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Trace metal concentrations in the offshore surficial sediments of Heraklion Gulf (Crete Island, East Mediterranean Sea)

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Abstract

The present study investigates the distribution of trace metals (Fe, Mn, Cr, Zn, Pb, Cu and Al) as pollution indicators in the surficial inner shelf sediments along the northern coast of Heraklion Gulf (Crete Island). Despite the fact that Heraklion Gulf is an industrialized urban area, hosting the third most important commercial harbour in Greece, the levels of trace metals in sediments are not considerably high. According to Sediment Quality Guidelines (SQGs), the sediments are considered unpolluted with low probability of adverse effects on biota in the case of Cu, Zn and Pb, and moderately to heavily polluted in the case of Cr. Moreover, Zn, Cu and Pb concentrations are lower than those measured in a previous study (1989). This improvement in the environmental status of the study area is a response to more efficient control of terrestrial pollution sources, following the enforcement of Directive 91/271/EEC (as amended by Directive 98/15/EU) on urban wastewater treatment and disposal.

Keywords: Geochemistry; pollution; ecosystem health; SQG; human impact; South Aegean.

Introduction

Coastal margins, especially those influenced by riverine inputs, are active interfaces between terrestrial and oceanic environments (Dagg *et al.*, 2004; Bianchi & Allison, 2009) where terrestrial fluxes, complex biogeochemical processes and anthropogenic inputs are present. Since ancient times humans have set their activities and civil-cultural foundations near the coast. Nowadays, more than 50% of the European population is gathered in coastal areas (EEA, 2008; Eurostat, 2013), with most of the terrestrial and coastal usage waste discharged into the marine environment.

Trace metal content in coastal sediments may derive from natural processes such as weathering, erosion and volcanic activity but is mostly considered as a pollution indicator related to anthropogenic activities such as mining, metallurgical and other (various) industrial wastewater, fossil fuel combustion and other atmospheric emissions, treated and untreated municipal sewage, urban and agricultural runoff, harbour activities and aquaculture (e.g., Morillo *et al.*, 2004; Luo *et al.*, 2006; Squadrone et *al.*, 2016).

Once trace metals enter the aquatic environment, they generally exhibit a preferential tendency to bind to suspended matter, and thus, through sedimentation, to accumulate in sediments. In addition, trace metals participate in various biogeochemical mechanisms, have significant mobility and can affect ecosystems through bioaccumulation and bio-magnification processes (GESAMP/UNESCO, 1994; Salomons & Förstner, 1984). Hence, trace metal concentrations could be regarded as environmental indicators, for both spatial and temporal trend monitoring of marine pollution, contributing to pollution control, as well.

For the assessment of sediment quality, Sediment Quality Guidelines (SQGs) have been developed by the U.S. Environmental Protection Agency (EPA), the U.S. National Oceanic and Atmospheric Administration (NOAA) and the Canadian Council of Ministers for the Environment (CCME, 1995). They include sediment quality classification categories, concentration ranges and thresholds that have been set after taking into account large series of chemical and biological field data collected from North American coastal regions. These concen-

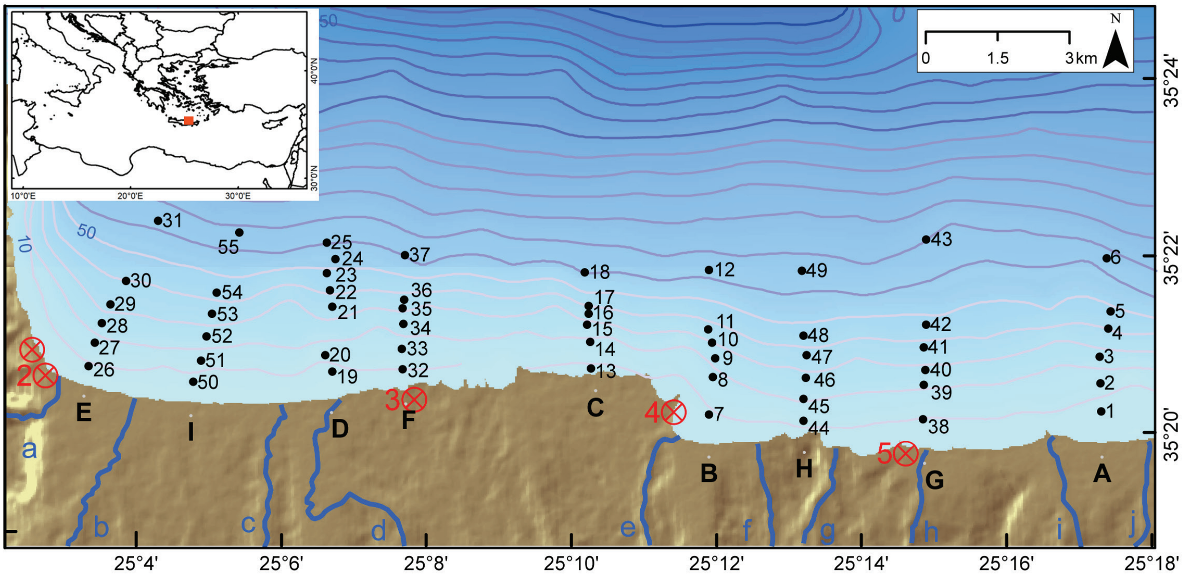

Fig. 1: Location map showing the bathymetry (in metres), sampling stations (1-55), river/torrent mouths (from west to east: a-Almiros, b-Gazanos, c-Xiropotamos, d-Giofyros, e- Krateros, f-Vathilagkos, g-Gournianos, h-Gouvianos, i-Aposelemis, j-Sfakoryako) and the most important potential terrestrial sources of pollution (1: oil storages; 2: Electric Power Station; 3: outfall of treated waste water; 4: former outfall of untreated waste water; and 5: former Gouves military base).

tration ranges and thresholds have been widely used in monitoring studies as guidelines or screening tools for the possible hazards and biological effects incurred by sediments on local aquatic biota (e.g. Long *et al.*, 1995; Long & Wilson, 1997; MacDonald *et al.*, 2000; Buchman, 2008). Since the beginning of the 21st century, several studies have been published on Mediterranean and Black Sea regions such as those concerning the Marmara Sea (Balkis & Çağatay, 2001), Evoikos Gulf in Central Aegean Sea (Dassenakis *et al.* 2003), the Spanish coast (Morillo *et al.*, 2004), the NW Aegean Sea (Karageorgis *et al.*, 2005), the south-central Black Sea shelf (Duman *et al.*, 2006), Saronikos Gulf in the Aegean Sea (Scoullos *et al.*, 2006), Thermaikos Gulf in the NW Aegean Sea (Christophoridis *et al.*, 2009), the Gulf of Corinth adjacent to the Ionian Sea (Iatrou *et al.* 2010), offshore the NE Sicilian Coast (Sacca *et al.*, 2011), the northern Cyprus shelf (Duman *et al.*, 2012), the Egyptian shelf (El Nemr *et al.*, 2007), the Adriatic coast of Italy (Goudeau *et al.*, 2013), the Alexandroupolis Gulf in the NE Aegean Sea (Karditsa *et al.*, 2014) and Ierissos Gulf in the North Aegean Sea (Pappa *et al.*, 2016).

The present study, investigates the distribution of certain trace metal (Fe, Zn, Mn, Cu, Cr and Pb) concentrations, as indicators of pollution, utilising a data set collected in June 2010, in the surficial inner-shelf sediments along the northern coast of Heraklion (region) (north coast of Crete Island), which hosts several potential sources of pollution (urban, industrial). The results of this study are then compared to those published by Poulos *et al.* (2009) for the same area during a sampling campaign that took place in September 1989. This comparison becomes more interesting as the first data set (in 1989) was collected prior to the transposition of Directive 91/271/EEC on urban wastewater treatment and disposal (as amended by Directive 98/15/EU) into Greek national legislation (Government Gazette 192B/14-3-1997).

