

Anthropogenic Heavy Metal Pollution in the Surficial Sediments of the Keratsini Harbor, Saronikos Gulf, Greece

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Abstract The contents of ten elements [Cd, Pb, W, Zn, Mn, As, Se, Cr, Cu, and organic carbon (C_{org})] have been determined in the surficial sediments of Keratsini harbor, Saronikos Gulf, Greece. The contamination of the sediments was assessed on the basis of geoaccumulation index and to corresponding sediment quality guidelines (SQGs) effects range low/effects range median. The results revealed highly elevated Cd, Pb, W, Zn, As, Se, Cr, Cu, and C_{org} values (Cd, 190–1,763 mg kg⁻¹; Pb, 521–1,263 mg kg⁻¹; W, 38–100 mg kg⁻¹; Zn, 409–6,725 mg kg⁻¹; Mn, 95–1,101 mg kg⁻¹; As, not detectable–1,813 mg kg⁻¹; Se, not detectable–58 mg kg⁻¹; Cr, 264–860 mg kg⁻¹; Cu, 195–518 mg kg⁻¹; and C_{org} , 0.69–4.41%). The enrichment of metals in the sediments results from the contribution of the central Athens sewage outfall through which the waste of the Attica basin ends up in Keratsini harbor as well as from industrial and ship contaminants.

Keywords Heavy metals · Pollution · Marine sediments · Keratsini harbor

1 Introduction

The Keratsini harbor, in the Saronikos Gulf, Greece (Fig. 1), is the commercial port of Pireaus, one of the most important ports of the Mediterranean Sea. The harbor is surrounded by the most industrialized and urbanized areas of Attica region including the greater Athens area. Until 1994, the Kerarsini bay accepted untreated waste from the greater Athens area through a central sewer outfall. Approximately 600,000 m³/day of sewage flow were discharging into the Kerarsini harbor during the central sewer operation (Theodorou and Perissoratis 1991). Now, the sewage outfall is almost entirely replaced by a new waste treatment and disposal system in Psitallia island, near Keratsini harbor.

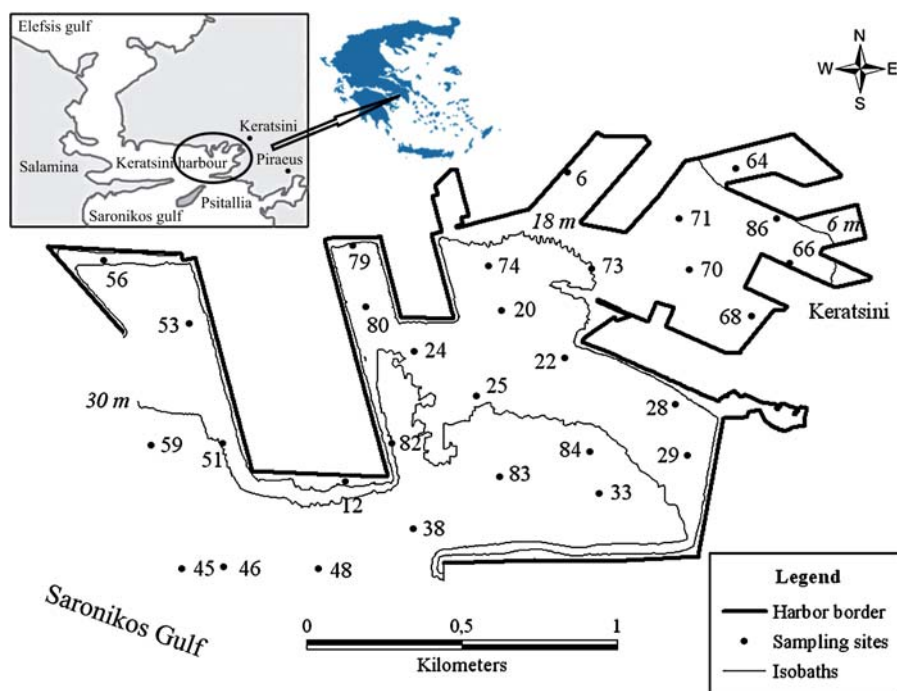
In a previous study (Galanopoulou et al. 2005), there have been detected highly elevated concentrations of dichloro-diphenyl-trichloroethanes and other chlorinated organic pesticides and polychlorinated biphenyls in the sediments of Keratsini harbor. Elevated concentrations of aliphatic and polycyclic aromatic hydrocarbons have also been reported in the near Elefsis bay (Sklivagou et al. 2001). The present study aims to assess the pollution of the sediments of the Keratsini harbor by heavy metals and to examine their distribution and their sources.

2 Materials and Methods

Eighty-six sediment samples were collected from the seabed of the Keratsini harbor by means of a

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Fig. 1 The study area and location of the sediment samples. Isobaths are in meters



Van Veen type grab sampler. The sediments were placed in plastic bottles and were kept at -18°C until the grain size, chemical, and mineralogical analyses were carried out. Taking into account their homogeneity, their grain size, and their mineralogical composition, 30 representative sediment samples (Fig. 1) were chosen for the analysis of nine metals (Cd, Pb, W, Zn, As, Se, Cr, Cu, and As). Nearly total extraction of the metals was achieved with KNaCO_3 and HCl as described by Galanopoulou (2005). The determination of metal content was carried out by applying inductively coupled plasma–atomic emission spectrometry. Accuracy of the determinations was checked by the analysis of the international standard reference material PACS-2 (National Research Council Canada). The analytical precision was generally better than 5%. Oxidable organic carbon (C_{org}) was also determined using the Walkley (1947) technique.

