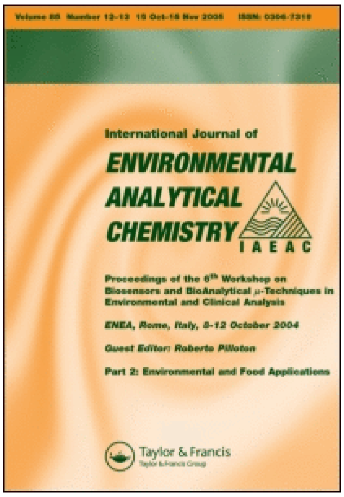

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ASSESSMENT OF METAL CONTAMINATION IN SHALLOW COASTAL SEDIMENTS AROUND MYTILENE, GREECE

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Different normalisation procedures were applied on a data set of metal concentrations of sediments from 28 stations in the harbour and coastal area of Mytilene, Lesvos island, Greece. Due to the great granulometric variability of the sediments the normalisation for grain-size was not applicable. Also, the normalisation to a carbonate-free basis did not provide additional information. On the other hand the normalisation to Al and the calculation of enrichment factors of metals enabled to distinguish between contaminated and non-contaminated areas. The harbour sediments were highly enriched in Cd, Cu and Zn and also slightly enriched in Pb. No enrichment was found in the sediments of the coastal area outside the harbour, indicating that the metal rich deposits of that confined area are not affecting the quality of the neighbouring coastal environment.

Keywords: Coastal sediments; metal contamination; normalisation

INTRODUCTION

Natural and anthropogenic metals are transported from land to the sea mainly through rivers and the atmosphere. In the marine environment, the land derived detrital metals along with the non-detrital metals which have been removed from the water column (biogenous, authigenic, hydrothermal, diagenetic) settle towards the bottom and form marine sediments.[1] The same general processes take place in the littoral environment, but the local runoff material plays the key role in the morphology and mineralogy of coastal sediments. This material is directly influenced by the local geology, as well as, the occurrence of local human metal sources (industrial and urban effluents). As a consequence, in order

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to evaluate metal concentrations in coastal marine sediments, these data have to be manipulated taking into consideration i) grain-size variability, ii) the geochemistry of the local material, iii) the effect of the human discharges into the marine environment.

Methods for the Normalisation of Geochemical Data

The manipulation of data usually aims at the elimination of some well known physical and chemical factors which affect the metal distribution process in marine sediments. Since trace metal concentrations usually increase with decreasing grain size of sediments, compensation for grain-size differences is one of the most important normalisation techniques for the detection and quantification of anomalous metal concentrations. Other manipulations include: correction for carbonate content and normalisation to a conservative element or to another parameter (e.g. organic matter).[2]

Correction for grain-size differences

The correction for grain-size differences is based on the tendency of trace metals to be concentrated in fine-grained sediment.[3,4] Therefore, the coarser material in the sediments plays the role of the «diluent» affecting the total (bulk) metal concentration. There are several approaches to solve this problem: a) Remove the finer sediment fraction through sieving and analyse it separately. This is not exactly a normalisation method and may be used when the fine material is abundant. This is not the case in coastal sediments, where the fine fraction (i.e. silt + clay $< 63\ \mu m$) may represent a small percentage of the bulk sediment. In such environments, the metals contained in the fine fraction represent only a small part of the total metal content in the sediment and clearly cannot solely been used to characterise the total sediment. b) Normalise metal concentrations by multiplying the bulk sample metal concentrations by the factor: 100/(100-percentage of the coarser fraction). This method assumes (although it is not true) that there is no metal content in the coarser sediment fraction. Although this may be an acceptable method when the coarse fraction is small (less than 50% of the bulk sample) and the coarse material is metal-poor (quartz), it cannot be used in coastal sediments which contain a great proportion of coarse material from natural and human sources.