The study area

Marine geomorphology and sedimentology

The coastal area under investigation is located in the Heraklion Prefecture of Crete Island (Greece), lying between Cape Panagia to the west and Malia Bay to the east and extending to depths between 10 and 70 m (Fig. 1). The area belongs to the southern continental margin of the central Cretan Sea which is narrow (<10 km) and relatively steep (1.5° slope gradient) becoming wider eastwards. The shelf brake is found at depths ranging between 100 m and 150 m, followed by relatively steep slope (2^o-4^o) and variable morphology (Chronis *et al.*, 2000). The nearshore zone consists of sands, while the outer part of the continental shelf by fine material, mainly terrigenous (silt and clay) (Poulos *et al.*, 2002 and 2009; Dounas and Papadopoulou, 1993; and Chronis *et al.*, 2000). The hinterland area of this coastal strip (1.67 km^2), is drained by ten ephemeral streams and torrents (Fig. 1).

Oceanographic conditions

The average tidal range is <10 cm (Tsimplis, 1994), while the meteorologically induced sea level rise may exceed 1 m (HNHS, 2005). According to the Wind and Wave atlas (Athanasoulis & Skarsoulis, 1992) the study area is influenced, on an annual basis, primarily by NW (23.62%), N (12.43%) and partially E (6.79%) wind-induced waves. The wave characteristics (significant height (H_s), period (T), closure depth (h_c), wave breaking zone (d_b) and depth of wave propagation in intermediate waters (L/4)) according to Komar (1976), of the most frequent and the highest incoming offshore waves, are presented in Table 1 and graphically in Figure 2. In addition, it is noteworthy that the coastal stretch to the west of Heraklio city receives reduced wave energy, as the predominant NW waves undergo refraction at the Panagia promontory (Alexandrakis *et al.*, 2013).

Anthropogenic sources of pollution

The coastal region under investigation concentrates vast trade, industrial (including tourism) and agricultural activities and a vivid urban area since the city of Heraklio is the administrative capital of Crete. Among the various human infrastructure, the most significant –from west to east– are (see Fig. 1): (i) The Electric Power Station located in the extreme west end of the bay, using the adjacent Almiros River water for its cooling systems and discharging it into the sea; (ii) crude oil storage facilities, which supply tankers through an underwater pipeline; (iii) the port of Heraklion, which is of major importance for Greece and the Eastern Mediterranean; (iv) the city wastewater treatment plant that discharges effluents in Heraklion Bay through a 1000 m long underwater outfall at a depth of 10 m; and (v) the mouths of five small rivers and some other ephemeral streams discharging farming and agricultural waste, urban runoff as well as eroded sediments from the hinterland area.

Materials and Methods

The sampling campaign was carried out in June 2010 with the R/V Philia conducting a field survey of 55 stations over 9 transects perpendicular to the coastline of Heraklion Gulf. The water depths ranged from 10 to 70 m except for the reference station sample at 200m in transect D (Fig.1). Positioning was established with FURUNO SFN-70 satellite navigator and depth was measured by SIMRAD K-400 echo sounder. At each station, a single undisturbed sediment sample was taken using a Smith McIntyre box corer (Smith & McIntyre, 1954). The uppermost 2 cm were collected and stored in plastic bags. Samples intended for chemical analysis were immediately stored and frozen at -20C° on board.

The standard sieve analysis technique (Folk, 1980) was used to determine the sand and mud percentages of each of the surficial sediment samples, while the silt and clay percentages were determined by Malvern's particle size "Mastersizer 2000 Hydro".

For geochemical analysis, sediment samples were lyophilized (freeze-dryed below minus 40C° and 133 mbar under vacuum pressure with a "LABCONCO" apparatus), slightly ground with an agate mortar and pestle and sieved for the estimation and separation of the fractions above and below 63 μm. The percentage of both fractions (sand and silt-clay) was calculated and further analytical procedures were carried out to those fractions with adequate mass (>10% of the total sediment).

The particulate organic carbon (POC) content was

Table 1. Wave characteristics of most frequent (mf) and highest (max) incoming waves.

	NW		N		NE	
	mf	**max**	**mf**	**max**	**mf**	**max**
Significant wave height (Hs in m)	1.6	6.3	1.7	5.9	0.5	3.2
Wave period (T in sec)	7.2	11.0	6.5	9.8	4.1	9.7
Intermediate waters (wave length/4 in m)	20.1	47.1	16.4	37.3	6.4	23.2
Water breaking zone (d_b in m)	2.5	9.0	2.6	8.2	0.8	4.6
Closure depth (hc, in m)	12.0		10.9		6.1	

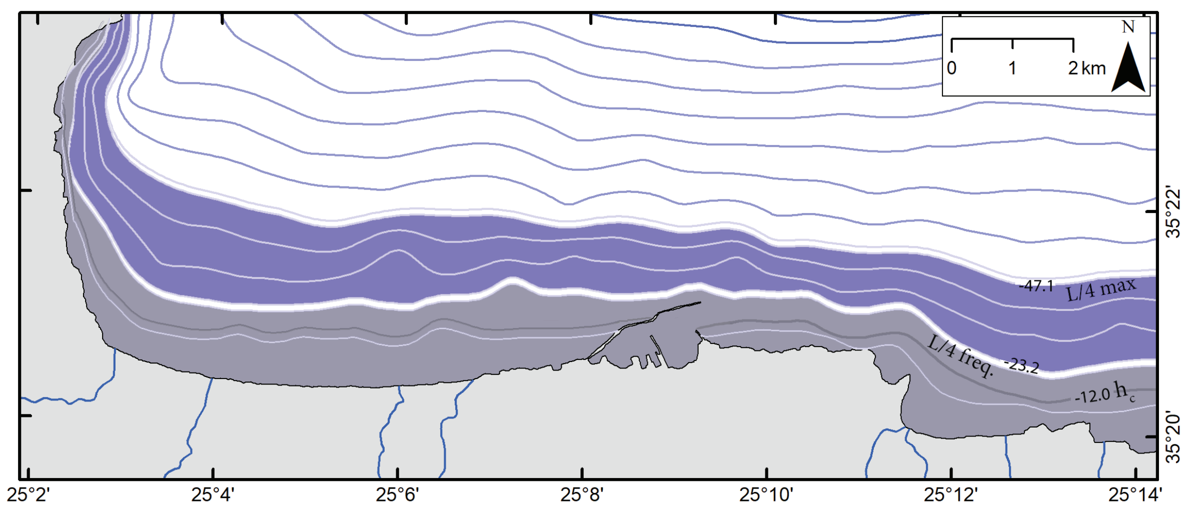

Fig. 2: Determination of the offshore zone (blue zone) by means of L/4 (according to Komar, 1976) for approaching waves of different wave lengths (L). Closure depth limit (hc) is also presented (12 m isobath).

measured using the standard Walkey method (Walkley, 1947) as modified by Jackson (1958) and Loring & Rantala (1992), which is based on the exothermic reaction (oxidation) of the sediment with potassium dichromate ($K_2Cr_2O_7$) and concentrated sulfuric acid (H_2SO_4), followed by back-titration with ferrous ammonium sulfate ($FeSO_4$) and ferroine indicator.

The carbonate content was determined by calculating the weight difference of the sample before and after the strong effervescence caused by adding hydrogen chloride (HCl) 6M (exothermic reaction followed by HCl gas and CO_2 emission, method modified from Loring & Rantala (1992).

Non-lattice held metals (nlh) were extracted by shaking the sediment samples overnight with HCl 0.5M. For the extraction of total metals, the samples were digested in Teflon beakers with concentrated acids (HF – $HClO_4$ – HNO_3). The concentrations of total and non-lattice held metal contents Cu, Zn, Fe, Mn, Cr, Pb, and Al) were determined by Flame Atomic Absorption Spectrophotometry (Varian SpectrAA 200-FAAS) with background correction (Dassenakis *et al.*, 2003). The software SPSS 17 was used for the statistical analysis of data.

