LEVELS AND DISTRIBUTION OF HEAVY METALS AND TOC IN THE SURFACE SEDIMENTS OF THE BAY OF SOUDA

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EXTENDED ABSTRACT

The bay of Souda is an important natural harbour in the north west of the island of Crete. Its area is about 21 Km^2 and its maximum depth 210m. The bay receives the inputs of the Moronis River that discharges at the inner part of the bay. The commercial and the naval port, as well as the city of Souda are located at the west-south coast of the bay.

The aim of this work is to assess the levels and the spatial distribution of several heavy metals and organic carbon of the surface sediments of the bay and identify the major sources of pollution.

A sampling cruise was carried out during February 2008 in a sampling network consisting of one estuarine, two coastal and ten marine stations within the bay of Souda. The sediment samples were collected using appropriate sediment samplers.

The contents of the sediments in nine metals (Zn, Mn, Pb, Ni, Cd, Cu, Fe, Al and Hg) were determined by Atomic Absorption Spectrometry after total dissolution of the sediment samples by strong acids. Total Organic Carbon (TOC) was determined by a standard volumetric method.

According to our results, elevated values for the majority of the studied metals were determined in the central and western part of the bay near the cove (mean values for Zn, Pb, Cu and Hg were 95.5, 42.4, 39.2 and 0.128 mg/Kg, respectively against 36.2, 22.2, 17.1 and 0.053 mg/Kg respectively at the rest of the bay) indicating that the discharges of the river Moronis, the activities of the Naval Base as well as of the Commercial Port, influence the bay's sediment as well as seawater (Dassenakis et al, 2012). In the case of Cadmium an opposite trend was observed, as the highest values were detected in the south part of the bay's entrance (0.144, 0.109 and 0.06 μg/g for the estuaries of the river, the entrance of the bay and the rest of the bay's area respectively). This trend is not clear for Nickel and Manganese. A statistically important correlation (according to the t-test) between Al and Fe as well as between Al and Mn (r = 0,989 and 0,809 respectively) was found, indicating a common origin, probably geological, for those three metals.

According to the SQGs, none of the metals studied exceeded the perspective ERMs/PELs, the values above which adverse effects on benthic biota are frequently observed. However, the levels of Cu, Pb, Zn and Hg found in the sediments of the river estuary and close to the naval base exceed the low-range values (ERLs/TELs). Therefore, pollution control measures and monitoring programs including toxicity tests on biota are needed for protecting and/or restoring the sediment quality. The values of TOC measured were lower than 0.3 % (w/w) indicating a relatively low content of the sediment in organic carbon.

In conclusion, we can say that the surface sediments of the bay are not enriched in metals and TOC, with the exception of the areas near the river's estuaries and near the naval and commercial harbour. Nevertheless, the values measured are lower than the ones prevailing in other Greek marine areas near big cities such as Saronikos gulf, Thermaikos gulf and South Evoikos gulf.

KEYWORDS: heavy metals, sediments, Souda, TOC, SQGs

1. INTRODUCTION

The bay of Souda is an important natural harbour in the north-west part of the island of Crete, 6 Km east of the city of Chania. Its area is about 21 Km^2 and the length of its coastline is about 24 Km. The bay's length is about 8.5 Km and its width varies between 2 and 3.3 Km. Its mouth is relatively small (1.5 Km) and its maximum depth reaches the 210m. The high mountain (Madares – 2,453 m) lying in the south of the bay in combination with the high hills that surround the bay, are natural obstacles that weaken and veer the winds. A weak anticlockwise surface current is recorded close to the coastline.

The bay's water and sediments are exposed to various activities that can be considered as potential pollution sources: The activities of the commercial harbour and the ones of the naval base, the dredging activities that take place almost continuously for the last 60 years, the discharges of the small Moronis River at the inner part of the bay, as well as the agricultural wastes consisting of residuals of fertilizers and pesticides that discharge into the bay via runoff. Furthermore, although the urban waste water of the city of Souda do not discharge into the bay, domestic untreated waste waters of various inhabited areas around the coastline are considered as a potential source of pollution.

2. MATERIALS AND METHODS

A sampling cruise was carried out at the area during February 2008 in a sampling network consisting of one estuarine (SD13), two coastal (SD19, SD17) and ten marine stations within the bay of Souda (figure 1), and surface sediment samples were collected from all locations using appropriate Van Veen sediment samplers.