Correction for carbonate content

This correction is based on the assumption that the carbonate component of the marine sediments does not contain substantial quantities of trace metals. The metal concentration of the bulk sample is multiplied by the dilution factor: 100/(100-percent carbonate). This manipulation may neutralise the effect of carbonate content but it is based on the assumption that carbonate does not carry any metals, an assumption which may not always be valid (for example Cd and Pb concentrations may not decrease with increasing carbonate content[2]). In any case this correction may give useful information, especially when comparing sediments of different carbonate content. Similar corrections can be made when sediments contain an important amount of another non-metal bearing material, such as quartz, coarse grained organic material etc.

Normalisation to a conservative element

The term «conservative element» is used for elements of natural origin which are structurally combined to one or more of the major fine-grained trace metal carriers. This normalisation aims to reduce the natural effect of grain size on metal distribution, to identify the predominant metal carriers and to estimate the extent of contamination.[5] Depending on the mineralogy of the marine sediments of an area, several conservative elements have been used for normalisation purposes: Al,[6] Li,[5] Cs and Sc[7] and Fe.[8] Each element that has been used for normalisation purposes has presented advantages and disadvantages (For a detailed review on normalisation procedures refer to Loring 1990[5]). Aluminium has been widely used as a conservative element for normalisation of metal data from marine sediments, because it is a major constituent of fine grained aluminosilicates with which the bulk of trace metals are associated. However, it cannot be used successfully in high latitude sediments composed mainly of material from glacial erosion of igneous rocks because the prevailing weathering conditions result in the production of immature weathering materials, such as feldspars, of variable grain size. In that case, the presence of Al in roughly the same amounts in the coarse as well as the fine fraction leads to poor or insignificant correlations between trace metals and Al.[9,10] In those sediments Li gives better results because the metals are associated in the same mineralogical components as Li, such as primary micas and ferromagnesium minerals, and secondary clay minerals.[11]

To normalise the metal data, the ratios of Metal/Al must be calculated. In non-contaminated sediments this ratio should be relatively constant, because it is assumed that a linear positive correlation exists between the concentration of the metal and that of Al (a linear correlation must also exist between the Al concentration and the percentage of fine-grained [silt + clay] content of the samples). Since human activities will add anthropogenic metals but not Al to the marine environment, it is expected that contaminated sediments will present higher Metal/Al ratios. Using these ratios it is possible to calculate an «enrichment factor» of a metal in the sediment by dividing the Metal/Al ratio of a sample by the Metal/Al ratio of a non-contaminated sediment sample from a pristine area.[12] The calculation of enrichment factors may be a very useful tool for assessing the contamination of marine sediments.

The Study Area

The study area is a shallow coastal marine environment located at the eastern part of the island of Lesvos. The only major metal source is the discharge of domestic effluents from the city of Mytilene (population 25,000) since there is no significant industrial activity in the area. The urban effluents are discharged without any treatment into the sea. Previous surveys in the area,[13,14] revealed that the sediments in the harbour of Mytilene had higher metal concentrations than the neighbouring coastal sediments, thus constituting a local metal-rich «hot-spot». However, due to differences in granulometry and geochemistry between the sediments along the coast of Mytilene, it is difficult to evaluate metal concentrations using only the raw data and a series of normalisation procedures were used to assess the extent of metal pollution in the marine sediments of the area.

METHODOLOGY

Surface sediment samples were collected from 28 stations from the harbour and the wider coastal area of Mytilene (Figure 1). Grain size distribution was measured by wet sieving and the following fractions were determined: silt + clay ($< 63\ \mu m$), sand ($1\ mm > x > 63\ \mu m$) and gravel (> 1 mm). Organic carbon, carbonate and metal contents were all determined in the < 1 mm fraction. Organic carbon was determined by the Walkley-Black method, as adopted and modified by Jackson.[15] According to this method 0.5 g of dried sediment are oxidized with 10 ml of 1 N $K_2Cr_2O_7$ and 20 ml of concentrated H_2SO_4. After 30 min 200 ml of distilled water, 10 ml of 85% H_3PO_4 and 0.2 g of NaF are added and the solution is back titrated with 0.5 N of $Fe(NH_4)_2SO_4$ in the presence of diphenylamine indicator to a one-drop end point.