The geospatial distribution of trace element contents was performed by Arc GIS desktop software. The Inverse Distance Weighted (IDW) algorithm was used to interpolate the data spatially, as, in a comparison of several different interpolation procedures, it has been found to be most consistent with the original input data (eg. Magesh *et al.*, 2011; Xie et *al.*, 2011; Mathes & Rasmussen, 2006). In order to evaluate the precision and accuracy of the method for total metal analysis certified reference materials (ISE 921, 80MS, PACS-2) from Wepal, Quasimeme and NRC-CNRC were carried through the analytical procedure along with the sediment samples. Accuracy was calculated as % recovery (percentage ratio of the measured to the certified value). The precision was evaluated by replicate analysis (n=3) of the reference materials under reproducibility conditions (different days of digestion and measurement) and the %RSD-Relative Standard Deviation (percent ratio of the standard deviation to the average concentration of the replicates) was calculated for each metal. The quality data for the total metal method, given in Table 2, show that all recoveries are between the recommended US EPA ranges (75-125%).

The extent of sediment pollution was estimated by calculating Ef (enrichment factor) as defined by Salomons & Förstner (1984) using the following formula, with aluminium as the normalization element:

$$Ef = \frac{\dfrac{Me_{sed}}{Al_{sed}}}{\dfrac{Me_{back}}{Al_{back}}}$$

where, Me_{sed} and Al_{sed} are the concentrations of each metal and aluminium, respectively, in the analysed sediment sample, while Me_{back} and Al_{back} are accepted background concentrations of the elements.

Two approaches are used in the selection of the background values. The safest approach is to use metal data from deep horizons (>50-100cm, depending on sedimentation rates) of dated core sediments from the same area. These values should prove to refer to metal contents, prior to any type of anthropogenic pollution by earliest or modern activities. When no background sediment core samples are available most researchers use trace metal levels proposed as representative of the average earth crust (Salomons & Förstner, 1984). In this study, both the average earth crust metal values and the values from a subsurface sediment recovered from 200 m of water depth have been used.

Subsequently, enrichment factor (Ef) has been applied to classify sediments into five (5) contamination classes (after Sutherland, 2000), which are:

1. Ef <2: Depletion to minimal enrichment suggestive of no or minimal pollution
2. Ef 2-5: Moderate enrichment, suggestive of moderate pollution
3. Ef 5-20: Significant enrichment, suggestive of a significant pollution signal
4. Ef 20-40: Very highly enriched, indicating a very strong pollution signal
5. Ef >40: Extremely enriched, indicating an extreme pollution signal.

Furthermore, sediment metal contents were compared

Table 2. Quality assurance data (%relative standard deviation and recovery) for total metal determination in sediments.

Certified Reference Material / Quality Measures		Al	Cr	Cu	Fe	Mn	Pb	Zn
80MS	%RSD	3.4	6.5	-	1.5	2.2	1.8	4.6
	%Recovery	87-92	87-95	-	93-95	87-90	101-104	96-104
PACS-2	%RSD	1.6	-	-	1.1	3.4	1.7	4.1
	%Recovery	79-80	-	-	90	78-83	93-96	98-104
ISE 921	%RSD	-	-	2.9	-	-	-	-
	%Recovery	-	-	97-101	-	-	-	-

Table 3. Sediment Quality guidelines for marine sediments (after Buchman, 2008).

	Background	TEL	ERL	PEL	ERM
Al	2600	-			
Cr	7-13	52.3	81	160	370
Cu	10-25	18.7	34	108	270
Fe	9900-18000	-	-	-	-
Mn	400	-	-	-	-
Pb	4-17	30.2	46.7	112	218
Zn	7-38	124	150	271	410

Table 4. Metal concentrations criteria for sediment quality classification.

	Cr	Cu	Pb	Zn
Non polluted	<25	<25	<40	<90
Moderate pollution	25-75	25-50	40-60	90-200
Heavy pollution	>75	>50	>60	>200

to Sediment Quality Guidelines (SQGs) commonly used, which provide scientific benchmarks, or reference points, for evaluating the potential of sediments to cause toxicity and adverse biological effects in aquatic systems. The SQGs used are given in Table 3, adapted from Buchman (2008). The numerical values of TEL (threshold effects level), ERM (effects range low), PEL (probable effects level) and ERM (effects range median) create the following ranges of biological effects: (1) adverse effects rarely occur (below TEL and ERL); (2) some adverse effects occur occasionally (between TEL - PEL, and ERL - ERM); and (3) adverse effects occur frequently (above PEL and ERM). The values of TEL and PEL are proposed as guidelines in Canada (CCME, 1995) while the values ERL and ERM in the US (Long *et al.*, 1995; Long & Wilson, 1997; Buchman, 2008).

Further characterization of the marine sediments has been enforced by applying the quality classification categories given by US EPA (Nichols, 1991) and presented in Table 4.

Also, it must be mentioned that EU has so far not adopted quality guidelines for metals in marine sediments, with the exception of Hg (the guideline was set at 20μg/kg in Directive 105/2008 EC). However, for the implementation and improvement of the Marine Strategy Framework Directive each Member State has submitted initial proposals for Good Environmental Status (GES) criteria in sediments. The suggested Greek GES thresholds for metals in sediments are 40mg/kg for Cu; 50mg/kg for Pb; and 150 mg/kg for Zn (Anagnopoulos *et al.* 2012).

Results and Discussion

Grain size distribution and sediment texture

The texture of the seafloor is presented in Figure 3, while the spatial grain size (sand-silt-clay) distribution in Appendix A (Fig. A1). The grain size analysis (see also Table A1 in Appendix A) shows that the nearshore zone is composed mainly of coarse sand (S) (90-100% content), reflecting the high-energy wave regime. It is worth mentioning that the seaward limit of this zone coincides with the closure depth (hc) that lies around 12 m of water depth (Fig. 3). Seawards sediments become finer (silty

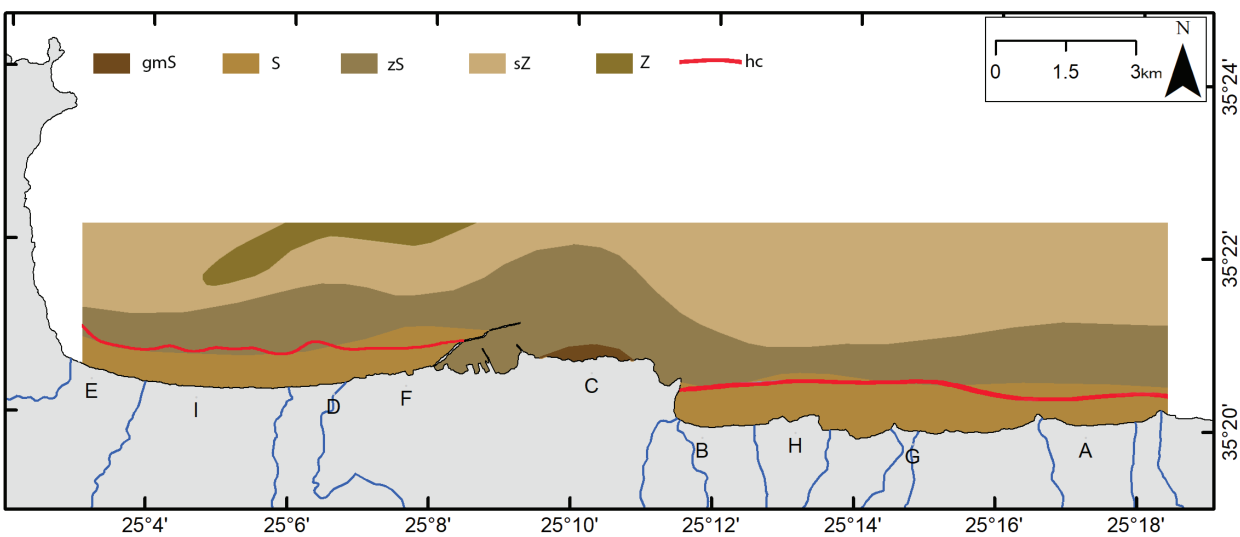

Fig. 3: Texture map based on grain size analysis according to Folk 1974. [gmS: gravelly muddy Sand; S: Sand; zS: silty Sand; sZ: sandy Silt; Z:Silt; C: Clay; M: Mud (=silt+clay) and hc: closure depth in red].

