sampling sites.

monitoring programs, interpretation of historical data, and for environmental assessments for future remedial actions etc. [26–29].

SQGs are developed using a variety of approaches, such as effect-range approach, effect-level approach and apparent effect-threshold approach. The selection of the most appropriate SQGs is not trivial; each derived numerical value may differ significantly based on the derivation procedure, the objective of the calculation and the ability of the Guideline to match the selected geological background of the specific area [26]. The most widely used SQGs for marine sediment samples, have been developed by the U.S. National Oceanic and Atmospheric Administration (NOAA) and they include sets of effect-range guidelines derived from a large series of chemical and biological data collected from North American coastal regions that incorporate field and laboratory data from many different methodologies, chemical and biological species [25]. Effect-range SQGs are empirically derived and do not include crucial factors such as bioavailability of the contaminant [25,26].

Chemical concentrations corresponding to the 10th and 50th percentiles of adverse biological effects were called the Effects-range-low (ERL) and Effects-range-median (ERM) respectively. The NOAA guidelines provide two values for each chemical, classifying the sediment either rarely (<ERL), occasionally (≥ERL and <ERM) or frequently associated with adverse biological effects [25,28].

The objectives of this study were: (i) to examine the spatial variations of the heavy metal concentration in the surface sediments regarding the Thermaikos Gulf (N. Greece, Thessaloniki), (ii) to evaluate the metal content using GIS software and to visualize and assess the distribution of the metals, (iii) to use the Geoaccumulation Index (I_{geo}), EF and modified degree of contamination (mC_d), in order to evaluate the level of anthropogenic participation in the pollution caused by heavy metals in the area, (iv) to demonstrate the potential association between the chemical contamination of the sediments and the adverse biological effects to aquatic organisms based on the widely accepted Sediment Quality Guidelines.

2. Materials and methods

2.1. Study area

The area studied is located in the Northwestern part of the Aegean Sea including the Bay and Gulf of Thessaloniki. The Gulf of Thessaloniki extends northerly of the line defined by the outfall of Axios River and Cape Megalo. The surface layer of the gulf sediments are primarily mixtures with low sand content; fine grained in the northern part and clay dominated in the deeper southern parts [30].

The city of Thessaloniki, the second largest metropolitan center of Greece with a population of over 1,000,000 inhabitants located in the northern part of the bay. Various point and non-point sources of contaminants, such as harbor facilities, industrial activities originating from the adjacent industrial zone and partially treated domestic effluents, have generated pollutant loads during the last 30 years, significantly degrading the water and sediment quality [31]. In addition, the gulf receives particulate matter, nutrients and dissolved elemental inputs from two major Rivers (Axios and Aliakmonas) and numerous minor rivers and streams. The intensively cultivated agricultural plains along the north and west coast of the gulf have been reported to introduce elevated amounts of nutrient and organic pollution through agricultural runoff [32,33].

2.2. Sample collection

Forty sediment samples were collected using a zinc-plated Petersen grab (10 cm of surface sediment) and fifteen water sam-

Table 2
Heavy metal content of sediments (μg/g dw, average of replicates), TOC content and calculated factors.

	Metal content (μg/g dw) and organic content (%)						Enrichment Factors based on average shale content				Enrichment Factors based on less contaminated sample				Contamination Factors C_f based on average shale content					Contamination Factors C_f based on less contaminated sample					Geoaccumulation Index			
	Fe %	Zn	Cu	Cr	Pb	TOC %	Zn	Cu	Cr	Pb	Zn	Cu	Cr	Pb	Zn	Cu	Cr	Pb	mC_d	Zn	Cu	Cr	Pb	mC_d	Zn	Cu	Cr	Pb
min	2.9	74	19	7	10	0.23	0.9	0.5	0.1	0.6	0.7	0.8	0.7	0.7	0.8	0.4	0.1	0.5	0.6	1.0	1.0	1.0	1.0	1.6	-0.9	-1.8	-4.3	-1.6
max	4.5	358	165	172	218	3.45	4.4	5.3	2.1	12.5	3.5	7.7	16.2	15.4	3.8	3.7	1.9	10.9	4.1	4.8	8.7	24.6	21.8	10.6	1.3	1.3	0.3	2.9
median	4.0	180	77	26	72	0.94	2.2	2.0	0.3	4.1	1.7	2.9	2.7	5.1	1.9	1.7	0.3	3.6	2.2	2.4	4.1	3.6	7.2	5.1	0.3	0.2	-2.4	1.3
mean	3.9	184	80	47	77	1.10	2.4	2.2	0.6	4.8	1.9	3.2	5.0	5.9	1.9	1.8	0.5	3.9	2.0	2.5	4.2	6.6	7.7	5.3	0.3	0.0	-2.1	0.9
SD	0.4	65	47	41	55	0.82	0.9	1.4	0.6	3.6	0.7	2.1	4.4	4.4	0.7	1.0	0.5	2.7	1.0	0.9	2.5	5.9	5.5	2.7	0.5	1.0	1.3	1.3

Table 3
Heavy metal content of water samples (μg/L).