The degree of contamination of the surficial sediments of the Keratsini harbor with heavy metals was assessed on the basis of the geoaccumulation index of Müller (1979) and the corresponding sediment quality guidelines (SQGs) effects range low/effects range median (ERL/ERM; Long et al. 1995).

3 Results and Discussion

3.1 Heavy Metal Pollution

Table 1 presents the concentrations of heavy metals and C_{org} in the sediments of the Keratsini harbor. The results show variable concentrations of Cd ($190\text{--}1,763\text{ mg kg}^{-1}$), Zn ($409\text{--}6,725\text{ mg kg}^{-1}$), Pb ($521\text{--}1,263\text{ mg kg}^{-1}$), Cr ($264\text{--}860\text{ mg kg}^{-1}$), Cu ($195\text{--}518\text{ mg kg}^{-1}$), Mn ($95\text{--}1,101\text{ mg kg}^{-1}$), W ($38\text{--}100\text{ mg kg}^{-1}$), As (not detectable– $1,813\text{ mg kg}^{-1}$), and Se (not detectable– 58 mg kg^{-1}).

A comparison of the abovementioned concentrations with the corresponding values of the metals given for the shales by Wedepohl (1969, 1978) grades the values of all the considered metals in the Keratsini harbor as high to very high (Table 2). However, earlier research in the broad area of Keratsini harbor has produced lower Zn, Pb, Cr, Cu, and Mn values (Grimmanis et al. 1977; Scoullou 1981; Voutsinou-Taliadouri 1981; Scoullou 1986; Sioulas et al. 1990; Zorpas et al. 2001). According to Table 2 the concentration levels of Cd, Pb, Zn, and Cu observed in the surface sediments of Keratsini harbor are also higher than the concentrations traced in similar harbors in Greece, e.g., in the harbor of Rhodes

Table 1 Results of the chemical analyses of the surficial sediments of Keratsini harbor

Sample	Cd (mg kg ⁻¹)	Zn (mg kg ⁻¹)	Pb (mg kg ⁻¹)	Cr (mg kg ⁻¹)	Cu (mg kg ⁻¹)	Mn (mg kg ⁻¹)	W (mg kg ⁻¹)	Se (mg kg ⁻¹)	As (mg kg ⁻¹)	C _{org} (%)
6	1,060	586	544	301	195	157	46	1	–	1.77
12	1,248	690	546	433	218	95	41	14	–	1.98
20	634	1,025	638	451	233	217	41	11	71	2.31
22	1,513	1,159	618	513	326	125	66	23	–	3.03
24	946	1,060	588	543	328	152	49	44	–	3.15
25	880	2,088	683	551	518	177	66	–	–	3.23
28	584	551	570	433	299	266	58	10	66	1.68
29	1,208	1,060	650	519	286	125	50	–	–	2.79
33	955	5,663	963	828	258	470	89	–	810	3.90
38	1,088	3,425	831	603	294	295	74	–	386	3.70
45	1,363	724	594	363	274	168	56	15	–	3.78
46	973	1,413	643	640	250	205	66	48	–	3.75
48	888	1,388	606	616	291	127	41	–	–	4.32
51	1,288	466	521	330	196	104	40	21	–	0.93
53	1,178	503	565	316	309	133	49	–	–	1.47
56	190	409	546	293	216	180	45	1	–	0.78
59	1,313	1,095	624	446	264	155	46	–	–	2.55
64	1,125	974	649	275	286	140	58	8	–	0.69
66	829	1,288	636	413	513	122	59	–	–	4.14
68	1,196	6,725	1,263	860	330	1,101	100	1	1,813	3.39
70	893	494	533	264	241	101	38	–	–	4.41
71	934	516	524	341	219	163	51	58	–	1.29
73	908	2,100	788	464	284	151	70	–	68	4.31
74	869	966	591	408	284	155	44	6	–	2.64
79	826	1,001	610	460	305	129	50	–	–	4.29
80	1,233	701	571	319	270	120	41	35	–	1.29
82	1,763	1,065	568	428	371	177	58	18	–	2.43
83	735	1,400	621	505	246	194	61	–	–	4.26
84	1,063	1,006	618	515	226	130	56	–	–	3.00
86	253	1,513	735	473	295	288	59	–	83	4.29

(–) not detected

(Angelidis and Aloupi 1995) and in the harbor of Mytilene (Cd, 0.30–0.495 $\mu\text{g g}^{-1}$, Aloupi and Angelidis 2001) and in highly industrialized and polluted areas and harbors worldwide, e.g., Port of Bangoli, Gulf of Naples, Italy (Romano et al. 2004), Tolo harbor, Hong Kong (Owen and Sandhu 2000), Victoria harbor Hong Kong (Wong et al. 1995), Montevideo harbor, Uruguay (Muniz et al. 2004), Kaohsiung harbor, Taiwan (Chen et al. 2007), and Barcelona harbor (Guevara-Riba et al. 2004). The values of Cu measured in Victoria and Barcelona harbor are exceeded. On the other hand higher Pb, Zn, and Cu concentrations have been observed in the East London harbor and Elizabeth harbor, UK (Fatoki and Mathabatha 2001).

