HEAVY METAL INVESTIGATION, AS POLLUTANT INDICATORS, IN BOTTOM SEDIMENTS, IN THE HARBOURS HERAKLION AND ALEXANDROUPOLIS (AEGEAN SEA, GREECE).

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EXTENDED ABSTRACT

This study examines the concentrations of Pd, Cu, Zn and Cd in two large Greek harbours located in the Aegean Sea; these are: the harbour of the city of Heraklion (Southern Aegean, Cretan Sea) and the harbour of the city of Alexandroupoli (NE coast of the Aegean Sea).The harbour of Heraklion city is located in the northern continental shelf of the island of Crete, which is very narrow (<2km) and relatively steep sloping. The harbour of Alexandroupolis has a length of 2km and it is located in the homonymous Gulf which belongs to the inner continental shelf of the NE Aegean (Samothraki Plateau).

The present contribution is based on thirteen and eleven samples recovered from the surrounding area of the Heraklion and Alexandroupolis harbour, respectively. The concentrations of the metals (Pd, Cu, Zn and Cd) have been determined with the use of the method of atomic absorption, whilst the enrichment factor has been calculated according to the standard values for the Mediterranean Sea, proposed by the World Health Organization (WHO, 1995).

The concentration of Cu in Heraklion harbour varies in between 13.65 and 70.31 ppm, slightly higher than those of Alexandroupolis harbour, where they vary from 6.9 to 69.9 ppm. Pb and Cd in Alexandroupolis present relatively higher values (Pb: 13.5-107.1, Cd: 0.08-1.47) compared to the Heraklion (Pb: 10.42-63.0 ppm and Cd: 0.8-14.7 ppm). Zn concentrations in Alexandroupoli, ranging from 55.8 to 172.0 ppm, are much higher than those of Heraklion (29.6-125.3 ppm).

In both coastal areas the environmental impact of the harbours can be identified as in most of the stations the enrichment factor is greater than 1 and for all metals except Pb. However, they cannot be characterized as highly contaminated areas. This is in accordance to the hydrodynamic conditions that favour the mobility of the sea bed sediments.

Keywords: Heraklion, Alexandroupolis, harbour, heavy metals

1. INTRODUCTION

Bottom sediments within harbour basin and their surrounding area have been often found to be polluted. This is due to: (i) the fact that harbours have been designed to minimise hydrodynamic energy within harbour basin, reducing, therefore, the ability of the water and seabed sediments to be renewed; and (ii) the presence of human activities relating to both the operation (e.g loading and unloading, accidental spills) and/or the utility of presence of the harbour nearby of coastal city for the disposal of urban and industrial wastes (Guerra et al., 2000). On the other hand, heavy metals have been widely used as pollutant indicators in sea bed sediments.

Within this framework, this study examines the concentrations of Pd, Cu, Zn and Cd in the surficial sea bed sediments outside the two large Greek harbours (Heraklion and Alexandroupolis) in order to identify the level of pollution (if any) related to their presence.