	Cu	Cr	Pb	Zn
Min	0.8	0.4	12.3	16.5
Max	5.5	5.4	24.4	75.9
Mean	3.2	2.1	17.5	40.0
SD	1.5	1.5	3.7	19.2
Median	2.6	1.5	17.8	37.8
EQS UK SAC's Project (Annual mean—dissolved metals)	5.0	15.0	25.0	40.0

ples (3 m depth) using a water sampler, from several areas of the Bay and the Gulf of Thessaloniki (north Thermaikos Gulf). Sampling sites along Thermaikos Gulf were selected to cover an impacted coastal area, based on known anthropogenic sources, intensively cultivated land along the coasts and nearby river effluents (Fig. 1). Water samples were collected only from Stations 16–30. Sediment samples 1–4 were collected by the southwestern coast of the gulf (Methoni and Makrigiallos areas), 5–9 were collected along the shore of the urban zone of the city, 10 and 11 represented the coastline sediments of a shipyard zone near industrial point sources and airport facilities, 12–15 represented the eastern shoreline of the gulf, 16–22 were selected in order to cover the sediments affected by the main industrial effluent discharge area western of Thessaloniki city, 23–26 covered the area affected by a former point source of untreated domestic waste disposal, and 31–33 were collected from the estuaries of Axios and Aliakmon Rivers. The remaining seven samples were collected from an area at a greater distance from the coast to represent sediments from greater water depths.

Sediment samples were transported to the laboratory at −4 °C, they were slowly air dried at 70 °C, gently homogenized, and dry sieved. The fraction with size less than 62.5 μm fraction was retained for heavy metal analysis. Water samples were analyzed for TOC, pH, salinity, conductivity, and filtered (<0.45 μm) portion was acidified and analyzed for metal content.

2.3. Analysis of sediments

Sediment samples were analyzed using an acid digestion method in which 1 g of dried sediment is accurately weighted into a 100 mL beaker and digested using consecutive amounts of HNO_3 and HCl (3 mL, duplicate digestions for each sample). This method of digestion ensures the dissolution of the total metal content, except for the silicate fraction that is generally stable and does not interfere with the ecosystem. The contents of the beaker are then transferred with as little distilled water as possible to a centrifuge tube (2500 rpm for 20 min). The supernatant is decanted into a 50 mL volumetric flask, and the residue washed with a small

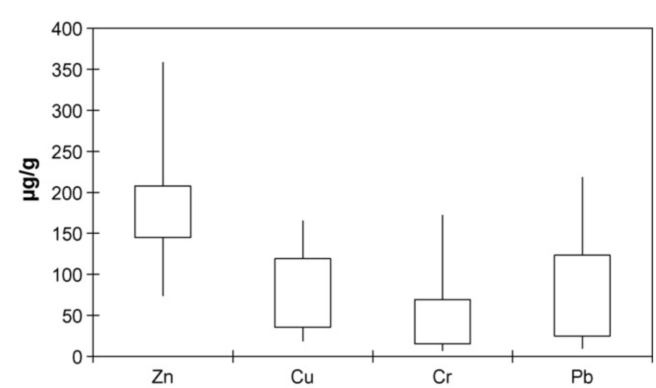

Fig. 2. Sediment metal content in the surface sediments of the Bay and Gulf of Thermaikos (includes min, max, 25- and 75-percentile of the values).

amount of distilled water. This is again centrifuged at 2500 rpm for 20 min, with the supernatant again being added to the flask. The flask is then made up to volume with distilled water, and the solution retained for analysis by Atomic Absorption Spectrometry. Zinc (Zn), copper (Cu), chromium (Cr) and lead (Pb) were analyzed using a Graphite Furnace (HGA 400 programmer) and Flame Atomic Absorption Spectrometry (Perkin Elmer 2380) depending on the metal concentration. TOC was determined using the Walkey–Black wet combustion method [34]. All reagents were of analytical grade.

Laboratory quality control (QC) for metal analysis and total organic carbon consisted of the certified reference material NRCC MESS-1 (marine sediment), analysis of triplicates, preparation blanks for each measurement and matrix matched calibration curves. The analytical results of the quality control samples show good agreement with the certified values (recoveries ranging 93.1–103.4%).

2.4. Analysis of water samples

Salinity, pH and Conductivity were measured using WTW instruments, models pH 330 and LF 330. 100 mL of sample were filtered through 0.45 μm filter and the pH was adjusted to 3.5 using HCl solution. An appropriate amount of fresh APDC solution (2% Ammonium pyrolidine dithiocarbamate) was added as well as 5 mL of methyl isobutyl ketone (MIBK) [35]. The solution was stirred for 30 min, the organic layer allowed to separate, and collected. Metal concentrations were determined in the organic phase using a Graphite Furnace (HGA 400 Perkin Elmer 2380). Accuracy was determined by repeated analyses of international reference materials.

2.5. Geographic information systems

The results of the pollution analysis were treated as a simple database, which was linked directly to the location editor. ESRI ArcGIS 9.1 was used for the area digitization. ESRI Spatial Analyst extension provided a series of GIS maps, which offer an overview of the surface sediment metal concentration and their spatial variability.