The Mn values of the sediments in the study area are comparable with those of the East London harbor

and Port Elizabeth harbor, UK (Fatoki and Mathabatha 2001; Table 2) as well as with those of Victoria harbor, Hong Kong (Wong et al. 1995; Table 2) and Portovesme harbor, Sardinia (Schintu and Deggetto 1999). However, the W concentrations of the sediments of the Keratsini harbor are lower in comparison to the ones observed in Portovesme, Sardinia (0.04–0.10%, Schintu and Deggetto 1999; Table 2), while the concentrations of As detected in the seven samples of the study area are higher than the corresponding values in other ports in the world polluted by arsenic, e.g., the Copenhagen harbor (3.4–15 mg kg^{-1} dry sample; Andersen et al. 1998).

These high values of heavy metals observed in the sediments of the study area are due probably to the central Athens sewage outfall as well as to pollutants

Table 2 Heavy metal pollution levels in marine surface sediments of different areas in the world (in mg kg⁻¹)

	Cd	Zn	Pb	Cr	Cu	Mn	W	Se	As	References
Average shale	0.3	95	20	90	45	850	1.8	0.6	1.3	Wedepohl (1969/1978)
Lesvos island, Greece	–	33–85	–	14–291	12–147	–	–	–	–	Kelepertsis and Andriopoulos (1995)
Lavreotiki Peninsula, Greece	<0.4–44	51–9,930	83–6,791	3–197	7–360	174–10,795	–	–	6–7,616	Kelepertsis and Alexakis (2004)
Northern Euboeos bay, Greece ^a	–	69–471	–	10.64–2,360	20.9–114.9	545–6,490	–	–	–	Voutsinou-Taliadouri and Vamavas (1993)
Thermaikos gulf, Greece	0.3–8.7	32–2,600	11–334	39–386	7–200	206–1,994	–	–	–	Voutsinou-Taliadouri and Vamavas (1995)
Kalloni bay, Lesvos, Greece	3.2	103	96	3,800	48	910	–	–	–	Vamavas (1989)
Astakos bay, Greece	3.25	89	28	166	23	687	–	–	12	Panagos et al. (1989)
Rhodes harbour, Greece	0.03–0.08	59–168	77.7–152	32.0–77.3	38.3–64.7	162–181	–	–	–	Angelidis and Aloupi (1995)
Mandraki harbour, Rhodes, Greece	0.03–0.04	211–242	133–230	19, 4–26.4	72.3–101	138–154	–	–	–	Angelidis and Aloupi (1995)
Navarino bay, Greece	0.047–2	299–352	9–59	–	30–66	–	–	–	–	Vamavas et al. (1987)
Patraikos bay, Greece	–	104–430	0–40	70–210	23–101	–	–	–	–	Vamavas and Ferentinos (1983)
Kalamata bay, Greece	–	–	8–40	–	11–56	–	–	–	–	Vamavas et al. (1984)
Gulf of Corinth, Greece	–	65–116	0–80	–	–	–	–	–	–	Vamavas et al. (1986)
Harbour of Portovesme, Sardinia ^b	–	–	–	–	–	500–800	–	–	–	Schintu and Deggetto (1999)
Victoria harbour, Hong Kong	2.61–3.33	97.9–610.4	47.4–138.1	57.5–601.2	45.2–3,789.5	371.5–568.8	–	–	–	Wong et al. (1995)
Southwest coast of Spain	0.19–2.5	141–649	20–197	32–92	41–336	180–576	–	–	–	Morillo et al. (2004)
Galicia, NW Spain	1.0–1.4	22–161	27–153	2–61	2–58	39–270	–	–	–	Evans et al. (2003)
East London harbour	120–1,630	26,100–332,000	3,200–84,200	–	12,700–183,000	87,400–549,000	–	–	–	Fatoki and Mathabatha (2001)
Elizabeth harbour	100–1,400	18,800–126,000	9–61.9	–	8,600–82,300	103,000–499,000	–	–	–	Fatoki and Mathabatha (2001)
Montevideo harbour, Uruguay	<1–1.6	174–491	44–128	79–253	58–135	–	–	–	–	Muniz et al. (2004)
Port of Bangoli, Italy	–	91–2,313	–	–	–	–	–	–	–	Romano et al. (2004)
Tolo harbour, Hong Kong,	–	270	144	14–30	84	–	–	–	–	Owen and Sandhu (2000)
Kaohsiung harbor, Taiwan	0.01–6.80	52–1,369	9.5–470	0.2–900	5.3–946	–	–	–	–	Chen et al. (2007)
Barcelona harbour	0.4–2.7	180–1,130	85–589	45–110	70–530	255–427	–	–	–	Guevara-Riba et al. (2004)

^a Cores (depth 0–4 cm)^b Cores (depth 0–2 cm)

from the ships (paint, etc.) and the industries. As a matter of fact, high Pb, Cu, and other heavy metal concentrations have been usually identified near the outlets of drainpipes (Förstner and Wittman 1983).