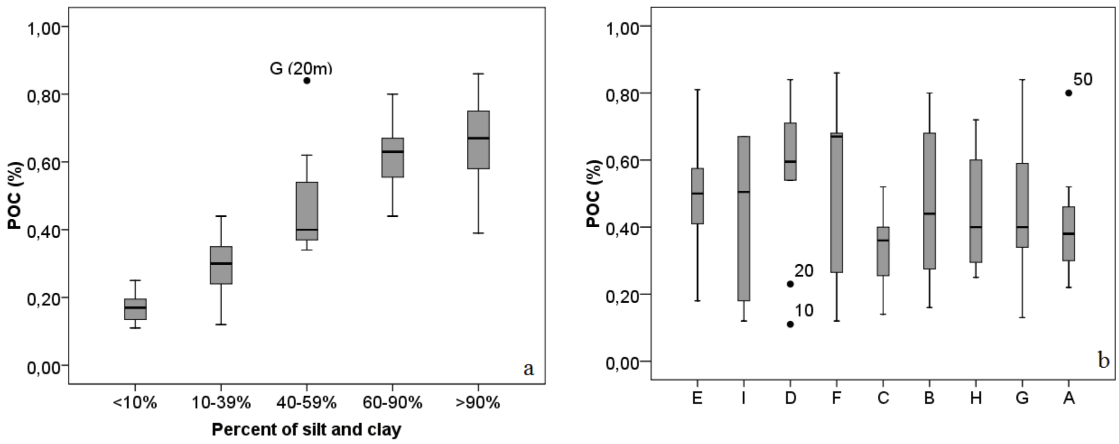

Fig. 4(a): Particulate Organic Carbon (POC) values box-plot grouped by percent silt+clay; ***(b):*** Particulate Organic Carbon (POC) values box-plot per transect (from west to east) [(•) outlier value symbol, numbers refer to the isobaths].

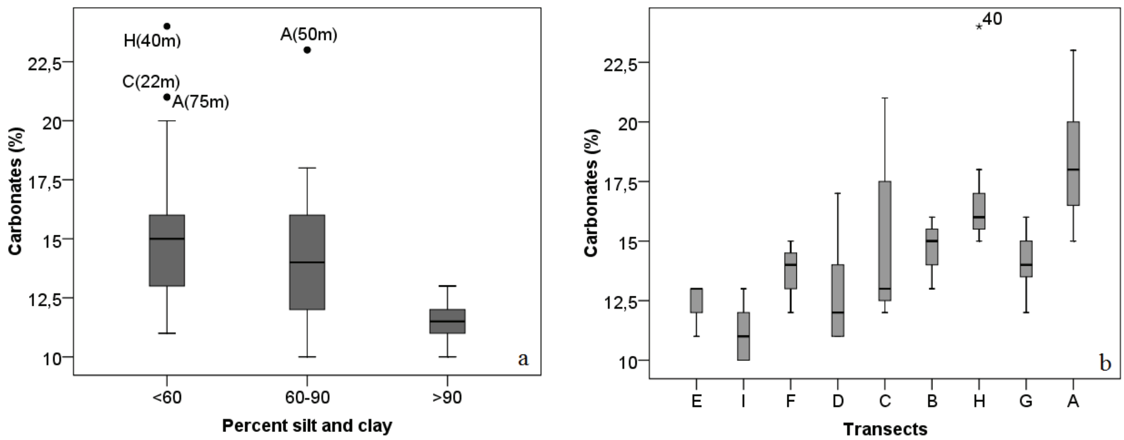

Fig. 5: (a): Carbonate content box plots grouped by percent silt+clay, b) Carbonate content box plots per transect (west to east) [(•) outlier value symbol, (*) extreme value symbol, numbers refer to the isobaths].

sand) following a zonal distribution, almost parallel to the coastline, with the silt content reaching almost 40% (Fig. 3). The sediments of the outer part of the west sub-region, which is partially protected by the NW incoming waves, present a silty zone (Z), which is not present in the east sub-region.

Organic carbon and carbonate content

The POC (particulate organic carbon) content in surface sediments varies between 0.11% and 0.86 % (mg/kg) (see Fig. A1 and Table A1, in Appendix A). The increasing content in POC seawards (see Fig. 4) indicates its association with the shift to finer sediments (i.e. increasing silt+clay content). A statistical difference of POC between the grain size groups is proven at the 95% confidence interval and thus the corresponding median POC values (Fig. 4a) follow the order: 0.17<0.30<0.40<0.63 = 0.67%.

The eastward transects, consisting of coarser material, present lower overall POC values (Fig 4b); while few samples with increased values (>0.40%) are found at the 40 m and 50m isobaths of transect A, at depths above 20m in transect B and above 40m at transect H and with the second highest POC value (0.84%) of the entire dataset located at 20m of transect G. The coarser material of transect C is associated with the lowest POC values (0.14-0.52%). In general, the western transects (E, I, D and F) present increased POC levels (>0.50%) seawards. The maximum observed POC value (0.86%), found in transect F at 50m of water depth, is most likely related to the nearby treated sewage outfall of Heraklion city. However, the detected increased POC value cannot be considered as a definite indicator of pollution since it is well below organic carbon content reported for polluted gulfs of Greece such as Thessaloniki Bay (1.2-3%; after Karageorgis *et al.*, 2005) and Elefsina Bay (2.6-3.0%; after Paraskevopoulou, *pers. comm.*). In general, the organic carbon content of Heraklion Gulf sediments is similar to values reported for Aegean Sea sediments, as in the case of Sporades basin (0.4-0.6%; after Karageorgis *et al.*, 2005) and Saronikos Gulf (0.33-0.52%; after Paraskevopoulou, *pers. comm.*). Undoubtedly, the operation of the urban wastewater treatment plant, the increased wave activity and the water circulation conditions contribute to the observed low organic carbon concentrations.