3. Results and discussion

3.1. General

The results of the sediment and water samples are shown in Tables 2 and 3. Fig. 2 shows the minimum and maximum metal content as well as the 25th and 75th percentile of the values. Sediments from the bay are samples 5–29 and sediments from the Gulf of Thermaikos are 1–4 and 30–40. The predominant of the four selected metals is Zn and the least abundant is Cr. Lead and zinc are the most variable, due to the difference between the northern more impacted area of the bay and the southern deep area in the Thermaikos Gulf. The spatial patterns of the selected metals are in agreement with previous work on the surface sediments of the bay [31,36]. Zn showed the highest mean total metal content (184 μg/g dw) while the rest of the metals were found in reduced concentrations (80 for Cu, 46.5 for Cr, 77.2 for Pb). These values refer to the deeper sediments of the southern Gulf. In general, the total metal content of the sediments of the Bay of Thessaloniki was higher for all metals, as opposed to sediments collected from the southern part of the gulf, due to the long-term exposure of these sediments to numerous anthropogenic activities near the city. Increased metal concentrations are encountered for samples collected near the shores of the Gulf of Thessaloniki as a result of inputs from coastal activity. A comparison of trace metal content between the Bay and Gulf of Thessaloniki is given in Fig. 3a, which shows the concentration of Cr in the Bay and Gulf of Thessaloniki.

3.2. Bay of Thessaloniki

The Bay of Thessaloniki, characterized by restricted water replenishment ratios, generally has a higher total metal content

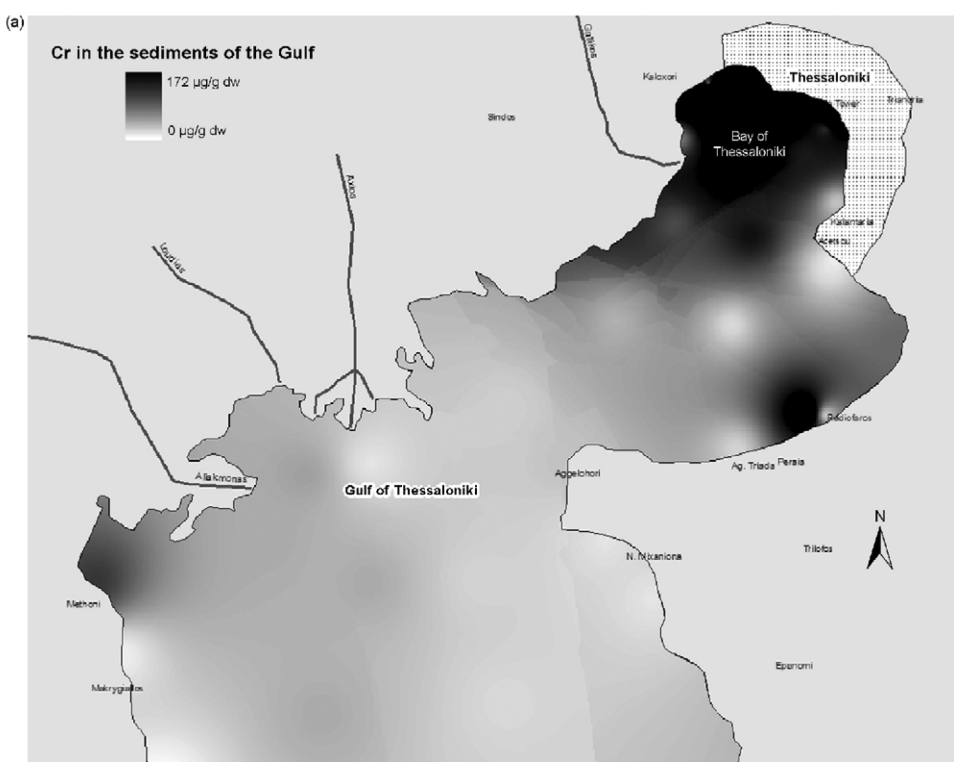

Fig. 3. (a) Cr distribution in the samples of the Gulf and the Bay of Thessaloniki (Northern Part). (b) Cr distribution in the samples of the Bay of Thessaloniki.