2. STUDY AREA

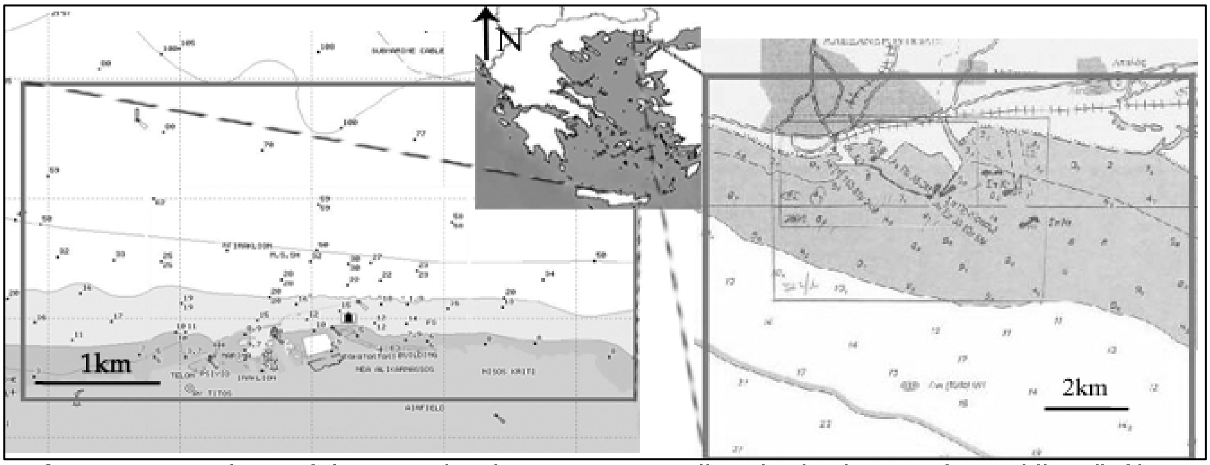

Figure 1: Locations of the examined areas surrounding the harbours of Heraklion (left) and Alexandroupolis (right) (charts provided by the Hellenic Hydrographic Service)

The harbour of Heraklion city is located in the northern continental shelf of the island of Crete, which is very narrow (<2km) and relatively steeply sloping (gradient: 1.5) with the shelf break to be generally in water depths of 100-150m (Chronis et al., 2000). The surficial seabed sediments according to their grain-size can be divided in three zones: the first zone (depths <40 m) in which prevails the sand, a transitional zone (40-70m) where the percentages of mud fraction are increased >50% and a third zone (depths >70 m), where mud fraction is the dominant (>90%) material (Alexandrakis et al., 2006). Offshore currents appear to be relatively weak (10 cm/s) with the main direction of variability to be along isobaths. Although during spring and summer there are periods when inner-shelf circulation is bi-directional, the overall annual (residual) direction is towards the east. The area is exposed mainly to wind generated waves of N, NE and NW direction, with the NW wind to be the dominant one annually (annual frequency 28.89%), whilst on a monthly basis is the most frequent with the exception of the period November to January, when north waves are prevailing. The highest expected waves exceed the 6m in height and the 11 sec in period (Athanasoulis & Skarsoulis, 1992). These high waves are capable to mobile surface sediments (closure depth) up to water depths of more than 11 m (Ghionis et al., 2004).

The harbour of Alexandroupolis is located in the homonymous Gulf which belongs to the inner continental shelf of the NE Aegean (Samothraki Plateau). The relief of the seabed is smooth with very low gradients (<1%), extending several km offshore. The harbor has its west pier extending to the ESE direction up to 2km seawards. Seabed has a zonal granulometric distribution with the nearshore area consisting of sand, the offshore zone of fine–grained (muddy) sediments, whilst in water depths larger than 20m relict sand deposits exist. Besides, 10 km to the east, the river Evros (drainage basin 52.500km^2), discharges annually some $3.2x10^6$ tonnes of sediment (Pehlivanoglou, 1989) with some of the riverine sediment to be transferred towards the harbour area.

Although coastal surface circulation is predominately westward due to the Coriolis Effect on the Evros outflow, with the exception of the period of maximum river discharge (around March) the currents near sea bed have an opposite direction. Current meter measurements indicate that the circulation is dictated mainly by the fringes of the

Samothraki anti-cyclone which implies an eastward circulation along the isobaths (~ 17 cm/s).
The gulf is exposed to waves, caused predominately by S and SW winds, while coastal sediment transport has a dominant east to west direction, especially for the region to the east of the harbour (Pehlivanoglou, 1989). Wave heights induced by average wind speeds (4-5 B) are in the order of 1,3 m, reaching values of 5 m during storms (Athanasoulis & Skarsoulis, 1992); these wave heights are expected to break at water depths of about 2,5m and 6.5 m, respectively; this results to the formation of an extended breaking zone which, in turn, implies an extended zone of resuspension of surficial seabed sediments (Karditsa, 2006).