Figure 2 shows a spatial distribution of Cd, Zn, Pb, Cr, Cu, Mn, W, As, and Se (obtained by Arcinfo GIS 8.3 software Inverse Distance Weighting). It seems a tendency in the distribution of certain metals showing maximum values of Zn, Pb, Cr, Mn, W, and As in the northeast and in the southeast part of the harbor, in the most protected areas from the open sea, where the hydraulic regime is rather weak. On the other hand, maximum values of Cd, Cu, and Se appeared, respectively, in the west and central part, in the central and northeast part, and at the entrance and in the central and northeast part of the harbor. It seems that the hydraulic regime within the harbor as well as the turbulence of the seabed caused by the ship engines are significant agents in the deposition of the contaminants in the Keratsini harbor.

Table 3 presents the Pearson correlation coefficient matrix between the various heavy metals and C_{org} . Zn, Pb, Cr, W, and As were significantly correlated with each other, indicating common origin, probably the Athens sewage outfall. Furthermore, the good correlation between W, As, Zn, Pb, and Cr with Mn probably reflects adsorption of the above metals by Mn oxides. Similarly, the positive correlation of Cr with C_{org} probably indicates that a part of the Cr content was adsorbed by the organic matter.

3.2 Organic Carbon

The concentrations of organic carbon are relatively high and vary between 0.69% and 4.41% (Table 1). These values are a little bit lower in comparison to previous studies in the area, like at the shore of Keratsini, close to the central sewer conduct (6.22%) and the Piraeus harbor (4.5%; Voutsinou-Taliadouri 1981). It appears that the biological purification plant that is operating in Psitallia island has restricted the organic pollution in the area.

It should be noted that in the wider Saronic gulf area, there have been measured significantly lower values of C_{org} that vary between 0.9% and 1.86% (Voutsinou-Taliadouri 1981). Lower concentrations have been determined also in other commercial ports in Greece, such as the commercial port of Rhodes (0.46–0.84%) and the Mandraki port in Rhodes

(1.90–2.74%; Angelidis and Aloupi 1995). On the other hand, higher concentrations of C_{org} are found in other polluted areas, such as the surficial sediments of the Mediterranean shores of Israel close to the sludge outlet from the biological sewage treatment system (0.18–10.3%, Kress et al. 2004).

3.3 Geochemical Strain of the Sediments with Toxic Heavy Metals

The elements that show the highest I_{geo} values are Cd, Pb, W, Zn, As, and Se (Table 4).

Concerning Cd, the whole port is characterized as heavily polluted, with the I_{geo} being at very high levels (8.72–11.94) and the I_{geo} class being equal to 6. The comparison of the Cd concentrations in the sediments of the research area (190–1,763 mg kg⁻¹) to the corresponding values SQGs ERL-ERM, according to Long et al. (1995), shows that all the sediments of the Keratsini harbor have toxic Cd concentrations, since they exceed both ERL (1.2 mg kg⁻¹) and ERM (9.6 mg kg⁻¹) guidelines.

The I_{geo} for Pb varies between 4.12 and 5.40, allocating it in the I_{geo} classes 5–6. Hence, the area is characterized as heavily contaminated up to polluted by Pb. In addition, the comparison of the Pb concentration in the sediments of the research area (521–1,263 mg kg⁻¹) to the corresponding SQGs ERL-ERM demonstrated that all samples of the Keratsini harbor contain toxic Pb concentrations, since they exceed both ERL (46.7 mg kg⁻¹) and ERM (218 mg kg⁻¹).

W I_{geo} index varying between 3.80 and 5.21 and the corresponding I_{geo} class of 4–6 classifies the sediments as highly contaminated up to polluted.

The I_{geo} index for As traced only in seven samples varies from 1.76 to 6.54 and is placed in the I_{geo} classes 2–6. In view of these results, therefore, the region is described as uncontaminated to polluted in regards to As. Moreover, a comparison of the As concentration in the sediments of the research area (not detectable–1,813 mg kg⁻¹) with the corresponding SQGs ERL/ERM established that:

- Twenty-three of the 30 samples (76.7%) present non-toxic concentrations.
- Two of the 30 samples (6.7%) exhibit concentrations higher than the toxic effect range ERL (8.2 mg kg⁻¹) and lower than ERM (70 mg kg⁻¹) and correspond to polluted marine sediments.