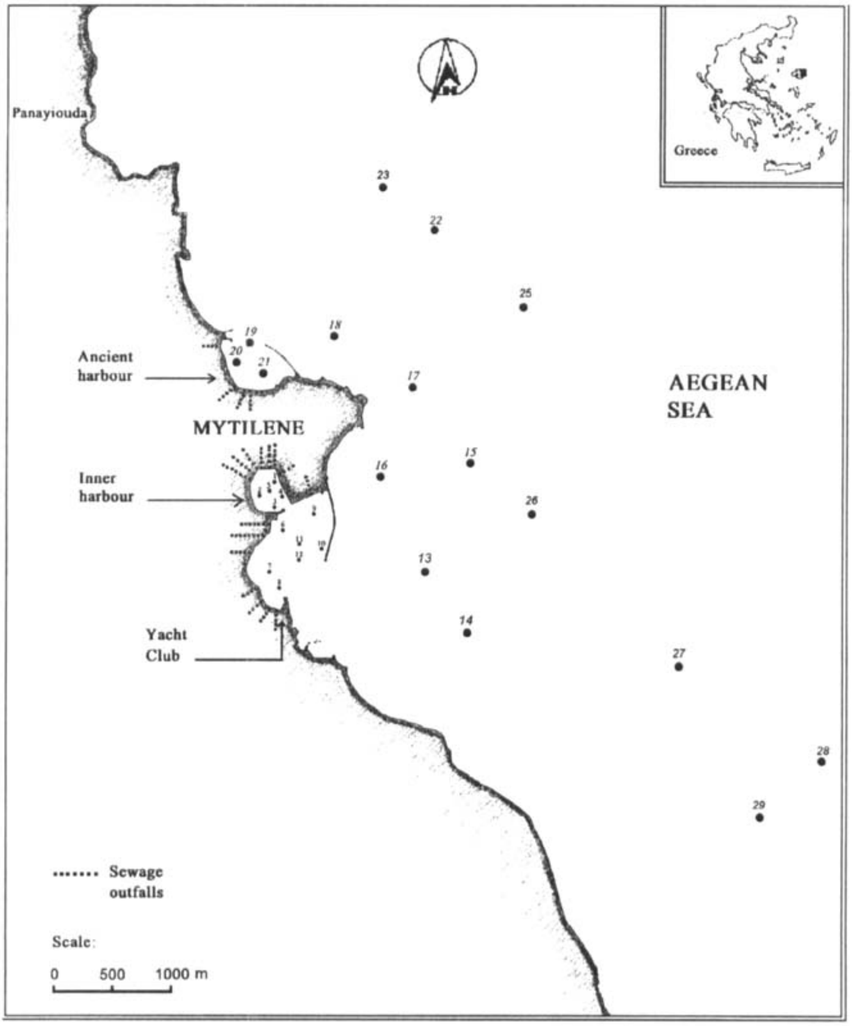

FIGURE 1 Sampling stations.

Carbonate content was measured using a method described by Loring and Rantala.[16] One g of dried ground sediment is treated with 5 ml of 4N HCl in a pre-weighed stoppered conical flask. After 2 h, the conical flask is weighed, the loss of weight due to the CO_2 evolution is calculated and compared to the loss of weight of 100 mg of $CaCO_3$, undergone the same procedure, so as to be used for the standardisation of the method. The total metal content of the samples was measured after total decomposition of 200 mg of dried ground sediment with 1 ml of *aqua regia* and 6 ml of HF, in Savillex teflon bombs

TABLE I Grain size distribution on gravel free basis, organic carbon content, carbonate content and total metal cncentrations in the sediments of the coastal area of Mytilene.