3. METHODOLOGY

Thirteen sediment samples have been collected from the surrounding area of the Heraklion harbour with the use of a van Veen grab. The sampling area is 6 km wide, reaching the depth of 70m. In the case of the Alexandroupolis harbour, eleven samples have been recovered from the area surrounding the harbour (some $20km^2$), in water depths less than 20m being in a distances of up to 5km from the shoreline due to the low-graded bathymetry (sampling positions are shown on Fig. 2).
The concentrations of the metals (Pd, Cu, Zn and Cd) have been determined with the use of the method of atomic absorption, whilst the enrichment factor (EF) has been calculated according to the standard values for the Mediterranean Sea, as given by the World Health Organization in 1995, by using the equation:

$$EF = \frac{Cm}{Cs}$$

Where C_m is the measured concentrations and C_s is the standard values, these are: Cu: 13ppm; Pb: 38ppm; Cd: 1ppm; and Zn: 45ppm. When the EF>1 then we can say that the sample has values higher than the natural ones.

4. RESULTS AND DISCUSSION

4.1 Heavy metal concentration values

The results of the analyses concerning the heavy metals under investigation for both harbour areas are presented on Table 1 and shown schematically in Figure 2.
The concentrations of Cu in Heraklion harbour varies in between 13.65 and 70.31 ppm (average value 34.30) being slightly higher than those of Alexandroupolis harbour, where they vary from 6.9 to 69.9 (average value15.25 ppm). On the other hand Pb and Cd presents relatively higher values in Alexandroupolis (Pb: 13.5-107.1, aver 50.78ppm Cd: 0.08-1.47, aver.0.62ppm) compare to the Heraklion (Pb: 10.42-63.0, aver. 46.39ppm and Cd: 0.8 ppm). Zn concentrations in Alexandroupoli, ranging from 55.8 to 172.0 (average value 107.72), are much higher than those of Heraklion (29.6-125.3; aver.72.48 ppm).
In the case of the Heraklion harbour area, the highest values of Pb, Cd and Zn being measured in station H8, which is located on the main route of navigation from and towards the harbour entrance, have been attributed to the navigation. The highest Cu value found in station H4, located to the west of the harbour, maybe related to the electricity power plan station established on the shore zone and the city's waste treatment plant which discharge in River Giofiros (2 km to the west of the Harbour). In general the lowest values are observed to the stations away from the harbour and close to the coastline. For Cu and Zn station H2 showed the lower values, while for the Pb and Cd the lower values were in station H1. Both of them are westwards to the harbour (figure2).

Table 1: Heavy metal concentration values (in ppm) for the Heraklion and Alexandroupolis harbour areas.

HERAKLION HARBOUR					ALEXANDROUPOLIS HARBOUR				
Stn	**Cu**	**Pb**	**Cd**	**Zn**	**Stn**	**Cu**	**Pb**	**Cd**	**Zn**
H1	23.14	10.42	0.08	41.27	**A1**	15.27	19.00	0.92	55.84
H2	13.65	29.33	0.29	29.63	**A2**	12.43	13.50	1.16	78.47
H3	21.66	37.25	0.38	35.90	**A3**	36.98	53.08	10.87	155.24
H4	**70.31**	47.17	0.61	77.02	**A4**	42.31	56.93	4.07	110.65
H5	51.19	45.62	0.58	79.64	**A5**	**69.87**	**107.14**	**11.95**	**171.64**
H6	52.52	48.23	1.36	99.23	**A6**	55.16	78.37	7.55	128.62
H7	35.88	45.56	0.79	82.07	**A7**	9.61	16.47	6.93	94.20
H8	37.12	**63.00**	**1.47**	**125.32**	**A8**	6.88	20.46	2.58	69.03
H9	29.72	61.09	1.39	110.76	**A9**	69.22	99.00	17.61	152.75
H10	23.43	57.92	0.83	61.70	**A10**	51.48	70.00	4.36	111.14
H11	33.72	58.06	1.22	52.17	**A11**	9.09	24.64	0.92	57.30
H12	25.10	51.70	0.79	81.33	**Aver.**	34,39	50,78	6,27	107,72
H13	29.72	47.69	0.61	66.24	All values are in ppm				
Aver.	34.40	46.39	0.80	72.48					

The Zn, Cu and Pb concentrations measured in Alexandroupoli harbour area present their highest values in Station 5, which is located within the harbour basin. The highest value of Cd, measured in Station 9 is attributed to nearby outflowing waste treatment plant and the offshore station of fuel loading. The lowest values were observed in station A8 for Cu , A2 for Pb, in stations A1, A11 for the Cd and A1 for Zn. These stations are located close to the coastline (figure2).