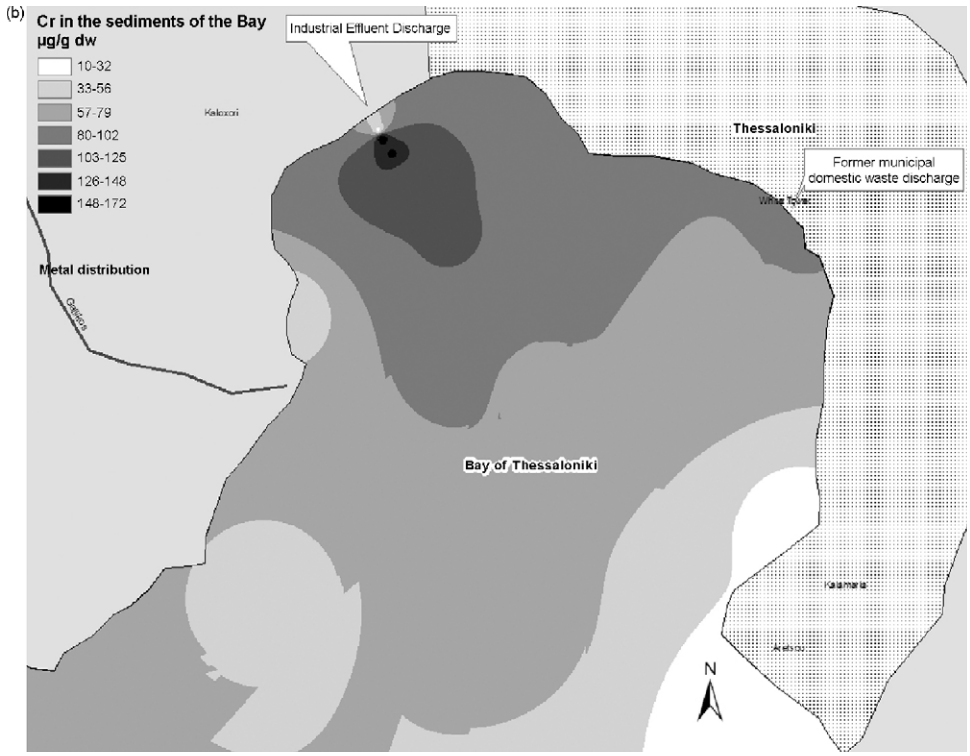

Fig. 3. (*Continued*).

(Fig. 4). In the western part of the bay and where industrial effluents were discharged, all four of the metals are found in increased concentrations. Zinc concentrations are less variable in the bay. Long-term discharges from tannery effluents and other facilities is reflected in the higher concentrations of copper and chromium. Fig. 3b shows that the total Cr content decreases with distance from the industrial effluent discharge zone. The maximum total Pb content found was near the eastern shipyard zone and along the eastern shores of the Bay of Thessaloniki, with concentrations varying 102–218 μg/g dw.

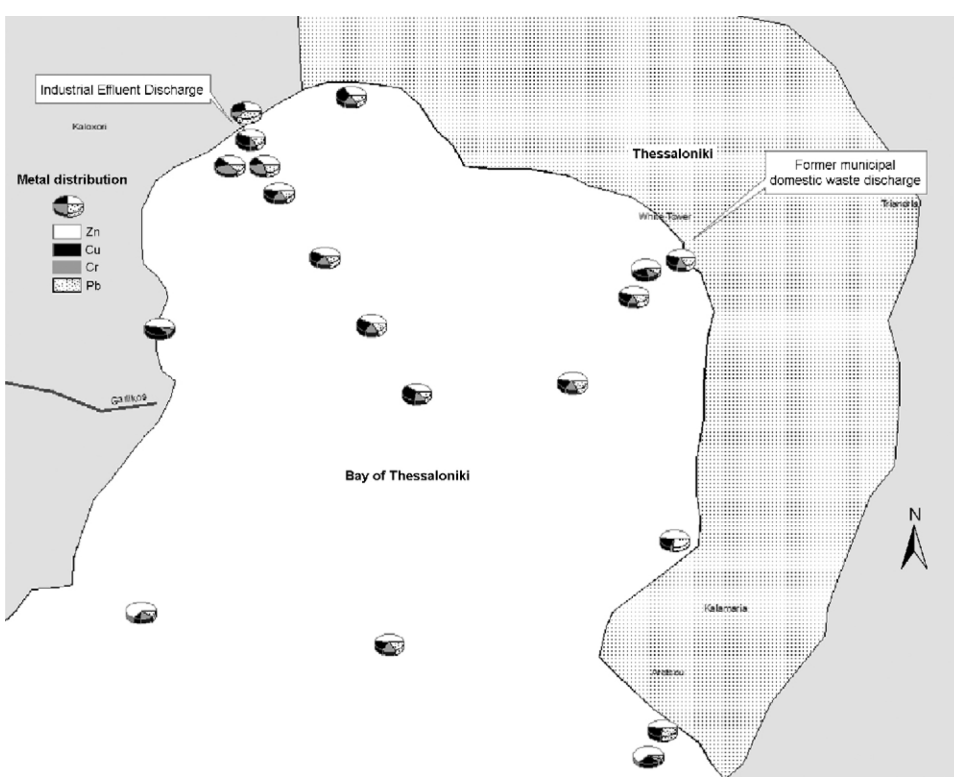

Fig. 4. Heavy metal distribution in the Bay of Thessaloniki.