Station	*Sand* %	*Silt - Clay* %	*OC* %	*$CaCO_3$* %	*Al* %	*Cd* μg/g	*Cu* μg/g	*Fe* %	*Li* μg/g	*Pb* μg/g	*Zn* μg/g
1	14.21	85.79	4.80	27.5	4.79	0.364	66.0	2.69	29.4	82.5	173
2	28.71	71.29	3.25	30.2	4.86	0.395	63.5	2.39	26.0	73.6	184
3	4.63	95.37	4.22	26.8	5.26	0.435	86.2	2.81	32.7	93.0	230
4	29.25	70.75	4.00	35.5	3.87	0.166	43.1	2.19	24.3	52.0	112
5	3.34	96.66	3.98	28.0	4.69	0.409	67.6	2.66	29.3	78.2	191
6	17.70	82.30	4.27	30.3	4.40	0.232	48.8	2.56	27.8	58.0	128
7	9.94	90.06	3.99	34.4	4.23	0.206	41.5	2.34	28.4	63.3	134
8	88.96	11.04	1.85	45.9	2.65	0.173	21.0	1.43	14.9	32.7	83.5
9	32.58	67.42	3.72	30.5	4.96	0.067	34.5	2.71	34.5	38.1	74.1
10	33.12	66.88	4.12	29.4	4.82	0.142	41.3	2.74	28.6	54.3	112
11	33.27	66.73	3.03	28.7	5.18	0.147	42.0	2.58	29.5	56.5	116
12	31.14	68.86	2.90	39.4	4.16	0.170	30.5	2.00	23.6	51.7	95.1
13	35.20	64.80	3.39	29.3	4.75	0.081	27.3	2.40	27.0	44.2	69.1
14	12.20	87.80	2.86	29.4	5.34	0.085	23.4	2.70	37.1	39.8	73.1
15	24.05	75.95	3.35	28.2	5.24	0.082	30.5	2.75	31.8	42.5	72.9
16	58.58	41.42	2.97	28.1	3.78	0.232	24.8	1.71	19.7	62.6	78.3
17	58.00	42.00	1.41	33.6	4.45	0.066	16.7	1.74	21.8	34.5	45.8
18	64.55	35.45	1.55	37.0	3.94	0.042	20.4	1.74	19.4	37.1	55.0
19	96.80	3.20	1.31	18.5	3.27	0.100	23.5	1.35	12.7	58.7	80.2
20	99.60	0.40	0.11	53.1	3.20	0.052	9.39	1.29	14.5	30.5	38.8
21	94.05	5.95	0.93	32.0	1.86	0.048	14.9	0.77	8.92	54.9	45.1
22	68.91	31.09	0.71	42.2	3.74	0.044	9.91	1.34	15.2	24.2	33.7
23	83.36	16.64	0.35	26.1	2.79	0.053	6.07	1.12	11.7	20.7	23.0
25	89.41	10.59	0.27	32.0	2.83	0.059	6.17	1.15	12.3	29.7	29.8
26	64.10	35.90	1.09	32.4	3.88	0.074	14.0	1.77	20.6	34.4	41.9
27	61.92	38.08	1.09	37.4	4.08	0.044	11.0	1.36	18.8	36.7	32.3
28	91.64	8.36	0.35	41.8	3.61	0.030	5.34	0.80	9.74	27.8	12.9
29	36.01	63.99	2.24	37.8	3.83	0.070	17.8	2.04	28.4	37.5	53.0

heated in a microwave oven. The resulting solution is transferred into a 50 ml volumetric flask containing 2.8 g of H_3BO_3 and made up to volume with distilled water.[16] The metal determinations were performed in a Perkin-Elmer 5100ZL Atomic Absorption Spectrometer with Zeeman background correction. Copper, Fe, Li and Zn were determined by FAAS, while Cd and Pb were determined by GFAAS with a mixture of 50 μg $NH_4H_2PO_4$ and 3 μg $Mg(NO_3)_2$ as matrix modifier. The quality assurance of the analytical results was controlled with the use of a Reference Material certified by NRCC (BCSS-1 marine sediment).