The two harbours under investigation in terms of heavy metal concentrations are comparable to other Greek harbours of similar size and traffic (e.g. Kavala, Stavros, Mitilini, Volos), whilst the more 'busy' harbours of Piraeus and Thessaloniki present much higher concentrations (Table 2).

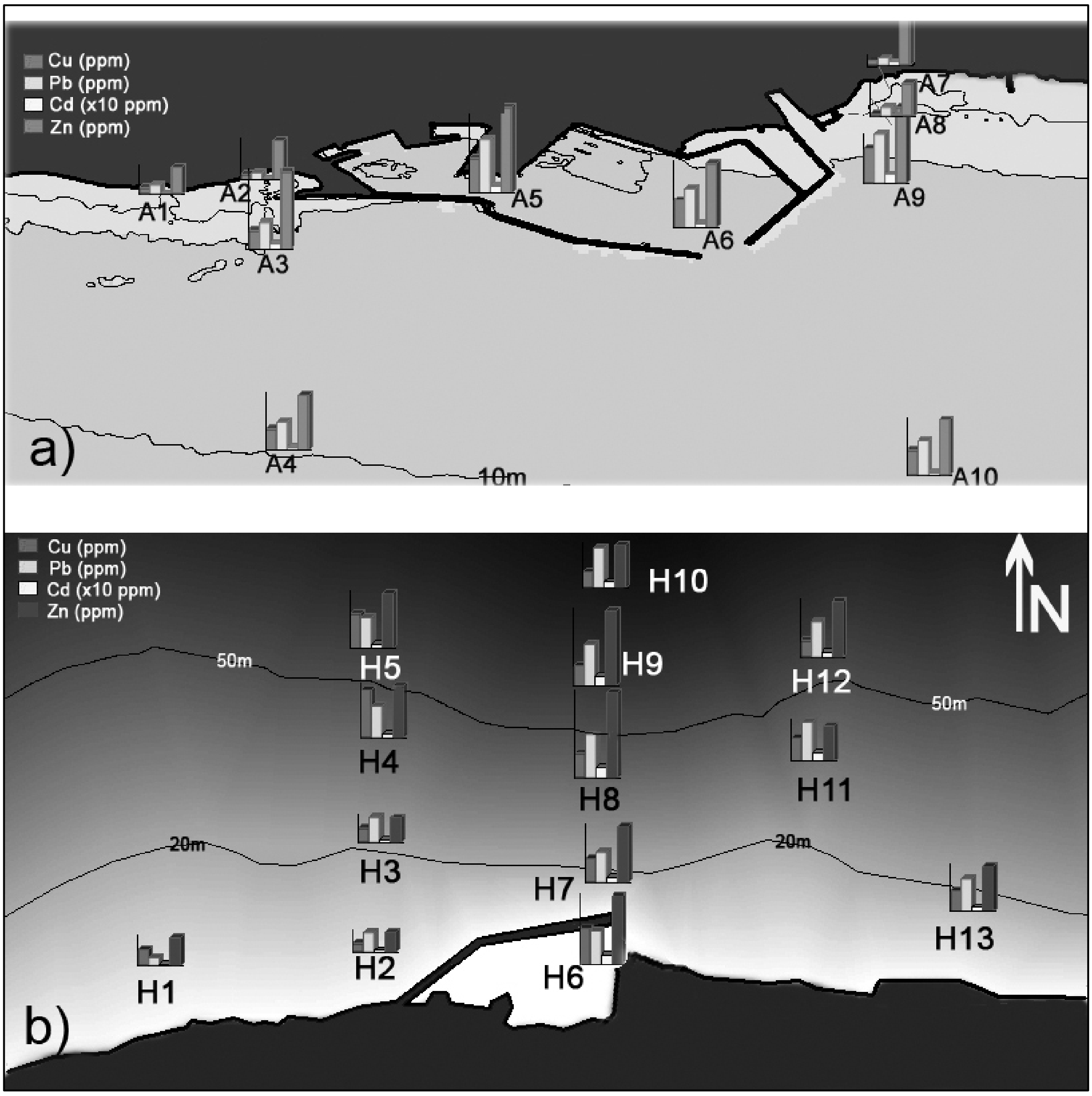

Figure 2: Heavy metal concentrations in the surface sediment of the Heraklion (a) and Alexandroupolis (b) harbour areas.

Table 2: A comparison of mean calculated values (in ppm) with those of other harbours (Sources: 1;NKUA, 2;NCMR)**.**

Port	Cd (ppm)	Pb (ppm)	Zn (ppm)	Cu (ppm)
Alexandroupolis	0,622	49,9	107,7	34,4
Heraklion	0,80	46,39	72,48	34,4
Thessaloniki[1]	0,620	146,2	220,6	66,9
Kabala[1]	0,452	72,0	129,1	36,1
Stavros[1]	0,164	23,6	53,6	18,0
Mitilini[1]	0,285	42,9	113,0	39,3
Volos[1]	0,129	37,1	89,5	25,3
Piraeus[2]		142-157	635-724	305-313

4.2. Enrichment Factor

The values of the calculated enrichment factor (EF), on the basis of standard values given by the WHO (WHO, 1995) for the Mediterranean Sea, for both harbour areas are listed on table 3 and presented graphically on figure 3.

Table 3: Enrichment factor (EF) calculated for the Heraklion and Alexandroupolis harbour areas.

HERAKLION HARBOUR					ALEXANDROUPOLIS HARBOUR				
Stn	**Cu**	**Pb**	**Cd**	**Zn**	**Stn**	**Cu**	**Pb**	**Cd**	**Zn**
H1	1.78	0.02	0.08	0.92	**A1**	1.17	0.02	0.09	1.24
H2	1.05	0.08	0.29	0.66	**A2**	0.96	0.03	0.12	1.74
H3	1.67	0.10	0.38	0.80	**A3**	2.84	0.29	1.09	3.45
H4	5.41	0.16	0.61	1.71	**A4**	3.25	0.11	0.41	2.46
H5	3.94	0.15	0.58	1.77	**A5**	5.37	0.31	1.19	3.81
H6	4.04	0.36	1.36	2.21	**A6**	4.24	0.20	0.75	2.86
H7	2.76	0.21	0.79	1.82	**A7**	0.74	0.18	0.69	2.09
H8	2.86	0.39	1.47	2.78	**A8**	0.53	0.07	0.26	1.53