Fig. 2 Spatial distribution of Cd, Zn, Pb, Cr, Cu, Mn, W, As, and Se in the Keratsini harbor

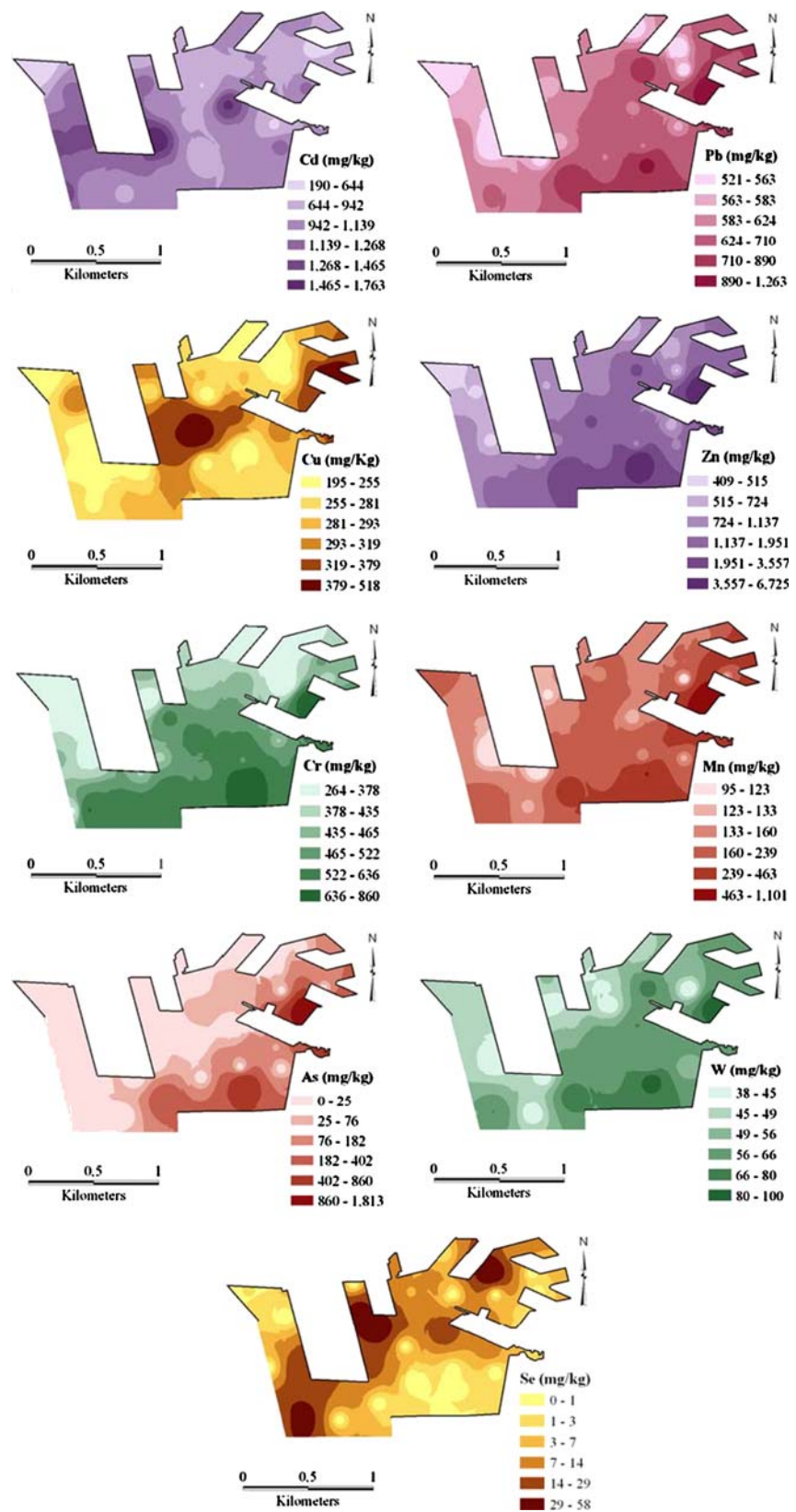


Table 3 Pearson correlation coefficient matrix between the trace elements and C_{org}

	Cd	Zn	Pb	Cr	Cu	Mn	W	Se	As	C_{org}
Cd	1.00									
Zn	0.05	1.00								
Pb	0.00	0.97	1.00							
Cr	0.04	0.85	0.79	1.00						
Cu	0.07	0.20	0.20	0.22	1.00					
Mn	0.02	0.87	0.90	0.68	0.09	1.00				
W	0.08	0.88	0.87	0.76	0.32	0.76	1.00			
Se	0.21	0.25	0.29	0.10	0.17	0.15	0.14	1.00		
As	0.07	0.92	0.93	0.70	0.07	0.98	0.76	0.18	1.00	
C_{org}	0.14	0.38	0.37	0.53	0.32	0.17	0.38	0.30	0.18	1.00

– Five of the 30 samples (16.7%) exhibit toxic As concentrations, since they exceed both ERL (8.2 mg kg^{-1}) and ERM (70 mg kg^{-1}) and correspond to polluted marine sediments.