The carbonate content is generally low (<20%). The

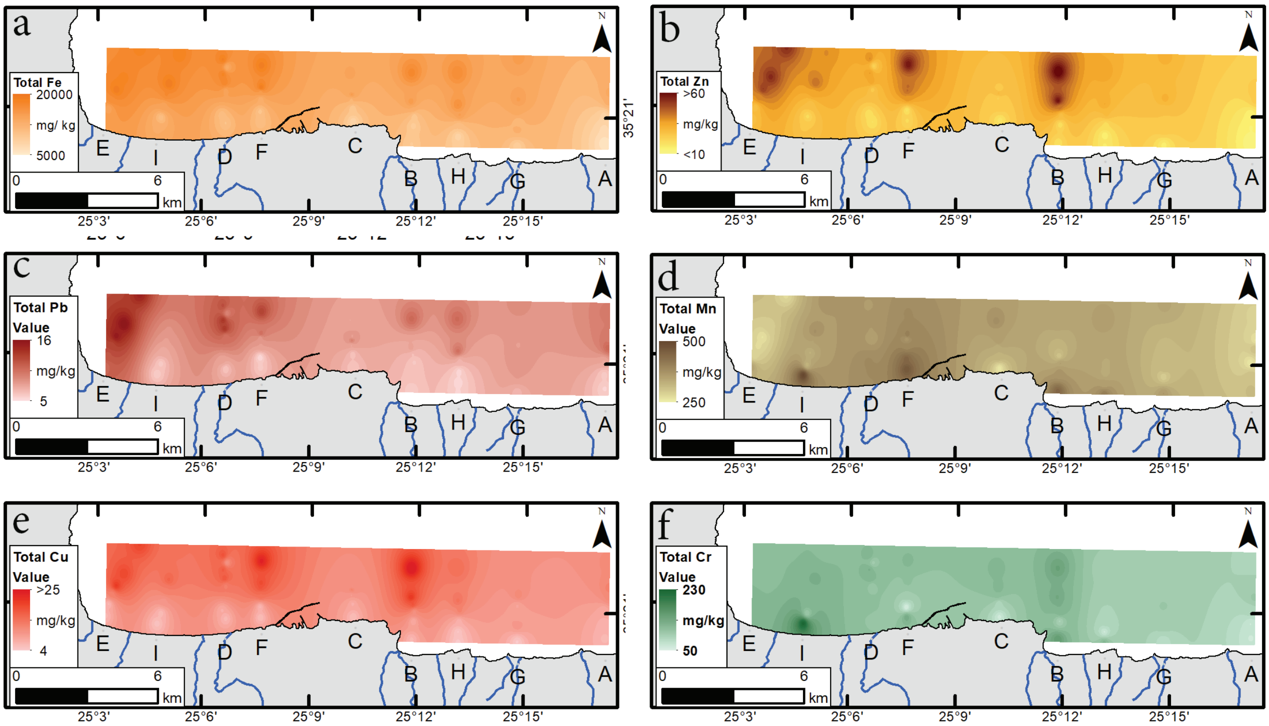

Fig. 6: Spatial distribution of total metal content in sediments (Al distribution is not presented, as it is similar to Fe) [a: Fe; b: Zn; c: Pb; d: Mn; e: Cu; f: Cr].

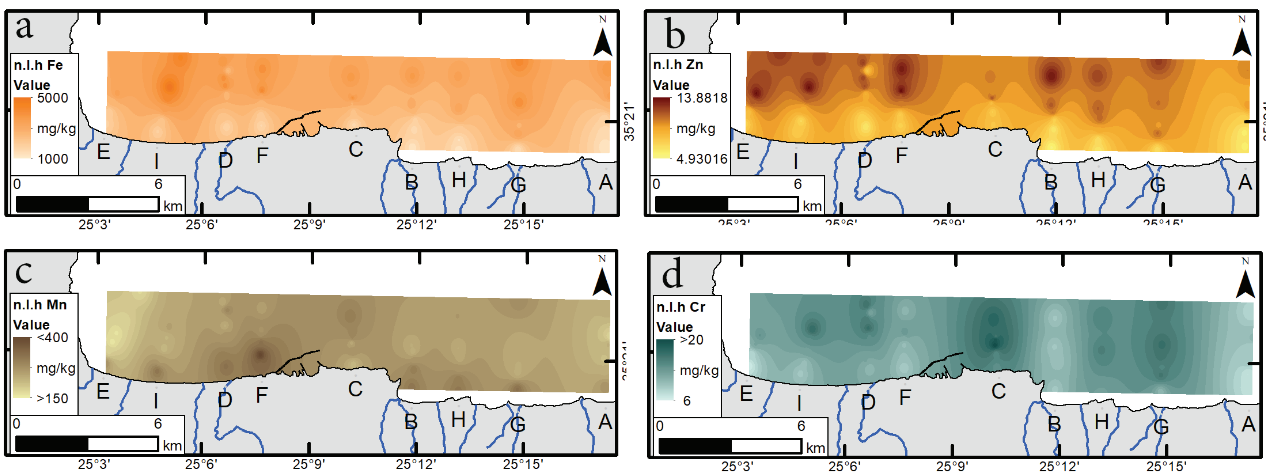

Fig. 7: Spatial distribution of non-lattice held (nlh) metals in surficial seabed sediments (a: Fe; b: Zn; c: Mn; d: Cr).

fine-grained sediments (silt+clay content>90%) present statistically lower carbonate contents (10-13%), compared to more coarse-grained sediments (with silt+clay content <90%) that have slightly increased carbonate percentages (13-15%). Carbonate contents above 20% are observed only locally (Fig. 5a). Figures 4b and 5b reveal that the trends of POC and carbonate contents are consistent with the established norms that carbonate minerals are mostly found in the coarser sediment particles, while the content of organic carbon increases with decreasing grain size (Salomons & Forstner, 1984).

The carbonate content of the inner shelf of Heraklion Gulf (<20%) is similar to that reported for the coastal areas of the North Aegean, but much lower than those reported for other marine areas of Greece (>40%) such as those of Evoikos and Saronikos gulfs, the Cyclades plateau and Alexandroupolis Gulf (Poulos 2009; Karditsa & Poulos, 2013).

Trace metals

The spatial distribution of the total and non-lattice held concentrations of Fe, Mn, Cr, Zn, Pb, Cu trace metals are shown in Figures 6 and 7 respectively, while the ranges of their abundances are given in Table 5. All the analytical results are presented in Table A1 (Appendix A).

Fe and Al present the highest concentrations among

Table 5. Total (tot in mg/kg), non-lattice held (nlh in mg/kg) and % non-lattice held metals.

		Min	Max	Average
	tot	51	234	108
Cr	nlh	6	24	14
	% nlh	4	27	14
	total	5120	26004	14563
Fe	nlh	1010	4942	2869
	%nlh	11	31	20
	tot	273	494	355
Mn	nlh	176	376	258
	% nlh	58	88	73
	tot	12	69	34
Zn	nlh	5	16	10
	%nlh	19	46	31
Al	tot	10326	52529	28984
Cu	tot	5	28	13
Pb	tot	5	23	9

Note: non-lattice held Cu and Pb are below detection limits and labile Al was not measured.

all metals with total values ranging between 5120-26004 mg/kg and 10326-52529 mg/kg, respectively. This is anticipated since Fe and Al are basic constituents in natural minerals (aluminosilicates) and mostly of lithogenic origin. Non-lattice held (nhl) Fe concentrations range between 1010 and 4942 mg/kg and the percentages of nlhFe to the total content varies between 11% and 31%. The values of total Al and Fe increase seawards and in the western transects wherein sediment becomes finer (see Fig 6a and Fig. A2a,b in Appendix A). Moreover, the differentiation between the western transects (more affected by riverine lithogenic contributions) and the eastern transects is more prominent for Al than for Fe. This is even more apparent in the case of nlhFe and %nlhFe, where the absolute difference between western and eastern transects ceases to exist. There is a degree of uniformity in non-lattice held Fe content among transects (Fig. A2c in Appendix A) but with some high values in transects I, D and F (river mouths of Gazanos, Xiropotamos and Giofyros), as expected, and also in transect G (former military base, Gouvianos). However, the percent of nlh Fe, more indicative of non-lithogenic sources is higher in transects C (navigation channel), G and A (former military base, Gouvianos, Aposelemis, Sfakoryako) followed by transect I (rivers Gazanos and Xiropotamos). Surprisingly, the lowest nlhFe percentages are found in transect E, where Almiros and Gazanos streams debouch spring water (Fig. A2d).

The total Mn content ranges from 273 to 494 mg/kg and the non-lattice held Mn content between 176 and 376 mg/kg. In contrast to Fe and Cr, that exhibit low non-lattice held percentages (20% and 14%, on average), the %nlhMn ranges from 58% to 88% (73% on average). Moreover, in the case of Mn, in contrast to Fe and Al, higher values are not observed in the finer sediments or the western transects. The highest values are found at 10m depth in transects I, D, B and H, in some samples of transect D (20m and 150m of water depth) and in all samples of transect F (waste treatment terminal outfall). The lowest values of total nlhMn are observed in transect E (Almiros, Gazanos) and the lowest percent nlhMn in transects E and I (Almiros, Gazanos and Xiropotamos river mouths) (see Fig. 6d, Fig 7c and Fig. A3a,b,c, in Appendix A).

The range of total Cr is 51-234 mg/kg and for nlhCr 6-24 mg/kg (Table 5). Similarly to Fe, Cr also exhibits low %nlh ranging from 4% to 27%. However, Cr presents a different spatial distribution (see Fig. 6f, Fig 7d and A4, a in Appendix A). In this case, higher levels of total Cr (>100mg/kg) are identified not only in transects E, I, D, and F (west of Heraklion harbour), similarly to Al and Fe,

Table 6. Correlation matrix for total metal concentrations, percentages of muddy (silt+clay) fraction M%, CaCO3 and particulate organic carbon (POC).