3.3. Thermaikos Gulf

The total metal content of sediments from the southern, deeper part of the gulf was less than that found in the bay. One of the most important rivers of the area, is Axios river with a mean annual water discharge of 3.2×10^9 m^3/yr and water flows varying from 35–220 m^3/s. Past studies have shown that the water discharges of the river are accountable for a significant metal input of the Gulf of Thermaikos [24]. Various metals enter the gulf following the course of the river, originating both from anthropogenic sources and the erosion of the catchment area. Zinc is the most abundant metal found in the water discharges of the river [37] and this is reflected in the sediments of the gulf. Nevertheless, the samples collected near the river estuaries only showed medium Zn concentrations (74–181 μg/g dw). It seems that the sediments collected from the delta of the rivers do not contain the expected amount of metal content, although past studies have shown that Zn from various anthropogenic sources finds its way to the sediments of the area. The low sediment content of the area in Zn may be attributed to a significant decrease in the river's metal input, as well as to the complex water currents of the gulf, as shown below. The slightly increased metal content of the eastern shores of the Gulf (Aggelohori, Mihaniona), as well as the presence of considerable Pb, Cu and Zn at the western shores of the Gulf (Makrygiallos, Methoni) could be attributed partly to unknown point sources (streams or anthropogenic activities) and partly to the complex water and particulate matter flow in the Gulf of Thessaloniki. It has been reported that under the influence of the predominant North–Northwestern wind regimes, the lower water masses of the gulf engage in the opposite circular patterns of flow, thus essentially moving the particulate and dissolved loads of the river flows to the western and eastern shores of the gulf [30].

3.4. Enrichment Factors

The Enrichment Factors are shown in Fig. 5a and b, respectively according to the reference values of Table 1. Zinc, copper and lead have EF values equal or greater than 1, suggesting anthropogenic sources; lower EF are encountered in the deeper part of Thermaikos Gulf (southern part). EF based on the less contaminated sample, shows values significantly higher (average and maximum values) than those based on the average shale content. They also exhibit a wider range of values (in the case of Cr, Enrichment Factors are almost eight times the maximum values of EF based on average shale content).

The EF for zinc and copper are higher along the shores of the Bay of Thessaloniki and the harbor, compared to the deeper sediments of the bay (where EF vary from 0.9 to 2 and from 0.5 to 1.2 for Zn and Cu, respectively). In the case of Cu, sediment samples 5–29 (obtained from the inner part of the bay and the shores of the bay) exhibit EF ranging 2–5, while the values of the southern and less contaminated Thermaikos Gulf vary 0.5–1.2, which reveals the anthropogenic contribution to the increased content of the surface sediments of the bay. Sediments show low Enrichment Factors for chromium with a maximum of 2.1 for the inner part of the bay, and values less than one (0.2–0.6) for the sediments of the Thermaikos Gulf. The background concentrations of Cr are four or five times less than the average shale content, which is considered to be 90 μg/g [22]. Taking into account the Cr content of the average of the seven deeper sediment samples, produces increased Enrichment Factors, reaching eight times higher values (Fig. 5b). This shows that despite this overestimation of the background levels for Cr, the historic tannery influence is still detectable in the sediments.

Based on past studies [31,36], lead was not considered to pose the greatest risk in the area; EF nevertheless are the highest among all other elements (Fig. 5), with the highest maximum value and also the highest range of values, indicating significant participation of anthropogenic sources, such as several urban and industrial activities, landfill leachates, as well as atmospheric deposition.

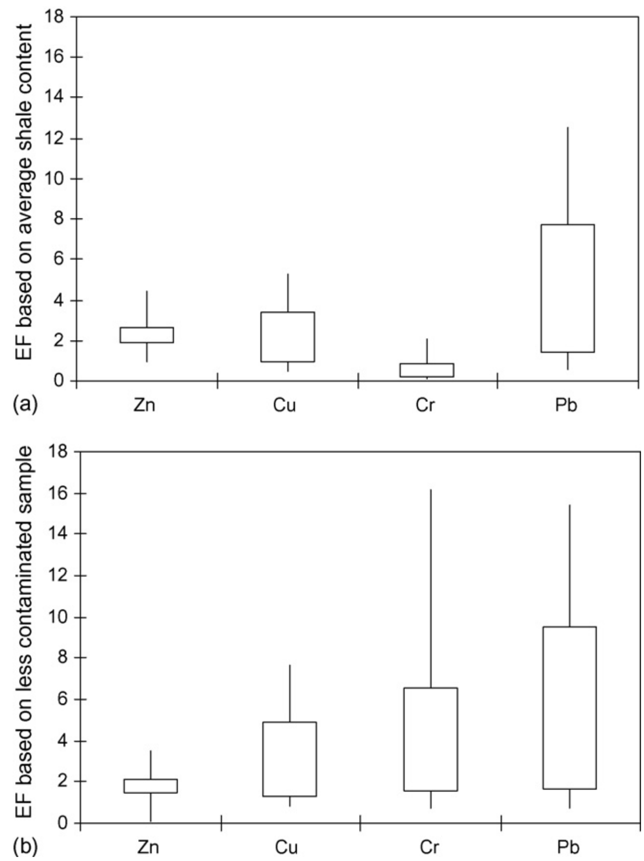

Fig. 5. Enrichment Factors based on (a) shale content and (b) less contaminated sample (includes min, max, 25- and 75- percentile of the values).