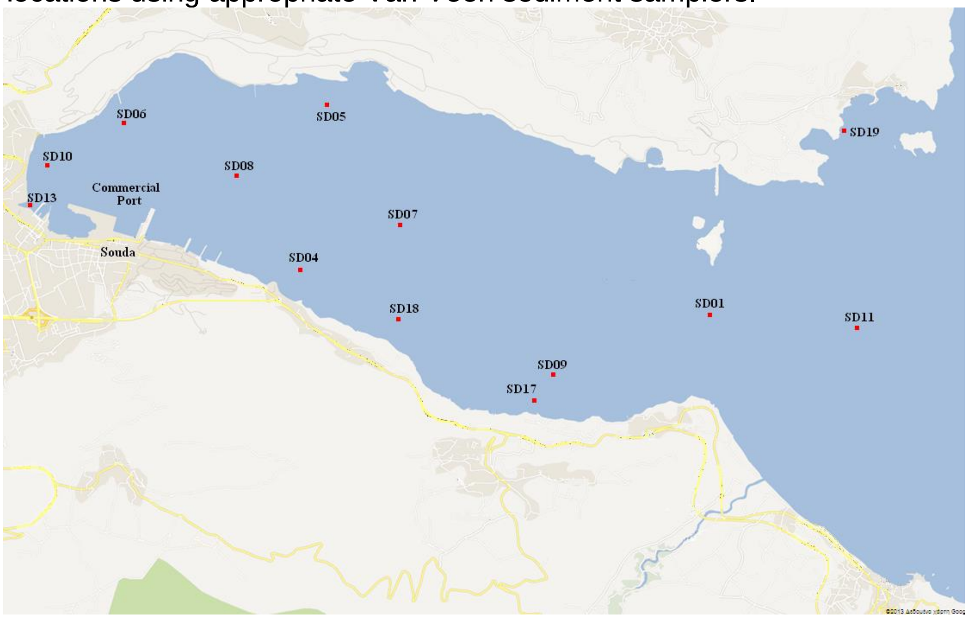


Figure 1: The bay of Souda and the sampling stations

The sediment samples were lyophilized with a LabCongo apparatus and then were sieved through a 63μm sieve. All determinations were carried out in the fraction having grain size < 63μm (mud); a portion of the sediment sample was treated with a mixture of strong acids ($HClO_4$-HNO_3-HF) into PTFE bakers at 200 ^oC to ensure total dissolution and the total metal contents of the sediments (Zn, Mn, Pb, Ni, Cd, Cu, Fe and Al) were determined in the obtained acid solution (Thompson and Walsh 1983, UNEP 1985).

For the determination of the Hg, a portion of each sediment sample was treated with extra pure concentrated HNO_3 into PTFE bakers at 100 ºC for 2h. After cooling to room temperature, the digests were diluted with MQ water to appropriate final volumes.
Flame and furnace atomic absorption spectrophotometry were used in order to determine the concentration of the acid solution in all metals but Hg, using a VARIAN SpectrAA 200 instrument (Flame AAS) and a VARIAN SpectrAA 640Z instrument (Graphite Furnace AAS) with Zeeman background correction.
The pseudo-total Hg contents were quantified by CVAAS with a Varian (SpectrAA-200) equipped with a vapour generation accessory (Varian VGA-77).
The content of the sediment in TOC was determined titrimetrically using the Walkey-Black method (Jacson 1958) as modified by Gaudette et al (1974) for marine sediments.
The accuracy and the reproducibility of the methods employed were tested through reference materials and replicate samples.

3. RESULTS AND DISCUSSION

3.1 Metals in the surface sediment

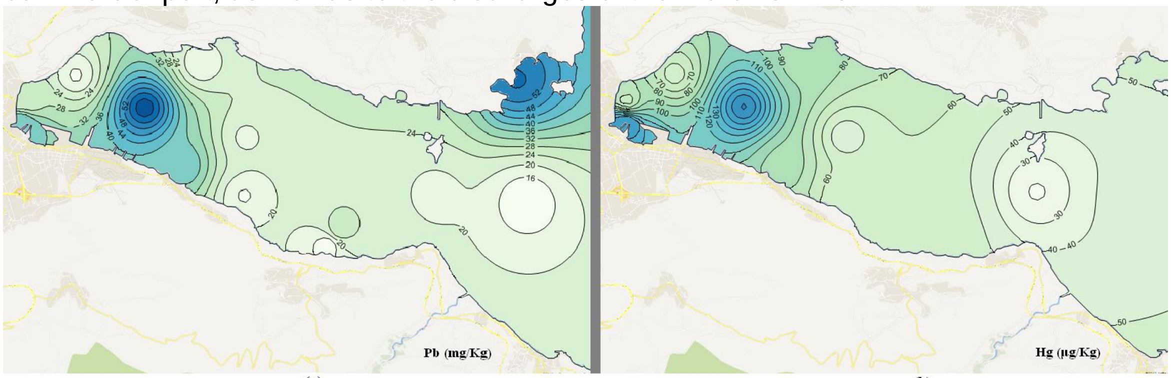
The average content of the surface sediment (3 replicates of each sample) in metals and TOC is presented in table 1:

Table 1: Metal contents and TOC of the surface sediments of Souda Bay

Sampling point	TOC (%)	Zn (mg/Kg)	Mn (mg/Kg)	Pb (mg/Kg)	Ni (mg/Kg)	Cd (mg/Kg)	Cu (mg/Kg)	Al (% w/w)	Fe (% w/w)	Hg (μg/Kg)
SD01	1,16	48,3	194	18,7	57,2	0,109	21,7	3,33	2,07	18,9
SD09	1,29	53,5	145	27,5	60,8	0,049	25,6	2,96	1,74	56,0
SD10	1,89	49,7	113	23,7	47,4	0,045	26,6	2,57	1,37	64,2
SD17	0,91	31,5	182	13,1	59,4	0,075	16,3	2,45	1,50	52,1
SD18	0,29	26,8	129	15,5	62,8	0,070	14,2	1,47	0,92	52,0
SD19	0,77	15,9	90	56,6	56,4	0,082	7,6	0,80	0,42	
SD04	0,95	67,0	210	39,7	52,2	0,050	33,9	3,44	2,06	86,0
SD05	0,70	28,7	170	16,4	56,9	0,042	12,1	1,52	0,97	85,1
SD06	0,94	26,8	125	15,2	31,2	0,045	11,6	1,70	0,95	54,9
SD07	1,50	52,2	308	19,0	68,9	0,076	19,1	4,05	2,31	43,0
SD08	1,18	85,4	208	62,8	56,6	0,055	46,4	3,32	2,13	171,3
SD11	1,34	44,4	212	12,9	50,8	0,066	18,3	3,16	1,98	41,9
SD13	2,93	177,4	201	48,0	53,9	0,144	57,6	2,53	1,54	213,3
Mean	1,22	54,4	176	28,4	55,0	0,070	23,9	2,56	1,54	78,2

The highest values for Zn, Cd, Hg and Cu were recorded at the sampling station SD13, near the estuary of the Moronis river, indicating that this small river is a considerable metal pollution source for the sediments of the bay of Souda.
Increased values for the most of the metals were also determined in the sampling stations close to the naval base and the commercial port (SD04, SD07 and SD08) indicating that they are responsible for the enrichment of the nearby sediments in metals and organic carbon.
On the other hand the lowest values for Zn, Mn, Cu, Al and Fe were detected in the coastal station SD19 that lies just outside the bay.
Low values for the most of the metals were also recorded in the sampling station in the mouth of the bay (SD01) as well as in sample station SD11 that lies outside the bay in the open sea.

All the metals but Cd are enriched in the sediments of the central part of the bay as well as in the one of the estuaries of the river Moronis (Zn, Mn, Al, Fe, Pb, Hg) as shown in figure 2 where the spatial distribution of Pb and Hg in the surface sediments of the bay is presented. This enrichment is attributed to the activities of the naval base and the commercial port, as well as to the discharges of the Moronis River.

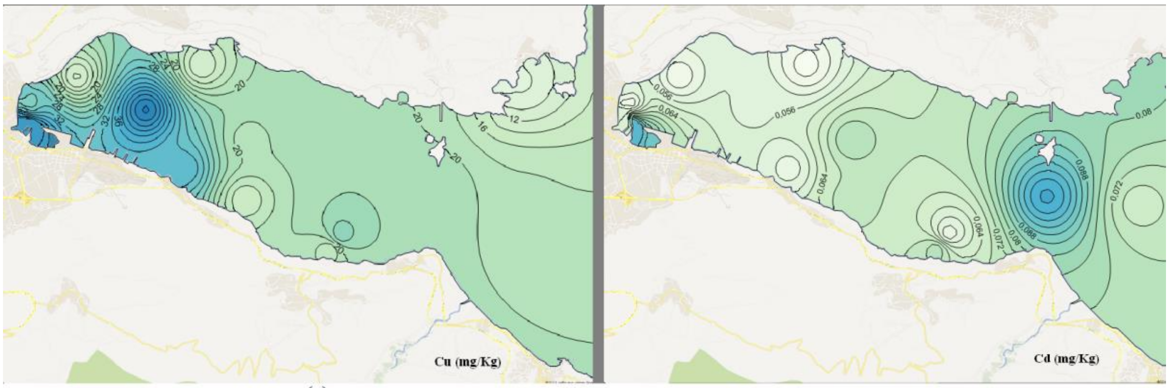


(a) (b)