	M (%)	$CaCO_3$	POC	Al	Fe	Zn	Pb	Cu	Cr	Mn
M (%)	1									
$CaCO_3$	-0.21	1								
POC	0.85**	-0.04	1							
Al	0.85**	-0.50**	0.67**	1						
Fe	0.84**	-0.43**	0.68**	0.93**	1					
Zn	0.82**	-0.34**	0.64**	0.85**	0.85**	1				
Pb	0.65**	-0.32*	0.55*	0.77**	0.82**	0.70**	1			
Cu	0.87**	-0.23	0.75**	0.84**	0.84**	0.95**	0.73**	1		
Cr	0,22	-0.50**	0.18	0.40**	0.40**	0.39**	0.24	0.30*	1	
Mn	-0.18	-0.34*	-0,26*	0.10	0.04	-0.08	-0,21	-0,11	0.40**	1

Note. (*) correlations statistically significant at the 95% confidence level; (**) correlations statistically significant at the 99% confidence level.

but also in transects C (navigation channel) and B (former outfall of untreated wastewaters, Krateros and Vathylagkos streams). Higher levels of nlhCr and %nlhCr in transects C (navigation channel) and G (former military base) are apparent in Fig. 7d and Fig. A4c, indicating slightly increased anthropogenic inputs, in contrast to the lower values in transects near the river mouths and ephemeral streams attributed to lithogenic non labile input.

Pb, Cu and Zn (usually considered as pollution indicators) present much lower concentrations 5-23, 5-28 and 12-69 mg/kg, respectively. Concerning the total contents of Cu, Pb and Zn, as well as nlhZn, there is a clear increasing trend with decreasing grain size. The spatial distribution of total Cu resembles to those of the other metals already discussed. Similarly to Al, the lowest levels of total Cu are found in transect C, while similarly to Fe, sediments of the western transects are slightly more enriched in Cu than the eastern ones. Moreover, the increased value of total Cr and total Cu in transect B (at depths of 50m and above) differentiate B from its neighbouring transects H, G and A (see Fig. A5a, in Appendix A). The highest values of total Pb are found in transects E and D (Fig. 6c), while in all other transects Pb presents lower contents. Total Zn is similar to Al and Cu, with transect C exhibiting the lowest total content, with relatively enriched presence in transects B former outfall of untreated wastewaters), F (waste treatment terminal outfall) and E (Almiros, Gazanos). Non-lattice held Zn levels are quite low (5-16mg/kg) at all transects, with the exception of transect A where it is slightly lower (see Fig. A5c in Appendix A). Finally, the spatial distribution of %nlh Zn is highly comparable to that of %nlh Cr (see Fig. A5d in Appendix A) with the lowest values in transects E, I, D, F and B located seawards to river mouths, while higher values are observed at the navigation channel and along the eastern transects.

Associations among (i) metals and (ii) metals and grain size, carbonates and total organic carbon

The associations among metal concentrations and the fine-grained, carbonate and POC percentages are given in Table 6, while Tables 7 and 8 present the correlations of the non-lattice held (nlh) metals and the percentages of the non-lattice held (%hlh) metals, respectively.

On the basis of the findings in Table 6, fine-grained sediments (silt+clay fraction) are strongly associated with organic carbon and all trace metals with the exception of Mn and total Cr, as they present correlation coefficients statistically significant at 99% confidence level. Organic carbon is positively correlated to all metals (total content and nlh content) except Cr and presents a strong negative correlation to total Mn, nlhMn and %nlhMn. Carbonates

Table 7. Correlation matrix of non-lattice held metals (nlh).

	M (%)	$CaCO_3$	POC	nlhMn	nlhZn	nlhFe	nlhCr
M (%)	1						
$CaCO_3$	-0.21	1					
POC	0.85**	-0.04	1				
nlhMn	-0.50**	-0.05	-0.52**	1			
nlhZn	0.87**	-0.28*	0.73**	-0.39**	1		
nlhFe	0.76**	-0.25*	0.69**	-0.28*	0.85**	1	
nlhCr	0.39**	-0.27*	0.37**	-0.12	0.48**	0.56**	1

Note. (*) correlations statistically significant at the 95% confidence level; (**) correlations statistically significant at the 99% confidence level.

Table 8. Correlation matrix of percent non-lattice held metals (nlh).

	M (%)	$CaCO_3$	POC	%nlhMn	%nlhZn	%nlhFe	%nlhCr
M (%)	1						
$CaCO_3$	-0.21	1					
POC	0.85**	-0.04	1				
%nlhMn	-0.61**	0.40**	-0.52**	1			
%nlhZn	-0.37**	0.34**	-0,22	0.55**	1		
%nlhFe	0.12	0.25*	0.21	0.35**	0.52**	1	**
%nlhCr	0.03	0.17	0.04	0.23	0.49**	0.37**	1

Note. (*) correlations statistically significant at the 95% confidence level; (**) correlations statistically significant at the 99% confidence level.

have strong negative correlations to all total metals, nlh Zn, Fe and Cr. Also, there are statistically significant positive correlations (99% confidence level) between the percentage of the fine fraction and nlhFe (r=0.76**), nlhZn (r=0.87**) and nlhCr (r=0.39**), and a strong negative correlation for nhlMn (r=0.50**). Finally, the percentage of the non-lattice held (%nlh) metal contents have either no correlation with %nlhFe, %nlhCr and organic carbon, or strong negative correlations with %nlhZn and %nlhMn and fine grained sediments. Strong correlations to carbonates exist especially for %nlhZn and %nlhMn and to a lesser degree for %nlhFe.

The clear trend of total Al, Fe, nlhFe, Cu, Pb, Zn, nlhZn and nlhCr to increase in finer sediments is anticipated because when the size of sediment grains decreases their surface area increases, as well as the concentrations of many geochemical phases known to bind trace metals (Fe and Mn oxides and hydroxides, organic carbon, and clay minerals). The existing strong correlation between metals (e.g. Cu, Zn, Fe, Pb, Al) and the organic carbon content results from this primary relation to grain size (Salomons & Forstner 1984; Horowitz & Elrick 1987, Calvert *et al.* 1985).

The strong association between Fe and Al is reasonable, as they are principal lithogenic constituents of natural minerals (aluminosilicates) in sediments and are present in high concentrations (i.e. one order of magnitude) above the mean value of the other metals.

The different spatial distributions of the main lithogenic metals, Fe and Al on one hand, and Mn on the other, along with the marked difference between the percentages of non-lattice held fractions, support the existence of very different lithogenic phases. Fe, Al, non-lattice held Cr, Zn, Pb and Cu are increased to the west, where seabed sediment is finer and most likely occur in alluminosilicate minerals of terrestrial origin. In contrast, Mn exhibits higher concentrations in coarse-grained sediments, indicating a correlation with other mineral phases. All samples with coarser grain sizes (sand > 50%) exhibit Mn/Al ratios quite above the average 106×10^{-4} shale ratio with a range of $122\text{-}312\times10^{-4}$ and an average value of 176×10^{-4}. Other researchers have also found similar associations of Mn to coarse-grained sediments and proposed the existence of authigenic manganese carbonate, or Mn oxyhydroxides, or Mn enriched mica grains (e.g. Pedersen & Price, 1982; Karageorgis *et al.*, 2005).

Sediment quality and enrichment evaluation

The US-EPA limits presented in Table 4 are used to evaluate the pollution status of the studied sediments. The average concentrations of Zn, Pb and Cu are low and according to US-EPA limits (90mg/kg for Zn, 40 mg/kg for Pb and 25mg/kg for Cu) indicate non polluted sediments. On the contrary, the average Cr content (108mg/kg) leads to the characterization of possible heavy pollution. In more detail, 11% of the samples could be considered as moderately polluted sediments with the remaining as heavily polluted.

The metal concentrations were also compared to the SQGs proposed by NOAA and CCME (see Table 3). For Cu, Zn and Pb, all samples present concentrations below TEL and ERL limits, which means that adverse effects on benthic biota due to exposure to these metals are unlikely to occur. However, in the case of Cr, the content in 63 out of 65 samples was in the range between TEL and PEL, which means that adverse effects are probable.