Similarly, the Se concentrations in the samples wherein they were traced exhibit a high fluctuation with the result that, regarding Se, the region is described from uncontaminated to polluted. The I_{geo}

Table 4 I_{geo} index values for heavy metals of the surficial sediments of Keratsini harbor

Sample	Cd I_{geo}	Zn I_{geo}	Pb I_{geo}	Cr I_{geo}	Cu I_{geo}	W I_{geo}	Se I_{geo}	As I_{geo}
6	11.20	2.04	4.18	1.16	1.53	4.10	0.47	–
12	11.44	2.28	4.19	1.68	1.69	3.93	3.93	–
20	10.46	2.85	4.41	1.74	1.78	3.93	3.64	1.87
22	11.71	3.02	4.36	1.92	2.27	4.62	4.64	–
24	11.04	2.90	4.29	2.01	2.28	4.17	5.60	–
25	10.93	3.87	4.51	2.03	2.94	4.62	–	–
28	10.34	1.95	4.25	1.68	2.15	4.41	3.47	1.76
29	11.39	2.90	4.44	1.94	2.08	4.21	–	–
33	11.05	5.31	5.00	2.62	1.93	5.04	–	5.38
38	11.24	4.59	4.79	2.16	2.12	4.77	–	4.31
45	11.56	2.34	4.31	1.43	2.02	4.38	4.06	–
46	11.08	3.31	4.42	2.25	1.89	4.62	5.72	–
48	10.95	3.28	4.34	2.19	2.11	3.93	–	–
51	11.48	1.71	4.12	1.29	1.54	3.89	4.56	–
53	11.35	1.82	4.24	1.23	2.19	4.17	–	–
56	8.72	1.52	4.19	1.12	1.68	4.06	0.47	–
59	11.51	2.94	4.38	1.72	1.97	4.10	–	–
64	11.29	2.77	4.43	1.03	2.08	4.41	3.06	–
66	10.85	3.18	4.41	1.61	2.92	4.44	–	–
68	11.38	5.56	5.40	2.67	2.29	5.21	0.47	6.54
70	10.95	1.79	4.15	0.97	1.84	3.80	–	–
71	11.02	1.86	4.13	1.34	1.70	4.25	6.00	–
73	10.98	3.88	4.71	1.78	2.07	4.70	–	1.79
74	10.91	2.76	4.30	1.59	2.07	4.02	2.80	–
79	10.84	2.81	4.35	1.77	2.18	4.21	–	–
80	11.42	2.30	4.25	1.24	2.00	3.93	5.28	–
82	11.94	2.90	4.24	1.66	2.46	4.41	4.28	–
83	10.67	3.30	4.37	1.90	1.87	4.50	–	–
84	11.21	2.82	4.36	1.93	1.74	4.38	–	–
86	9.13	3.41	4.61	1.81	2.13	4.44	–	2.08

classes where these samples are placed according to their indices are 1–6, with index values from 0.47 to 6, respectively.

The I_{geo} index for Zn ranges between 1.52 and 5.56 and the I_{geo} class from 2 to 6. The sediments are therefore classified as slightly contaminated up to polluted. A comparison of the Zn concentrations in the sediments of the research area (409–6,725 mg kg⁻¹) to the valid SQGs ERL-ERM resulted in the following:

- One of the 30 samples (3.3%) exhibits concentrations that are higher than the toxic effect range ERL (150 mg kg⁻¹) and lower than ERM (410 mg kg⁻¹) and corresponds to medium polluted marine sediments.
- Twenty-nine of the 30 samples (96.7%) exhibit toxic concentrations of Zn, since they exceed both ERL (150 mg kg⁻¹) and ERM (410 mg kg⁻¹) and correspond to polluted marine sediments.

The I_{geo} index for Cu is between 1.53 and 2.94 and the class from 2 to 3. Therefore, the sediments are described as slightly up to heavily contaminated. From comparison of the Cu sediment concentrations in the research area (195–518 mg kg⁻¹) to the SQGs ERL-ERM, it was established that:

- Twelve of the 30 samples (40%) exhibit concentrations that are higher than the toxic effect range ERL (34 mg kg⁻¹) and lower than ERM (270 mg kg⁻¹) and one sample (3.3%) is at the limit of ERM (270 mg kg⁻¹), so they correspond to medium polluted marine sediments.
- Seventeen of the 30 samples (56.7%) exhibit toxic Cu concentrations, since they exceed both ERL (34 mg kg⁻¹) and ERM (270 mg kg⁻¹) and correspond to polluted marine sediments.

The I_{geo} index values for Cr, ranging between 0.97 and 2.67, are placed into classes 1–3, thus varying from not contaminated to slightly contaminated and from slightly contaminated to highly contaminated areas. From the comparison of the Cr sediment concentration in the research area (264–860 mg kg⁻¹) to the SQGs ERL-ERM, it results that:

- Nine of the 30 samples (30%) exhibit concentrations that are higher than the toxic effect range ERL (81 mg kg⁻¹) and lower than ERM

(370 mg kg⁻¹) and correspond to medium polluted marine sediments.

- Twenty-one of the 30 samples (70%) exhibit toxic Cr concentrations, since they exceed both ERL (81 mg kg⁻¹) and ERM (370 mg kg⁻¹) and correspond to polluted marine sediments.

4 Conclusions

The results of the chemical analysis of the Keratsini harbor surficial sediments showed that the sediments present highly elevated Cd, Pb, W, Zn, As, Se, Cr, and Cu concentrations. Based on the I_{geo} indices, these sediments can be characterized as heavily polluted in regard to Cd, Pb, W, As, Se, and Zn and highly contaminated concerning Cu and Cr. Moreover, according to the SQGs as established by Long et al., the concentrations of Cd, Pb, As, Zn, Cu, and Cr of most of the sediments exceed the toxic effect range.