H9	2.29	0.37	1.39	2.46	**A9**	5.32	0.46	1.76	3.39
H10	1.80	0.22	0.83	1.37	**A10**	3.96	0.11	0.44	2.47
H11	2.59	0.32	1.22	1.16	**A11**	0.70	0.02	0.09	1.27
H12	1.93	0.21	0.79	1.81					
H13	2.29	0.16	0.61	1.47					

In the basin of Heraklion harbour the enrichment factor (EF) for the heavy metals showed that their values are higher than the standard values of the Mediterranean Sea (WHO, 1995). The values of the nearby area outside the harbour basin present concentrations above the standard values but lower than those inside the harbour basin and presenting increased values along the navigation routes. An exception is the EF for Pb, which is below the standard value proposed by WHO. For all the metals, the enrichment factor is larger to the stations located eastwards of the harbour entrance, which is also towards east (Cu: 1,93 & 2,59 , Pb: 1,53 & 1,36, Cd: 0,79 & 1,22, Zn: 1,16 & 1,81). In addition, the highest observed EF value of Cu, outside the harbour basin (station H4), is related to the outfall of the waste treatment plant of the city of Heraklion.
Similarly, in the basin of Alexandroupolis harbour the EF values (Cu: 4,81; Pb: 0,03; Cd: 0,97; Zn:3,34) have been found to be greater than the standard Med-values given by the WHO (1995). Outside the harbour basin, values, in general, have been found to be lower than those of the harbour basin, but still greater than the standard WHO values. The only exception comes again from the station nearby the waste treatment plant and the fuel loading pipe, both located about 0.5 km eastwards of the harbour, where all values appear to be higher (Cu:5,32; Pb:0,05; Cd:1,76; Zn:3,39) than the other values of the samples outside the harbour. The lowest values for all metals were referred to the deepest station seawards.