Furthermore, in order to examine whether the pollution origin is anthropogenic or not, the Enrichment Factor (Ef) was used. Thus, the enrichment factors of metals in the sediments, after normalisation with respect to Al, were calculated using two sets of metal background levels. The first set refers to metal contents proposed for the earth's crust (Salomons & Förstner, 1984) and the second set refers to metal levels of a subsurface sediment (approximately 15cm beneath the seafloor) collected at the reference station (D-200m). The metal background values (in mg/kg) are given in Table 9, while the results of the Ef calculations are summarized in Table 10.

Efs based on local background levels (reference area subsurface sediment) are considered to be more reliable compared to those of the average crust metal levels. According to the contamination classes of Sunderland (2000), the so-called anthropogenic metals (Cu, Pb and Zn) - along with Fe present Enrichment Factors below 2, against the background value of the reference station - are characterized as causing minimal pollution. In the case

Table 9. Metal background values for Enrichment Factor (Ef) calculations.

Background	Al	Cr	Cu	Fe	Mn	Pb	Zn
Average Crust	82000	100	50	41000	950	14	75
Reference station	53761	139	27	25740	390	20	54

Table 10. Enrichment Factors (Ef) based on Al as a normalization element for both the average crust and the reference station background.

	Fe		Mn		Cr		Cu		Pb		Zn	
	Crust	Ref	Crust	Ref	Crust	Ref	Crust	Ref	Crust	Ref	Crust	Ref
Min	0.7	0.7	0.6	0.9	1.8	0.8	0.4	0.4	1.1	0.5	0.9	0.6
Max	1.4	1.4	2.2	3.6	8.4	4.0	1.4	1.7	3.3	1.6	2.1	1.9
Average	1.0	1.0	1.1	1.7	3.2	1.5	0.8	0.9	1.8	0.9	1.3	1.1

Table 11. Minimum, maximum and averaged total values of the common trace metals (Cu, Pb, Zn in mg/kg) and Particulate Organic Carbon (POC in %) for the sampling campaigns of 1989 (Poulos *et al.,* 2009) and 2010 (present study), along with changes expressed in percentages.

	2010			1989			Change (in %) from 1989 to 2010		
	min	**max**	**aver**	**min**	**max**	**aver**	**min**	**max**	**aver**
Cu	5.0	28.0	13.0	2.07	126.10	27.11	+43.2	-45.3	-21.6
Pb	5.0	23.0	9.0	8.26	63.00	24.26	-54.4	-78.1	-50.4
Zn	12.0	69.0	34.0	6.89	125.32	42.74	+38.9	-63.5	-62.2
POC (%)	0.11	0.86	0.5	0.002	1.01	0.55	+98.2	-15.5	-53.1

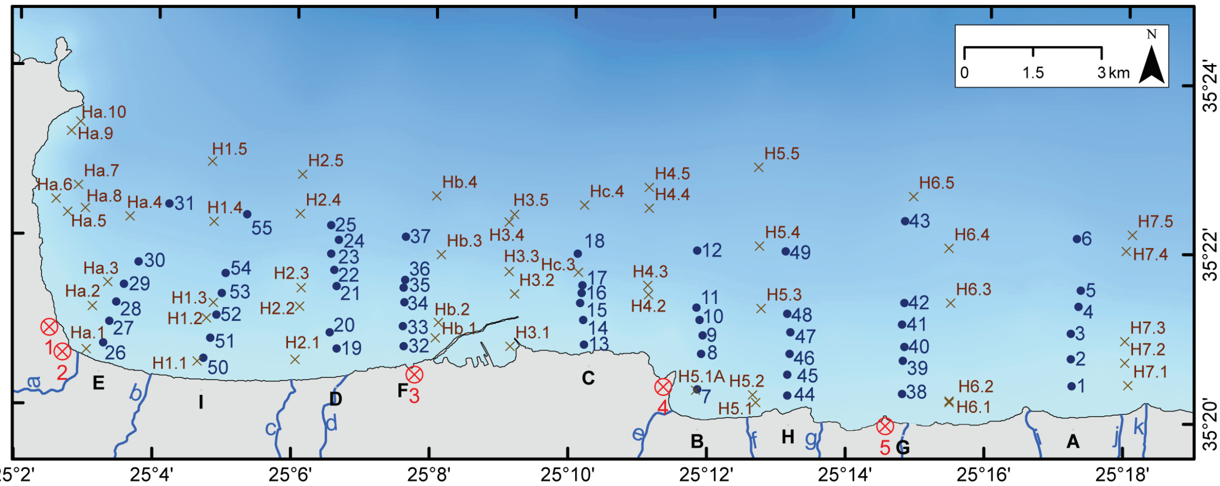

Fig. 8: Map showing the sampling stations in 1989 (referred by Poulos et al., 2009) (·) and those of the present investigation (x) over the bathymetry.

of Cr, 12 samples (19% of the total number of samples) present Enrichment Factors in the range of 2-5, suggesting moderate pollution. The highest Enrichment Factors for Cr are found near the mouth of Gazanos river (transect I), east of the harbour (transect C), west of the harbour near the outfall of treated waste waters (transect F), near a former site of untreated waste outfall (transect B) and, finally, in some samples of transect A. Unfortunately, the available dataset does not allow to fully identify the reasons (e.g. lithology, human intervention) involved in the occurrence of the aforementioned increased Cr concentrations and Enrichment factors.

Comparison between 1989 and 2010 datasets

A comparison between the 2010 dataset (present study) and the 1989 dataset (Poulos *et al*. 2009) is presented in Table 11 (locations of both sampling campaigns presented in Figure 8).

The 2010 dataset shows reduction of metal concentrations in bottom sediments, while the POC contents are consistent with those of the previous study, where most samples exhibited values of approximately 0.5% (5 mg/g) with a maximum value of 1.013% (i.e. 10.13mg/g). This improvement of environmental conditions could be both attributed to the restriction of sources of pollution (e.g. installation and operation of the Heraklion Municipality sewage treatment plant and marine outfall) and to the circulation (renewal) of shelf waters.

Comparisons with other costal Greek and Mediterranean sediments

From the referenced sediment data presented in Table 12, it is observed that the values of the lithogenic elements Fe, Mn and Cr in the sediments of Heraklion Gulf are similar to most in other Mediterranean areas. In addition, the maximum Cr concentrations in Heraklion are lower than those in other Greek areas characterised by either specific (i.e. the red mud input in the Gulf of Corinth, after Iatrou *et al.*, 2010) or other natural sources (i.e. geologic/ophiolithic -volcanic input in NW Saronikos, after Paraskevopoulou 2009). Fine-grained offshore sediments and sediments affected by mining activities (Pappa *et al*. 2016), riverine inputs (Karageorgis *et al.*, 2005 and Karditsa *et al.*, 2014), industrial activities (Dassenakis et *al.*, 2003) and the aforementioned red mud industrial discharge in the Gulf of Corinth (Iatrou et *al.*, 2010) are also characterized by higher concentrations of Fe and Mn. The maximum and mean concentrations of Cu, Pb, Zn (the so-called anthropogenic elements) in the sediments of Heraklion Gulf are generally much lower

Table 12. Ranges and mean or median values (in parentheses) of trace metal concentrations in coastal sediments of Greece and the Mediterranean Sea (nd: non detected).