Figure 2: The spatial distribution of the content of the surface sediments of the bay in Pb (a) and Hg (b)

The lowest values of the sediments' contents for all the metals (with the exception of Pb) were recorded in the sampling point SD19 which lies outside the bay.

Regarding the entrance of the bay (sampling points SD01 and SD11), the sediments' content in all metals (with the exception of Cd) is lower than the respective ones in the sediments inside the bay (figure 3a). Cd shows a different accumulation trend than the other metals; its highest content was recorded in the entrance of the bay as shown in figure 3b.



(a) (b)

Figure 3: The spatial distribution of the content of the surface sediments of the bay in Cu (a) and Cd (b)

The dendrogram extracted by the hierarchical cluster analysis using the "Nearest neighbour" method and the "Pearson correlation" algorithm is presented in figure 4.

According to this dendrogram, the metals can be clustered into two groups: the first group includes the metals Al, Fe and Mn and the second one the metals Zn, Cu, Pb and Hg. On the other hand, Ni and Cd present an independent behaviour so they cannot be placed in any group. The strong correlation (statistically significant according to the t-test at the 0.01 level) of Al, Fe and Mn indicates the geological origin of Fe and Mn (Al/Fe: 0.989, Al/Mn: 0.809 and Fe/Mn: 0.820).

The clustering of metals of the second group indicates their common origin from diffused pollution sources.

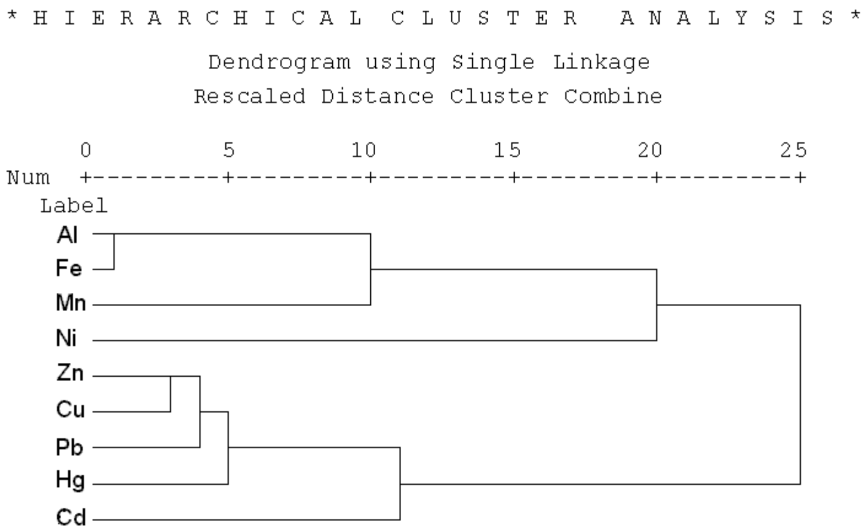


Figure 4: The dendrogram of the correlation of the metals between each other.

The empirically derived Sediment Quality Guidelines (ERL/ERM and TEL/PEL; McDonald et al. 1996; Long et al., 1998a, 1998b) were used in order to evaluate the potential toxicity of the surface sediments on the benthic organisms. None of the metals studied exceeded the perspective ERMs/PELs, the values above which adverse effects on benthic biota are frequently observed. However, the levels of Cu, Pb, Zn and Hg found in the sediments of the river's estuary and close to the naval base exceed the low-range values (ERLs/TELs), suggesting that further geochemical and biological studies (including toxicity tests) are needed for estimating the actual incidence of toxicity. Since the Moronis River could be considered as a point source of pollution for the marine environment (Dassenakis et al., 2012), control measures of the anthropogenic load should be considered. Furthermore, decision making of future dredging activities at the area of the port and the naval base should be accompanied by a comprehensive ecological risk assessment.