RESULTS AND DISCUSSION

The concentrations of the metals in the coastal sediments of Mytilene are presented in Table I. In the same Table are presented the grain size distribution (on a gravel free basis) the organic carbon content and the carbonate content of the samples. From these data it is obvious that higher metal concentrations were found in the sediments of the harbour of Mytilene and lower metal concentrations were found in the furthest seaward stations. However, with the exception of that general conclusion, the raw data cannot provide any other information on the geographical extent of the contaminated sediments in the area. Furthermore, it is not possible to evaluate the degree of metal contamination in the coastal stations. In order to clarify the picture the metal data were manipulated using different normalisation procedures.

Normalisation to Grain Size

Before any attempt to normalise to grain size, the correlation coefficients of the raw metal data to silt + clay content of the sediments, on a gravel free basis, were examined. Strong positive correlations of Cd ($r = 0.53$), Cu ($r = 0.78$), Pb ($r = 0.62$) and Zn ($r = 0.74$) with increasing fine grain content were detected (in all cases $p < 0.01$), implying that the highest metal concentrations are associated for the most part with the fine grained sediments in the study area.

The raw metal data were normalised to grain size by multiplying the metal concentration by a dilution factor: 100/percentage of silt + clay. The normalised concentrations presented great variability which was caused by the granulometric variability of the sediment samples. The normalised values were relatively low in the sediments which had a high percentage of silt + clay (e.g. station 5 [polluted]: silt + clay 96.7%, normalised Zn 197.1 $\mu g g^{-1}$) and extremely high in coarse sediments (e.g. station 25 [non-polluted]: silt + clay 10.6%, normalised Zn 281.4 $\mu g g^{-1}$; station 20 [polluted]: silt + clay 0.40%, normalised Zn 9611 $\mu g g^{-1}$). From these results it is apparent that the presence of sediments with a small percentage of fine material (less than 50%) renders it difficult to handle statistically the normalised data set, thus restricting the usefulness of this kind of normalisation. Furthermore, in the coastal zone, coarse material may act as a substrate of metal-rich coatings (iron oxides, organic substances, etc) as well as a carrier of lattice bound metals of terrigenous origin. The latter could determine the total metal concentrations, especially in a moderately polluted area such as the Mytilene coastal zone. The above processes could result in enhanced metal concentrations in that granulometric fraction thus contradicting the original assumption of the normalisation method. Therefore, the normalisation for grain size cannot be applied successfully to our data set.

Normalisation to Carbonate-free Basis

The correlation coefficients of the carbonate content to the silt + clay and the metal content of the sediments were calculated. The calculation revealed inverse relationships ($p \leq 0.02$–0.07) between carbonate and silt + clay content, as

TABLE II Correlation coefficients among metal concentrations in the sediments of the coastal area of Mytilene

	Al	*Cd*	*Cu*	*Fe*	*Li*	*Pb*	*Zn*
Al	1,00						
Cd	0,42	1,00					
Cu	0,62	0,92	1,00				
Fe	0,89	0,57	0,77	1,00			
Li	0,90	0,45	0,67	0,97	1,00		
Pb	0,44	0,89	0,91	0,58	0,48	1,00	
Zn	0,55	0,95	0,99	0,72	0,61	0,92	1,00

Significance level 0.05

well as between carbonate and metal contents. This fact would imply that the carbonates are associated rather to the sand than to the mud fraction of the sediments and that they act as a diluent of metal contents.