3.5. Degree of Contamination

The modified degrees of contamination (mC_d) for the sediments are shown in Fig. 6a and b. The Gulf of Thermaikos mC_d are less than 1.5 indicating zero to very low contamination. The area of Methoni suggests moderate contamination, attributed to the currents of the bay. The Inner Bay of Thessaloniki shows mC_d values ranging from 2.2 to 4.1, which is interpreted as moderate contamination based on the analyzed elements. mC_d based on the least contaminated sediments ranged 2.7–10.6 indicate "moderate" to "very high toxicity". Deeper areas of the gulf can be characterized as moderately contaminated.

mC_d values are calculated based only on the separate Contamination Factors, which do not consider the normalizing factor of Fe, therefore it gives values not reproducible to every environment with the same degree of contamination and not easily compared to other areas studied in the past with different geological backgrounds.

3.6. Geoaccumulation Index

The Geoaccumulation Index calculated for the selected metals, indicates that the majority of the samples can be characterized as "unpolluted (<1) to moderately polluted" for Zn, Cu and Cr, while I_{geo} values for Pb describe sediments as "moderately to strongly polluted".

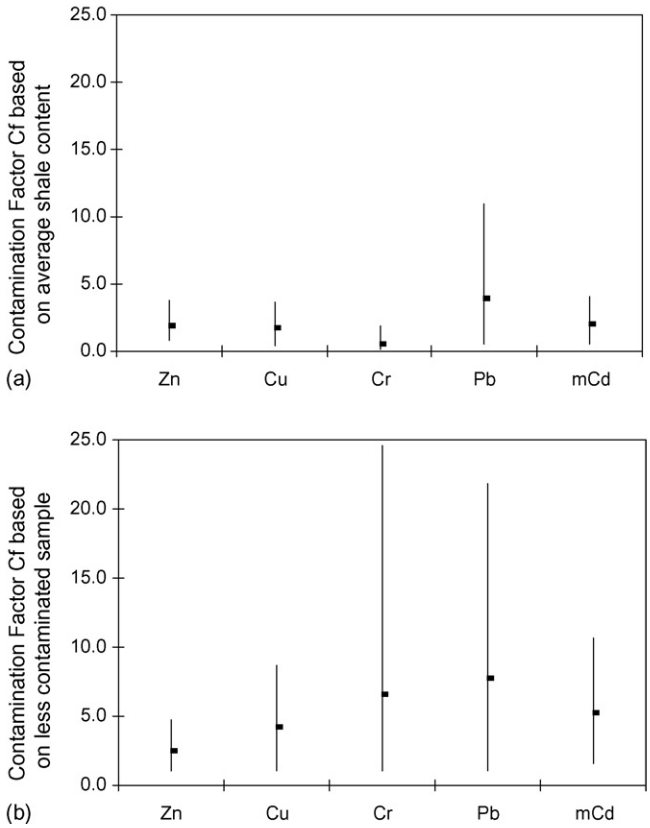

Fig. 6. (a) Degree of contamination based on average shale content and (b) less abundant sample.

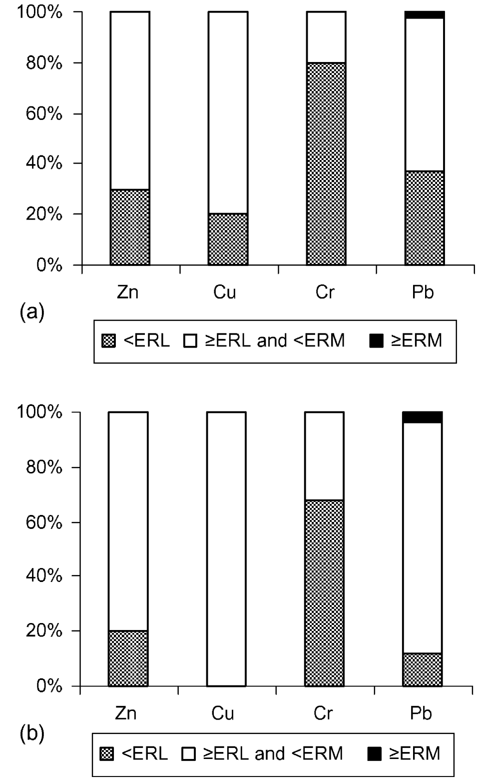

Fig. 7. Classification of samples based on the propose SQGs taking into account (a) all samples and (b) sediments collected from the bay area.

The values obtained from variable calculated factors, may point to different conclusions and may mislead to coinciding or colliding assessments. Bearing in mind that I_{geo} values are calculated without considering the spatial geological variations and arbitrarily introducing the factor 1.5 in the formula, as well as the average shale content, it is clear that this factor should not be used as a unique assessment tool for the specified area. Nevertheless, I_{geo} shows the general tendency already proved by the EF, C_f and visual representations of the area, that the content of Pb in the sediments of the bay are clearly of anthropogenic origin and have accumulated over a long period of time on the surface sediments of the area.