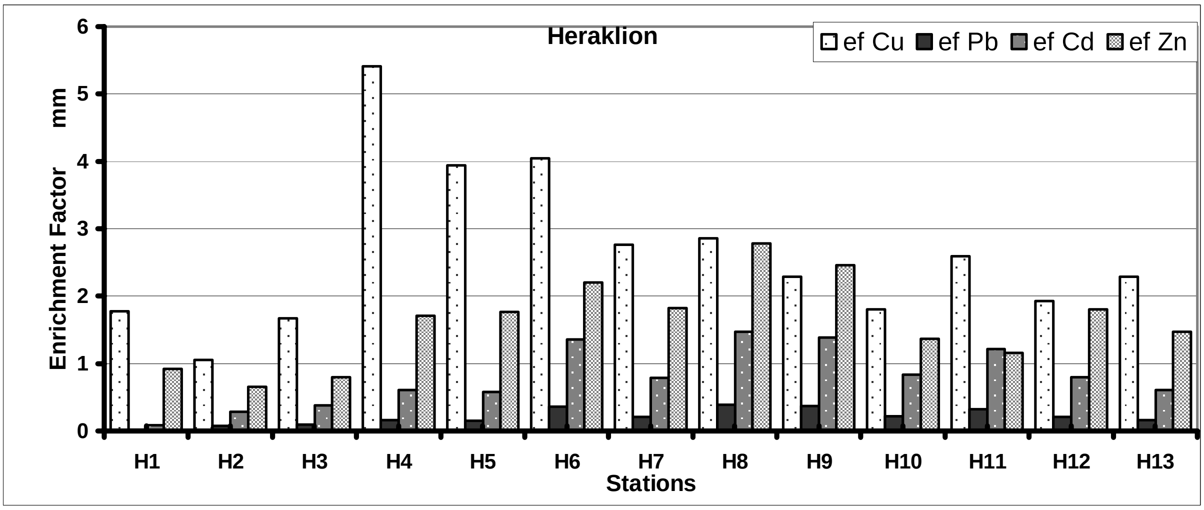

Figure 4: Graphic presentation of the enrichment factor for the Heraklion area.