The raw metal data of Table I were normalised to carbonate-free basis by multiplying the metal concentration by a dilution factor: 100/(100-percent of carbonate). The results did not give a drastically different distribution of metals in the coastal area of Mytilene. Table II presents the correlation coefficients of the metals determined in the sediments of the coastal area of Mytilene (raw data) and Table III presents the correlation coefficients after normalisation of the metal data to carbonate-free basis. No important changes were detected in the correlation coefficients among the anthropogenic metals (Cd, Cu, Pb and Zn) but weaker correlations were found between Al and the group of the effluent

TABLE III Correlation coefficients among metal concentrations in the sediments of the coastal area of Mytilene after normaliation for $CaCO_3$

	Al	*Cd*	*Cu*	*Fe*	*Li*	*Pb*	*Zn*
Al	1,00						
Cd	0,26	1,00					
Cu	0,45	0,91	1,00				
Fe	0,80	0,51	0,73	1,00			
Li	0,83	0,38	0,60	0,96	1,00		
Pb	0,25	0,89	0,89	0,50	0,39	1,00	
Zn	0,39	0,95	0,98	0,68	0,55	0,91	1,00

Significance level 0.05

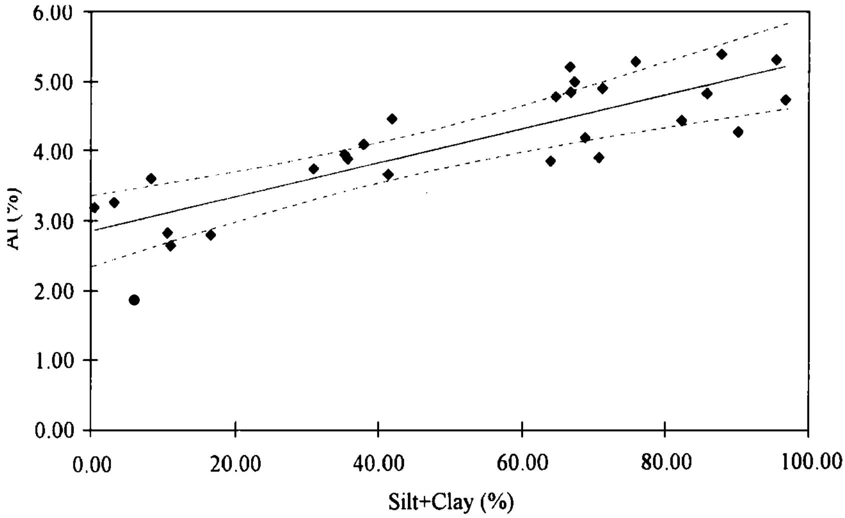

FIGURE 2 Al: Silt + clay (<63 μm) fraction plot for the sediments of the coastal area of Mytilene. Solid line represents the regression line, dashed lines define the 99% confidence band.

related metals. The limited effect of carbonate content to the normalisation of metal concentrations could be attributed to the more or less uniform distribution of carbonates in the study area (mean 33.1%, sd 7.0%), as opposed to the greater variability of the granulometric structure of the sediments (mean mud content 51.2%, sd 31.2%), which leads to more pronounced differences of the grain size normalised data.

Therefore, normalisation of the metal concentrations on a carbonate-free basis cannot provide additional information for the specific data set without further mineralogical analysis.

Normalisation to a Conservative Element

The metal concentrations were normalised to the most commonly used conservative element, Al. However, before using this method, it was necessary to check if such a normalisation procedure can be applied to our data set. According to Loring[11] in order to use this method a linear positive relationship must exist between the concentrations of metals and the concentrations of Al and, also, a linear positive relationship must exist between the Al concentration and the percentage of fine-grained material content of the samples. In the data set of the coastal sediments of Mytilene both conditions applied. Figures 2 and 3 present the regression of Al on the percentage of silt + clay ($r^2 = 0.70$, $p < 0.01$)