3.7. *Application of Sediment Quality Guidelines*

The Sediment Quality Guidelines for the selected metals and a classification of the samples based on these guidelines are shown in Table 4. The data from the SQG classification suggest that for Zn, Cu and Pb, the majority of the sediments may occasionally be associated with the adverse biological effects and most of these samples were localized in the Bay of Thessaloniki. Fig. 7 illustrates that the percentage of samples occasionally and frequently associated to toxic biological effects is increased when taking into account only the sediments from the Gulf of Thermaikos. Only a small percentage of samples show frequent association with adverse biological effects due to lead content of the sediments. Examining the whole gulf area and for Zn and Cu, 70% and 80% of the samples respectively may occasionally be associated with the toxic effects on aquatic organisms. In the Bay of Thessaloniki over 80% of the samples are considered as an occasional threat to organisms, as far as Zn, Cu and Pb are concerned. Only a small percentage of the samples, mainly those obtained by the southern, deeper part of the gulf, are rarely associated with negative biological effects. The SQG classification of the samples collected from the bay is given in Fig. 8.

The evaluation of the analytical data, along with the assessment of various factors, such as: the Contamination Degree, the Enrichment Factors and the Geoaccumulation Index, suggests that Pb and Cr originate from various anthropogenic activities associated with pollution and may pose a serious threat to the area. Nevertheless, the data obtained by the SQG classification suggest that most of the sediments show little to no association with negative biolog-

Table 4
Classification of sediment samples based on the proposed SQGs.

	Sediment Quality Guidelines[a] (μg/g dw)		% Of samples amongst ranges of Sediment Quality Guidelines (*all sediments considered*)			% Of samples amongst ranges of Sediment Quality Guidelines (*only bay area*)		
	ERL	ERM	<ERL	≥ERL and <ERM	≥ERM	<ERL	≥ERL and <ERM	≥ERM
Zn	150	410	30.0%	70.0%	0.0%	20.0%	80.0%	0.0%
Cu	34	270	20.0%	80.0%	0.0%	0.0%	100.0%	0.0%
Cr	81	370	80.0%	20.0%	0.0%	68.0%	32.0%	0.0%
Pb	46.7	218	37.5%	60.0%	2.5%	12.0%	84.0%	4.0%

[a] [27].

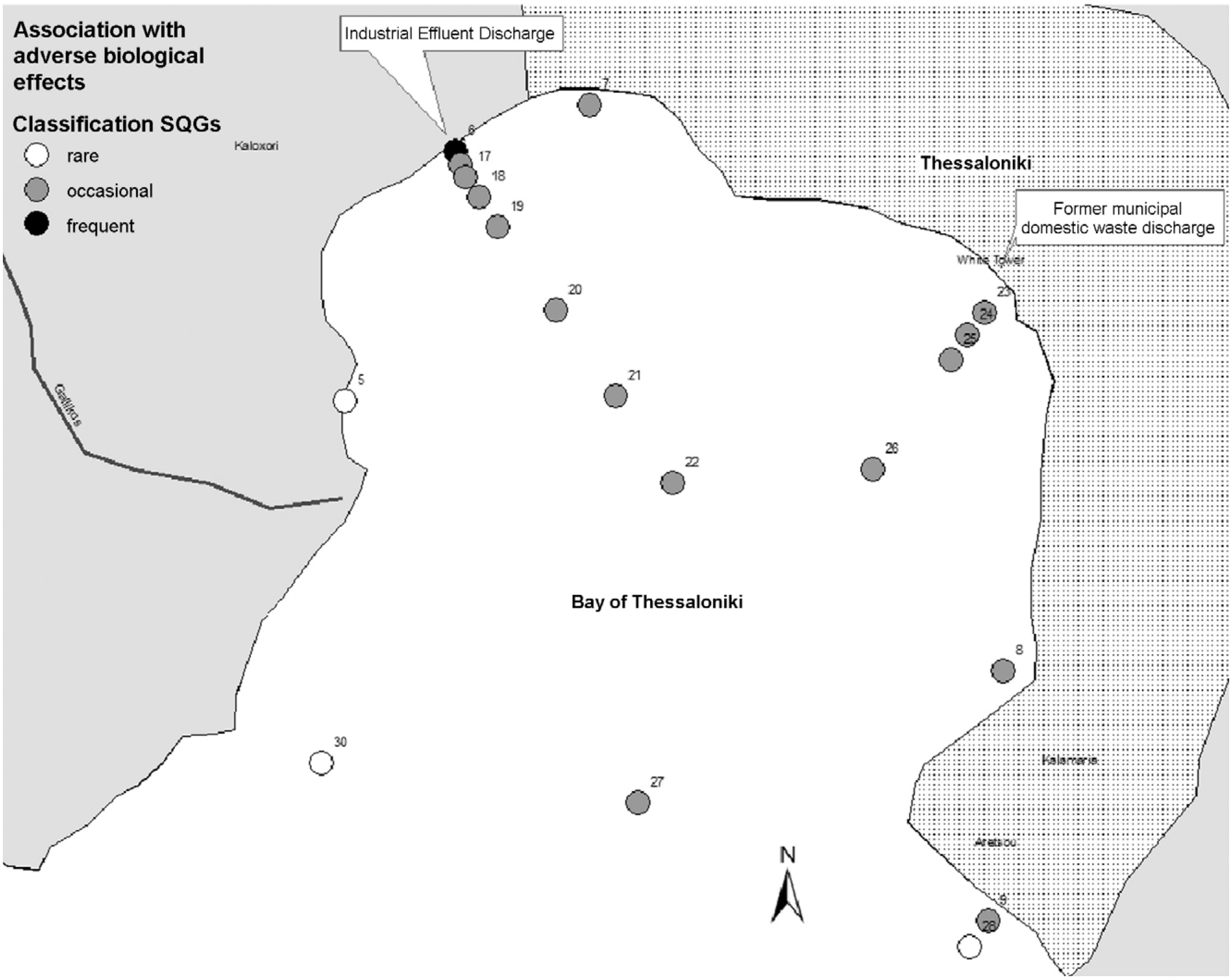

Fig. 8. Classification of the sediments based on SQGs.