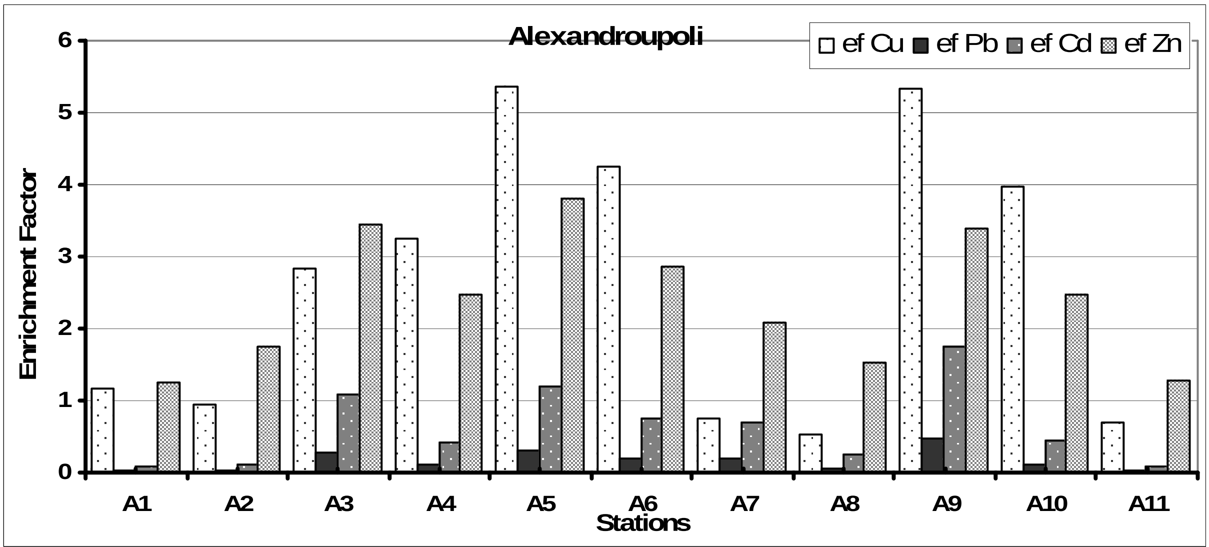

Figure 5: Graphic presentation of the enrichment factor for the Alexandroupolis area.

The comparison between the two areas shows that the heavy metal concentrations from Heraklion harbour present slightly lower EF values than those of Alexandroupoli, despite the fact that it is characterized by heavier traffic compare to the harbour of Alexandroupolis. This may be explained firstly by the fact that the sea bed sediments in Crete are coarser (heavy metals are better connected to fine-grained sediment) and secondly by the more intensive hydrodynamic (e.g. waves) regime associated with increased water depths, favouring self-cleaning of the coastal system.

5. CONCLUSIONS

In both coastal areas the environmental impact of the harbours can be identified, although they can not be characterized as highly contaminated areas. Relatively increased heavy metal concentrations are observed within the harbour basins and along the navigational routes, whilst the highest values found to be associated with sewage outflows that discharge close to the harbours. In the overall heavy metal distribution seems to play a role the local sedimentological and hydrodynamic conditions which favour either the absorption of the pollutants and/or increase the mobility of the surficial sea bed sediments.

REFERENCES

1. Alexandrakis G., Dounas C. and Poulos S., 2006. The relation between the grain-size and heavy metal concentrations in the surficial bottom sediments of the gulf of Heraklion, Crete. *8th Panhellenic Symposium of Oceanography and fishery*, Thesalloniki 4–8 June 2006
2. Athanasoulis, G.A. and Skarsoulis, E.K., 1992. Wind and wave atlas of the Mediterranean Sea. *Hellenic Navy General Staff*, Athens.
3. Chronis G., Lykousis V., Anagnostou C., Karageorgis A., Stavrakakis S., Poulos S., 2000 Sedimentological processes in the southern margin of the Cretan Sea (NE Mediterranean) *Progress in Oceanography 46 pp 143–162*
4. Guerra RM, Martın R, Vila J, Romo J. 2000 Informe de Caracteritzacio delssediments en el Port de Barcelona. *Servei de ´Medi Ambient de l'Autoritat Portuaria de Barcelona*.
5. Ghionis G., Poulos S., Bouziotopoulou N., Dounas C. 2004. The role of a natural submerged breakwater in controlling the hydrodynamic and sedimentological conditions of Ammoudara beach (Heraklion, Crete)., *7th Panhellenic geographical conference of the Hellenic geographical society , April 2004 Mitilini*
6. Karditsa,. 2006. Coastal environmental study in Alexandroupolis gulf, in relation to its harbour expansion. *Unpublished MSc Thesis*, University of Athens, School of Science, 117pp.
7. National Centre of Marine Research (NCMR), "Quality of materials from the dredging of central port of Piraeus", *Technical study for the Organism of Piraeus Port* (OLP), 1996.
8. Pehlivanoglou, K. 1989. Evros delta, evolution of continental shelf sediments. *Marine Geology 87: 27- 29.*
9. University Athens, Department of Chemistry (2005). Results of the monitoring program for the quality of the environment of Greek seas (Network of laboratories of monitoring the quality of the environment of the Greek Seas), April 2005.
10. WHO/UNEP, 1995 Health risks from marine pollution in the Mediterranean . Part II. Review of hazards and health risks. *Document EUR/ICP/EHAZ94 01/MT 01 (2*) World Health Organization, Regional office for Europe, Copenhagen