The enrichment of heavy metals in the sediments could be attributed to the deposition of the dissolved and particulate heavy metals and their compounds in the water column through the Athens central sewage outfall. In addition to this source, other inputs of heavy metals include inputs from the ships (cargo, fuel, paints etc.) and from the industrial activity in the wider area.

References

- Aloupi, M., & Angelidis, M. O. (2001). Geochemistry of natural and anthropogenic metals in the coastal sediments of the island of Lesbos, Aegean Sea. *Environmental Pollution*, 113, 211–219. doi:10.1016/S0269-7491(00)00173-1.
- Andersen, H. V., Kjølholt, J., Poll, C., Dahl, S., Stuer-Lauridsen, F., Pedersen, F., & Bjørnstad, E. (1998). Environmental risk assessment of surface water and sediments in Copenhagen harbour. *Water Science and Technology*, 37(6–7), 263–272. doi:10.1016/S0273-1223(98)00207-8.
- Angelidis, M. O., & Aloupi, M. (1995). Metals in sediments of Rhodes harbour, Greece. *Marine Pollution Bulletin*, 31(4–12), 273–276.
- Chen, C. -W., Kao, C. -M., Chen, C. -F., & Dong, C. -D. (2007). Distribution and accumulation of heavy metals in the sediments of Kaohsiung harbor, Taiwan. *Chemosphere*, 66(8), 1431–1440. doi:10.1016/j.chemosphere.2006.09.030.
- Evans, G., Howarth, R., & Nombela, M. (2003). Metals in the sediments of Ensenada de San Simón (inner Ría de Vigo), Galicia, NW Spain. *Applied Geochemistry*, 18, 973–996. doi:10.1016/S0883-2927(02)00203-2.