ical effects, as far as Cr is concerned. This is true even in the area of the bay where the sediments have received increased amounts of chromium rich effluents due to industrial activities; only 32% of the sediments appear to occasionally pose a threat to aquatic organisms.

3.8. Seawater analysis

In this study several selected water samples (corresponding to sediment sampling stations) were taken to determine the concentrations in the water column and determine any relationship to metal content in the sediments (Table 3). The results indicate that all metals show low concentration in the water column, and there appears to be no obvious relation between dissolved metals and the corresponding sediment content at the sampling sites. Compared to Environmental Quality Standards set by UK authorities for the Quality of Marine Environment [38], the concentrations of the metals in the water column are below the values set for the protection of marine life (Table 3). pH, redox and salinity values are in the typical range for the specific area. pH ranged 7.6–7.8, salinity 49.6–56.2 mS/cm and ORP 299–401 mV. Under the present physicochemical conditions (pH, salinity and low organic content) and in combination to the very low concentration of dissolved metals in the water samples (Tables 2 and 3), it appears that the dissolution of metals back to the water column is not presently favored, but it could be an issue in the future. Bearing in mind that the dissolution of accumulated metals back to the water column is frequently triggered by low redox potentials and decreased pH values the present physicochemical conditions do not seem favorable for any further dissolution of the accumulated metals (Table 3) [9].

Sediments have the ability to accumulate various contaminants and especially heavy metals, after a long-term exposure to various contaminant loads [2,3]. The sediments of the Bay of Thessaloniki

Table 5
Comparison of total metal content (μg/g dw) of the center of Thessaloniki Bay with past studies.

Research		Zn	Cu	Cr	Pb
Voutsinou-Taliadouri, F., Varnavas, S.P., 1995	*Municipal effluents outfall area*	235–500	100–200	137–187	100–330
	Industrial effluents outfall	220–375	68–85	214–386	120–245
Present Study (corresponding sampling sites)	*Municipal effluents outfall area*	172–358	66–161	57–94	56–123
	Industrial effluents outfall	126–285	85–165	26–153	47–143

have endured great ecological pressures in the last 30 years however improvement in the recent past, possibly because of the implemented environmental strategies and the innovative technologies of environmental remediation is apparent. Table 5 shows that the total metal content has not increased over the last 20 years, although the problem is not yet totally obliterated.

4. Conclusions

The sediments collected from the Bay of Thessaloniki have shown elevated total metal content but in comparison to the past, the situation seems to have improved significantly. The areas with the highest metal inputs are along the shoreline of the Bay of Thessaloniki and along the west and east coasts of the Gulf of Thessaloniki. Zinc and lead are the most abundant elements with higher concentrations in the Bay of Thessaloniki.

Enrichment Factors suggest that anthropogenic contribution has been significant, in the cases of Cr, Cu and Pb, especially in the Bay of Thessaloniki. In the case of Cr, although the tannery facilities have been removed from the area of the bay, enrichment is still detectable, despite the fact that the chromium background is significantly lower than found in average shale (90 vs. approx. 19, average of 7 deep stations). Pb has accumulated in the sediments of the bay (especially those along the coast of the bay), requiring prolonged time periods in order to be removed through natural pathways. The spatial distribution of the metals in the sediments of the bay, show a gradual decrease towards the deeper parts of the bay.

The concentration of lead in the sediments mainly contributes to the degree of mC_d, which characterizes the sediments of the bay as “moderately contaminated”. Considering only Pb the sediments could be classified as “highly to very highly contaminated”.

The Geoaccumulation Index is not in total agreement with the other contamination indicators. The majority of the sediments were classified as “unpolluted to moderately polluted” with the exception of Pb that indicated some sediments were “moderately to strongly polluted”, especially in the area of the bay.

The majority of the sediment samples can be “occasionally” or “frequently associated to toxic biological effects”, according to the effect-range classification for Zn, Cu and Pb. This is not the case for Cr, since most of the samples show rare association to adverse biological effects, probably due to the proposed ERL value. Samples obtained by the southern and deep part of the Gulf of Thermaikos have shown no relation to adverse biological effects, based on the effect-range approach.

Analysis of the overlying seawater columns, demonstrates that under the present physicochemical conditions, only small concentrations of dissolved metal are found in seawater and that dissolution of the accumulated metals from the sediments is unlikely to occur, although this closed and sensitive ecosystem is labile to various anthropogenic threats that could disturb its balance.

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