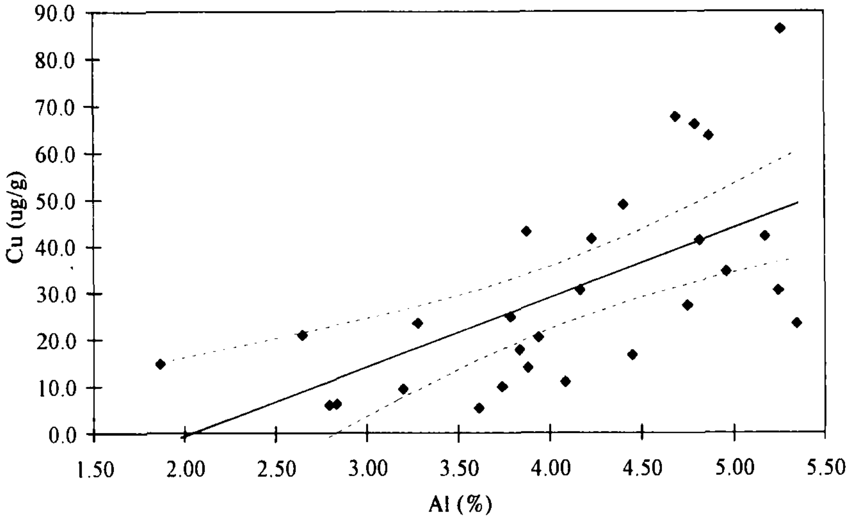

FIGURE 3 Cu: Al plot for the sediments of the coastal area of Mytilene. Solid line represents the regression line, dashed lines define the 99% confidence band.

and the regression of Cu on Al (r^2 = 0.39, $p < 0.05$) respectively. For the regression of the other metals on Al, the values of r^2 were: Cd: 0.18, Fe: 0.79, Li: 0.80, Pb: 0.19, Zn: 0.31. All coefficients were statistically significant at a 0.05 probability (those for Cu, Fe, Li and Zn, were statistically significant at a 0.01 probability).

The normalised data were used to calculate the enrichment factors of the metals in the different stations by dividing the ratio Metal/Al of each station by the ratio Metal/Al of a reference non-contaminated area. These enrichment factors (EF) are presented in Table IV. For the calculation of EFs the mean of the normalised concentrations from the 6 most remote stations of the area (stations 22, 23, 25, 27, 28 and 29) was used as reference (non-contaminated area). The mean normalised values of the non-contaminated reference area were: Cd/Al = 0.015 ± 0.005, Cu/Al = 2.64 ± 1.08, Fe/Al = 0.376 ± 010, Li/Al = 4.55 ± 1.55, Pb/Al = 8.48 ± 1.54, Zn/Al = 8.86 ± 3.37.

The calculated EFs revealed that only the sediments of the harbour of Mytilene (stations 1 to 8) can be considered as polluted with Cd, Cu and Zn, because the EFs of these metals in the above mentioned stations were higher than 2. It was assumed that sediments with an EF < 2 may be considered as non-contaminated due to natural mineralogical differences of the sediments and analytical uncertainty. Cadmium, Cu and Zn presented the highest EFs in the inner harbour of Mytilene (stations 1–5). These metals have relatively high concen-

TABLE IV Enrichment factors [$(Me/Al)_r$ is the ratio in the reference area]