In table 2 the metal contents of the sediments of the Souda Bay are compared to literature data of gulfs of the Greek coastline, being under various degrees of environmental pressures. In general, the sediments of the Souda Bay are less enriched in metals in comparison to other polluted gulfs, although some values are higher than the corresponding values of the open Aegean Sea.

Table 2: The contents in metals for some surface sediments originating from various Greek coastal areas (mg/Kg)

	Cd	Cu	Mn	Pb	Zn	Reference
Gulf of Mitilini	0,17-0,50	21-86	248-360	32,7-93	74-230	Aloupi et al, 2002
N. Evoikos gulf	0,095-0,141	22,6-35,0	523-552	21,3-29,4	93-129	Angelidis et al, 2000
Kotinthiakos gulf	0,10-0,50	29,3-46,4	681-1545	11,1-25,5	34-102	Kipriadis, 2007
Saronikos gulf	0,26-1,3	18-164	232-991	30-204	83-713	Giannopoulou, 2005
Thermaikos gulf	-	2,9-47,9		16,5-48,6	33-124	Karageorgis, 2003
Maliakos gulf	0,061-0,085	47,8-52,4			121-134	Rousselaki, 2007
Bay of Souda	0,042-0,144	7,6-58	90-308	13-63	16-177	present work

3.2 TOC in the surface sediment

The content of the bay's sediment in TOC ranges between 0.29 and 2.93 % w/w with a mean value of 1.22 % w/w; it is in accordance to the typical coastal sediment (Chester 1990). The relatively low values of TOC indicate a rapid oxidation of the organic matter in the well oxygenated water column (Gavriil et al, 2006) and/or low inputs of organic matter originating from the nearby urban areas. The highest value for TOC was recorded in the estuaries of the river Moronis (SD13) followed by the area in the centre of the bay (SD10).

The spatial distribution of the TOC in the surface sediments of the bay of Souda is presented in figure 5.

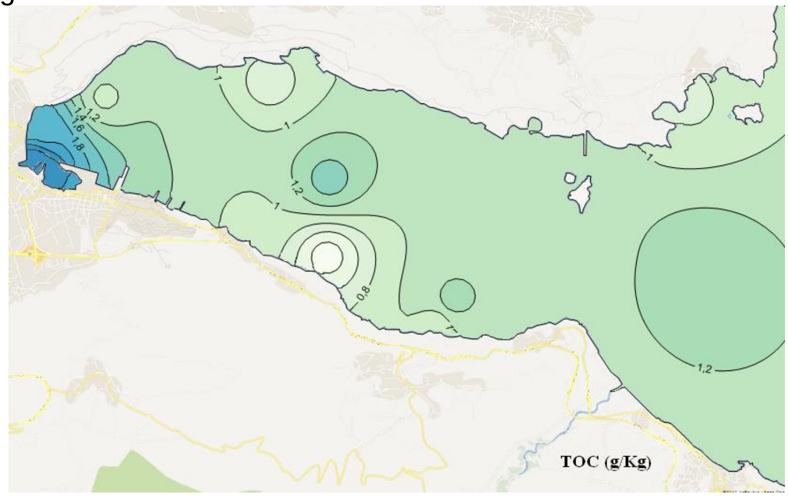


Figure5: The spatial distribution of the content of the surface sediment of the bay in TOC

As extracted from this figure, the TOC accumulates in the sediments of the south-west part of the bay, probably due to the anticlockwise circulation and the discharge of the river Moronis.

4. CONCLUSIONS

The present study is the first sediment quality assessment of the Bay of Souda. The conclusions extracted from this study could be summarized as follows:

- Despite the fact that the bay hosts a number of anthropogenic activities, the levels of metals are in general relatively low. Slightly higher metal levels are recorded close to point sources of pollution. On the basis of Sediment Quality Guidelines, adverse effects on benthic biota would rarely be observed.
- The Moronis River carries a significant load of metals into the bay. However, the deterioration of the sediment quality is limited to a restricted zone of 100 m off the mouth of the river.
- The metal contents of the sediments of the Bay of Souda are lower than those found in various gulfs of the Greek coastline with intense environmental pressures, but higher than the open sea.
- The sediment of the bay is poor in organic carbon, a fact that is attributed to the oligotrophic character of the bay's water column and the prohibition of discharging urban wastes into the bay.
- The levels and the distribution of metals and TOC show that the deterioration of the sediment quality, at the moment, is restricted to specific areas close to pollution sources. However, for protecting and/or restoring the sediment quality, control measures of pollution should be considered both for the current anthropogenic activities and for any new establishment at the enclosed bay of Souda.

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