- Fatoki, S. A., & Mathabatha, S. (2001). An assessment of heavy metal pollution in the East London and Port Elizabeth harbours. Water research commission. *Water S. A.*, 27, 233–240.
- Förstner, U., & Wittman, G. T. W. (1983). *Metal pollution in the aquatic environment*. Berlin: Springer.
- Galanopoulou, S. (2005). Mineralogical and geochemical study of surface sediments of Keratsini harbour. Ph.D Thesis, National Technical University of Athens, Greece (in Greek).
- Galanopoulou, S., Vgenopoulos, A., & Conispoliatis, N. (2005). DDTs and other chlorinated organic pesticides and polychlorinated biphenyls pollution in the surface sediments of Keratsini harbour, Saronikos gulf, Greece. *Marine Pollution Bulletin*, 50, 520–525.
- Grimmanis, A. P., Vassilaki-Grimmani, M., & Griggs, G. B. (1977). Pollution studies of trace elements in sediments for the upper Saronikos gulf, Greece. *Journal of Radioanalytical Chemistry*, 37, 761–773. doi:10.1007/BF02519388.
- Guevara-Riba, A., Sahuquillo, A., Rubio, R., & Rauret, G. (2004). Assessment of metal mobility in dredged harbour sediments from Barcelona, Spain. *The Science of the Total Environment*, 321, 241–255. doi:10.1016/j.scitotenv.2003.08.021.
- Keleperstis, A. E., & Andrinopoulos, A. D. (1995). Sediment provenance from geochemistry—Recent sediments off Lesvos island, Greece. *Annales Geologiques des Pays Helleniques*, 1° serie, T, 36, 747–770.
- Keleperstis, A., & Alexakis, D. (2004). The impact of mining and metallurgical activity of the Lavrion Sulfide deposits on the geochemistry of bottom sea sediments east of the Lavreotiki Peninsula, Greece. *Research Journal of Chemistry and Environment*, 8(1), 40–46.
- Kress, N., Herut, B., & Galil, B. S. (2004). Sewage sludge impact on sediment quality and benthic assemblages off the Mediterranean coast of Israel—a long term study. *Marine Environmental Research*, 57, 213–233. doi:10.1016/S0141-1136(03)00081-3.
- Long, E. R., MacDonald, D. D., Smith, S. L., & Calder, F. D. (1995). Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine ecosystems. *Environmental Management*, 19, 81–97. doi:10.1007/BF02472006.
- Morillo, J., Usero, J., & Gracia, I. (2004). Heavy metal distribution in marine sediments from the southwest coast of Spain. *Chemosphere*, 55, 431–442. doi:10.1016/j.chemosphere.2003.10.047.
- Muller, G. (1979). Schwermetalle in den sedimenten des Rheins Veränderungen seit (1971). *Umschau*, 79, 778–783.
- Muniz, P., Danulat, E., Yannicelli, B., García-Alonso, J., Medina, G., & Bicego, M. C. (2004). Assessment of contamination by heavy metals and petroleum hydrocarbons in sediments of Montevideo harbour (Uruguay). *Environment International*, 29, 1019–1028. doi:10.1016/S0160-4120(03)00096-5.
- Owen, R. B., & Sandhu, N. (2000). Heavy metal accumulation and anthropogenic impacts on Tolo harbour, Hong Kong. *Marine Pollution Bulletin*, 40(2), 174–180. doi:10.1016/S0025-326X(99)00201-5.
- Panagos, A., Papadopoulou, N., Alexandropoulou, S., Synetos, S., & Varnavas, S. (1989). Geochemical study of sediments from the Astakos Bay, Greece. Proceedings of the Conference “Environmental Science and Technology” Lesvos, Greece, pp. 231–242.
- Romano, E., Ausili, A., Zharova, N., Mangno, M., Pavoni, B., & Gabellini, M. (2004). Marine sediment contamination of an industrial site at Port of Bagnoli, Gulf of Naples, Southern Italy. *Marine Pollution Bulletin*, 49, 487–495. doi:10.1016/j.marpolbul.2004.03.014.
- Schintu, M., & Deggetto, S. (1999). Sedimentary records of heavy metals in the industrial harbour of Portovesme, Sardinia, (Italy). *The Science of the Total Environment*, 241, 129–141. doi:10.1016/S0048-9697(99)00336-8.
- Scoullou, M. J. (1981). Zinc in seawater and sediments (of the gulf of Elefsis, Greece). *Water, Air, and Soil Pollution*, 16, 187–207. doi:10.1007/BF01046854.
- Scoullou, M. J. (1986). Lead in coastal sediments: The case of the Elefsis gulf, Greece. *The Science of the Total Environment*, 49, 199–219. doi:10.1016/0048-9697(86)90240-8.
- Sioulas, A., Anagnostou, C., & Kersten, M. (1990). Heavy metals in the modern sediments of Elefsis gulf, as an index of anthropogenous impact in the marine environment of the area. 2nd Chemistry Congress of Greece and Cyprus, Athens, vol. 1, pp. 280–285.
- Sklivagou, E., Varnavas, S. P., & Hatjianestis, J. (2001). Aliphatic and polycyclic aromatic hydrocarbons in surface sediments from Elefsis Bay, Greece (Eastern Mediterranean). *Toxicological and Environmental Chemistry*, 79, 195–210. doi:10.1080/02772240109358988.
- Theodorou, A. J., & Perissoratis, C. (1991). Environmental considerations for design of the Athens sea outfall, Saronikos gulf, Greece. *Environmental Geology and Water Sciences*, 17(3), 233–248. doi:10.1007/BF01701704.
- Varnavas, S. P., & Ferentinos, G. (1983). Heavy metal distribution in the surface sediments of Patraikos bay, Greece. Proceedings of XXVIII International Congress of the International Commission for the Scientific Exploration of Mediterranean (I.C.S.E.M.), Cannes, France, pp 405–409.
- Varnavas, S. P., Panagos, A. G., & Laios, G. (1984). Heavy metal distribution in surface sediments from the Kalamata bay, Greece. Proceedings of International Conference of the International Commission for the scientific exploration of the Mediterranean (I.C.S.E.M.) Lucerne, Switzerland, pp 267–274.
- Varnavas, S. P., Ferentinos, G., & Collins, M. (1986). Dispersion of bauxitic red mud in the Gulf of Corinth, Greece. *Marine Geology*, 70, 211–222. doi:10.1016/0025-3227(86)90003-4.
- Varnavas, S. P., Panagos, A. G., & Laios, G. (1987). Trace elements in surface sediments of Navarino bay, Greece. *Environmental Geology and Water Sciences*, 10(2), 1–10.
- Varnavas, S. P. (1989). Metal Pollution of the Kalloni Bay, Lesvos Greece. Proceedings of the conference “Environmental Science and Technology”, Lesvos, Greece, pp 211–220.
- Voutsinou-Taliadouri, F. (1981). Metal pollution in the Saronikos Gulf. *Marine Pollution Bulletin*, 12(5), 163–168. doi:10.1016/0025-326X(81)90228-9.
- Voutsinou-Taliadouri, F., & Varnavas, S. P. (1993). Geochemical study of sediments from northern Euboikos Bay, Greece, with regard to the presence of submarine mineral

- deposits. *Marine Geology*, 110, 93–114. doi:10.1016/0025-3227(93)90108-8.
- Voutsinou-Taliadouri, F., & Varnavas, S. P. (1995). Geochemical and sedimentological patterns in the Thermaikos gulf, North-west Aegean Sea, formed from a multisource of elements. *Estuarine, Coastal and Shelf Science*, 40, 295–320. doi:10.1016/S0272-7714(05)80012-5.
- Walkley, A. (1947). A critical examination of a rapid method for determining organic carbon in soils—Effect of variations in digestion conditions and of inorganic soil constituents. *Soil Science*, 63, 251–264. doi:10.1097/00010694-194704000-00001.
- Wedepohl, K. H. (1969/1978). *Handbook of geochemistry*. Berlin: Springer.
- Wong, Y. S., Tam, N. F. Y., Lau, P. S., & Xue, X. Z. (1995). The toxicity of marine sediments in Victoria harbour, Hong Kong. *Marine Pollution Bulletin*, 31(4-12), 464–470.
- Zorpas, A. A., Vlyssides, A. G., Zorpas, G. A., Karlis, P. K., & Arapoglou, D. (2001). Impact of thermal treatment on metal in sewage sludge from the Psittalias wastewater treatment plant, Athens, Greece. *Journal of Hazardous Materials, B*, 82, 291–298. doi:10.1016/S0304-3894(01)00172-8.