Station	$(Cd/Al)/(Cd/Al)_r$	$(Cu/Al)/(Cu/Al)_r$	$(Fe/Al)/(Fe/Al)_r$	$(Li/Al)/(Li/Al)_r$	$(Pb/Al)/(Pb/Al)_r$	$(Zn/Al)/(Zn/Al)_r$
1	5,11	5,23	1,49	1,35	2,03	4,08
2	5,46	4,95	1,31	1,17	1,79	4,28
3	5,56	6,21	1,42	1,36	2,08	4,93
4	2,88	4,21	1,50	1,37	1,58	3,26
5	5,87	5,46	1,51	1,37	1,97	4,59
6	3,54	4,21	1,55	1,39	1,56	3,30
7	3,28	3,72	1,47	1,47	1,76	3,57
8	4,38	3,01	1,44	1,24	1,46	3,56
9	0,90	2,64	1,45	1,53	0,91	1,69
10	1,99	3,25	1,51	1,30	1,33	2,63
11	1,91	3,07	1,33	1,25	1,29	2,52
12	2,74	2,78	1,28	1,25	1,46	2,58
13	1,15	2,18	1,34	1,25	1,10	1,64
14	1,07	1,66	1,35	1,52	0,88	1,54
15	1,06	2,20	1,39	1,33	0,96	1,57
16	4,12	2,49	1,20	1,14	1,95	2,34
17	1,00	1,42	1,04	1,07	0,92	1,16
18	0,71	1,97	1,17	1,08	1,11	1,58
19	2,06	2,71	1,10	0,85	2,11	2,77
20	1,08	1,11	1,07	1,00	1,13	1,37
21	1,73	3,02	1,10	1,05	3,47	2,73
22	0,78	1,01	0,96	0,90	0,76	1,02
23	1,29	0,82	1,07	0,92	0,87	0,93
25	1,41	0,83	1,08	0,96	1,24	1,19
26	1,28	1,37	1,21	1,17	1,05	1,22
27	0,72	1,02	0,89	1,01	1,06	0,89
28	0,56	0,56	0,59	0,59	0,91	0,40
29	1,23	1,76	1,42	1,62	1,15	1,56

trations in the city effluents[13] and are deposited in the harbour mud forming an important depository of human related metals. Lead enrichment was much smaller in the harbour sediments, although Pb is considered as an effluent related metal. This is probably because apart from the presence of the metal in the city effluents, traffic derived Pb is transported to the sea mainly through the atmosphere, thus affecting the Pb concentration of the relatively remote marine sediments. Therefore, the EF of Pb calculated for Mytilene harbour sediments may have been underestimated because of relatively enhanced Pb concentrations in the sediments used as reference.

The process of metal enrichment in the harbour sediments described above is also supported by the strong positive correlations ($r > 0.9$, $p < 0.001$) between the concentrations of the effluent associated metals with each other (e.g. Cd, Cu, Pb and Zn) (Table II), together with the strong positive correlations of these metals with organic carbon content (i.e. Cd: $r = 0.69$, $p < 0.001$; Cu: $r = 0.85$, $p < 0.001$; Pb: $r = 0.74$, $p < 0.001$; Zn: $r = 0.81$, $p < 0.001$). These correlations indicate that Cd, Cu, Pb and Zn may be considered as metals with a common anthropogenic origin, as opposed to Al, Fe and Li, which may be considered of natural origin. These latter metals correlated very strongly with each other but had weaker correlations with the effluent associated metals.

From the EFs presented in Table IV it is clear that the wider coastal area of Mytilene is not contaminated by effluent derived metals. It seems that the harbour area acts as a trap for the metal bearing particles. Furthermore the fine metal-rich particles that may escape towards the coastal environment are dispersed by the strong current that prevails in the straight of Mytilene (between Lesvos island and the coast of Asia Minor).

CONCLUSIONS

The normalisation to a conservative element (in this case Al) and the calculation of enrichment factors of the metals, was a method that helped to assess the geographical distribution of the metal contamination in the coastal area of Mytilene.

The metals which are related to the city effluents (Cd, Cu and Zn) were highly enriched in the sediments of the harbour of Mytilene. Lead was also slightly enriched in the harbour sediments but it was apparent that it is transported to the marine coastal environment through a different process (probably through the atmosphere).

The sediments of the wider coastal area, outside the harbour, were not metal enriched. This is an indication that the important deposits of metal-rich mud of the harbour do not influence the wider coastal environment.

The normalisation procedure applied seems to be very effective in assessing metal contamination of relatively coarse coastal sediments.

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