Area (reference)	Sediment type, metal sources	Cr mg/kg	Fe mg/kg	Mn mg/kg	Cu mg/kg	Pb mg/kg	Zn mg/kg
Heraklio Gulf (this study)	Sandy, various	51.3-234 (104)	5120-17329 (11294)	273-494 (365)	4.5-16.0 (8.8)	5.0-11.9 (7.3)	12.1-39.2 (23.8)
	Muddy, various	83.8-152 (114)	12558-26004 (18345)	279-421 (348)	8.9-27.6 (18.9)	6.5-23.0 (11.3)	24.6-68.5 (45.0)
Central Evoikos Gulf (Dassenakis *et al.,* 2003)	<63μm, industrial,urban	-	14040-39680	309-702	29.9-240	-	66.5-435
Northern Cyprus (Duman *et al*., 2012)	Sandy, Urban,Cu mining	9.0-46	1800-84400	141-1241	1.6-74	1.6-9.2	5.0-78
Gulf of Alexandria, Egypt (El Nemr *et al*., 2007)	Sandy Industrial, urban,	11.6-110 (58.2)	124-37852 (9314)	13.5-1384 (469)	6.9-192 (41.7)	39.9-120 (78.7)	16.6-167 (75.3)
	Muddy, Industrial, urban	16.1-413 (78.6)	225-51006 (11823)	26.5-2257 (815)	10.4-190 (70.4)	59.9-220 (92.9)	24.1-241 (79.9)
Antikyra bay-Gulf of Corinth (Iatrou *et al*., 2010)	Red mud fine sediments, industrial	1030-4312 (2281)	30400-36700 (35400)	800-3501 (2119)	110-148 (133)	111-195 (146)	95-143 (122)
	Natural coarser sediments, industrial, urban	nd-753 (207)	4920-16920 (8420)	1292-8674 (4044)	29-101 (57)	nd-101 (30)	89-326 (218)
NW Aegean Sea (Karageorgis *et al.,* 2005)	Mostly muddy, industrial, urban, riverine input	39-458 (222)	4790-28575 (20808)	286-4336 (1378)	4-108 (34)	17-265 (52)	33-429 (120)
Alexandroupolis Gulf, NE Aegean (Karditsa *et al.,* 2014)	Both fine and coarser, industrial, urban, agricultural, riverine input	23-221 (66)	12800-48400 (30800)	271-1332 (557)	3-78 (20)	9-113 (38)	37-248 (93)
Ierissos gulf, North Aegean (Pappa *et al.,* 2016)	Mostly sandy, Mining	-	-	3835-25982 (10150)	31-206 (143)	567-1698 (1146)	936-4078 (1863)
NW Saronikos (Paraskevopoulou, 2009)	Mostly coarse grained, few muddy, oil refinery, vacation area, volcanic	180-5642	8108-44069	264-4822	5.6-40.4	4.5-56.6	27.7-120
NE Sicilian coast, SE Tyrhennian Sea, Italy (Saccà *et al*., 2011)	Mostly muddy, industrial, urban, riverine, volcanic	68-205 (137)	22731-34972 (31124)	(774)	40.9-105 (75.3)	-	127 339 (202)

than the corresponding levels in all the areas referenced in Table 12. This is due to the fact that the north coast of Crete (Heraklion Gulf) is subjected to fewer and relatively small-scale anthropogenic pressures compared to the other areas examined in Table 12.

Conclusions

The surficial sediments of the coastal area of Heraklion region present a zonal, textural distribution that generally follows the bathymetry, presenting a decreasing grain size (S→zS→sZ→Z) trend seawards. This zonal distribution is related to the wave propagation in the intermediate zone, where water depths are smaller than the ¼ of the length of incoming waves. The maximum depth of wave-induced sea-bed mobility is 10-12 m coinciding with the sandy zone.

The values of $CaCO_3$ content, ranging from 10% to 24% with an eastward increasing trend, are attributed mostly to biogenic fragments.

The total values of Fe, Zn, Pb, Cu and Al increase with increasing water depth and are associated with the decrease in the size of the sediment granules as confirmed by the SPSS correlations.

On the basis of the spatial distribution of trace metals, POC and the location of potential pollution sources onshore the coastal area under investigation could be divided into two sections relative to the port of Heraklion: (1) the hydrodynamically semi-protected western province, where there are more sources of potential pollution; and (2) the open eastern province with much less potential sources of pollution and more energetic hydrodynamic conditions. This is evidenced by the relatively lower concentrations of most trace metals and POC in the eastern province compared to the western one.

The relatively lower values of trace metal concentrations, presented by the currently analysed dataset of 2010, compared to that of 1989, indicate an improvement of the coastal environmental status of the examined area; the latter is believed to be the outcome of a better control of terrestrial pollution sources, following the transposition of Directive 91/271/EEC (as amended by Directive 98/15/EU) into Greek national legislation in March 1997 entitled "Measures and Conditions for the Treatment of Urban Wastewater" and its implementation.

Overall, the concentrations of Cu, Zn and Pb in all sediment samples show values below the TEL and ERL limits indicating zero to very low probability for adverse effects on benthic biota due to exposure to these metals. However, in the case of Cr, most samples were in the range between TEL and PEL, increasing the probability of adverse effects on benthic biota; hence, more detailed monitoring of Cr concentrations, including non-lattice held levels, is recommended.

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APPENDIX A

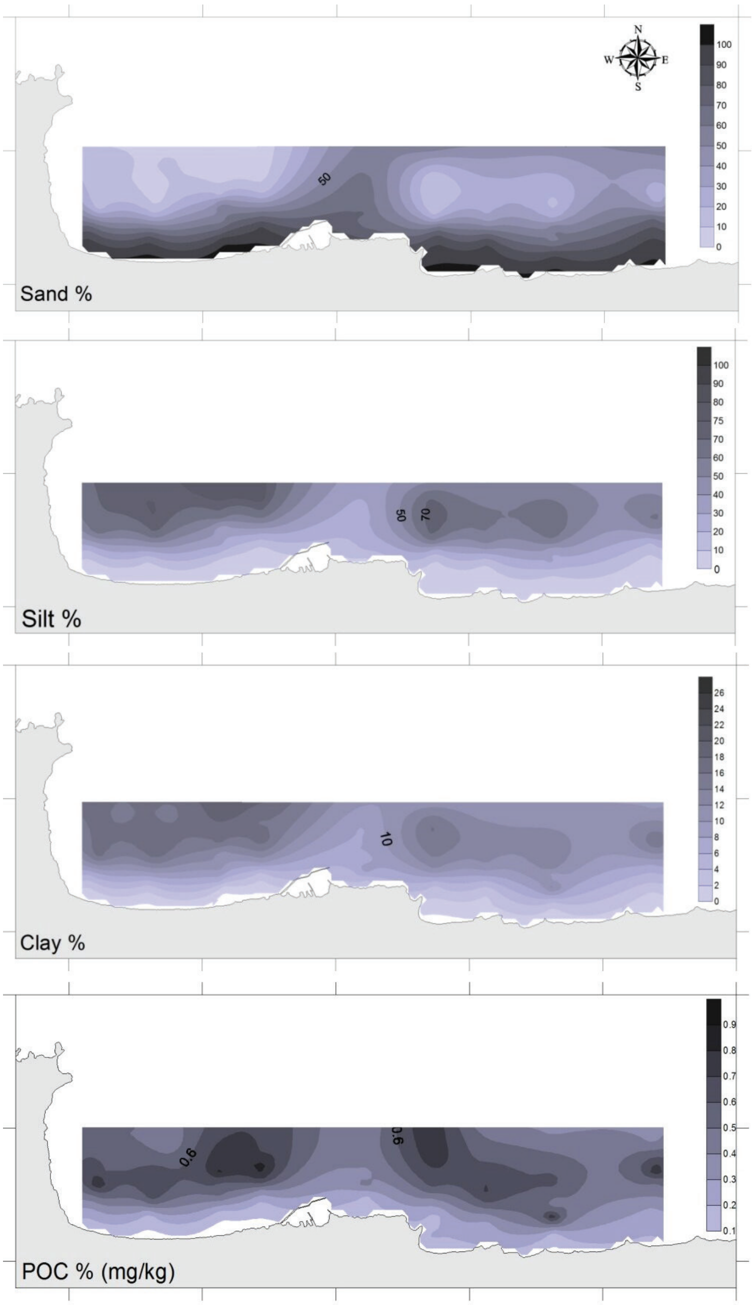

Fig. A1: Schematic presentation of sand, silt, clay distribution and Particulate Organic Carbon (POC) percentages.

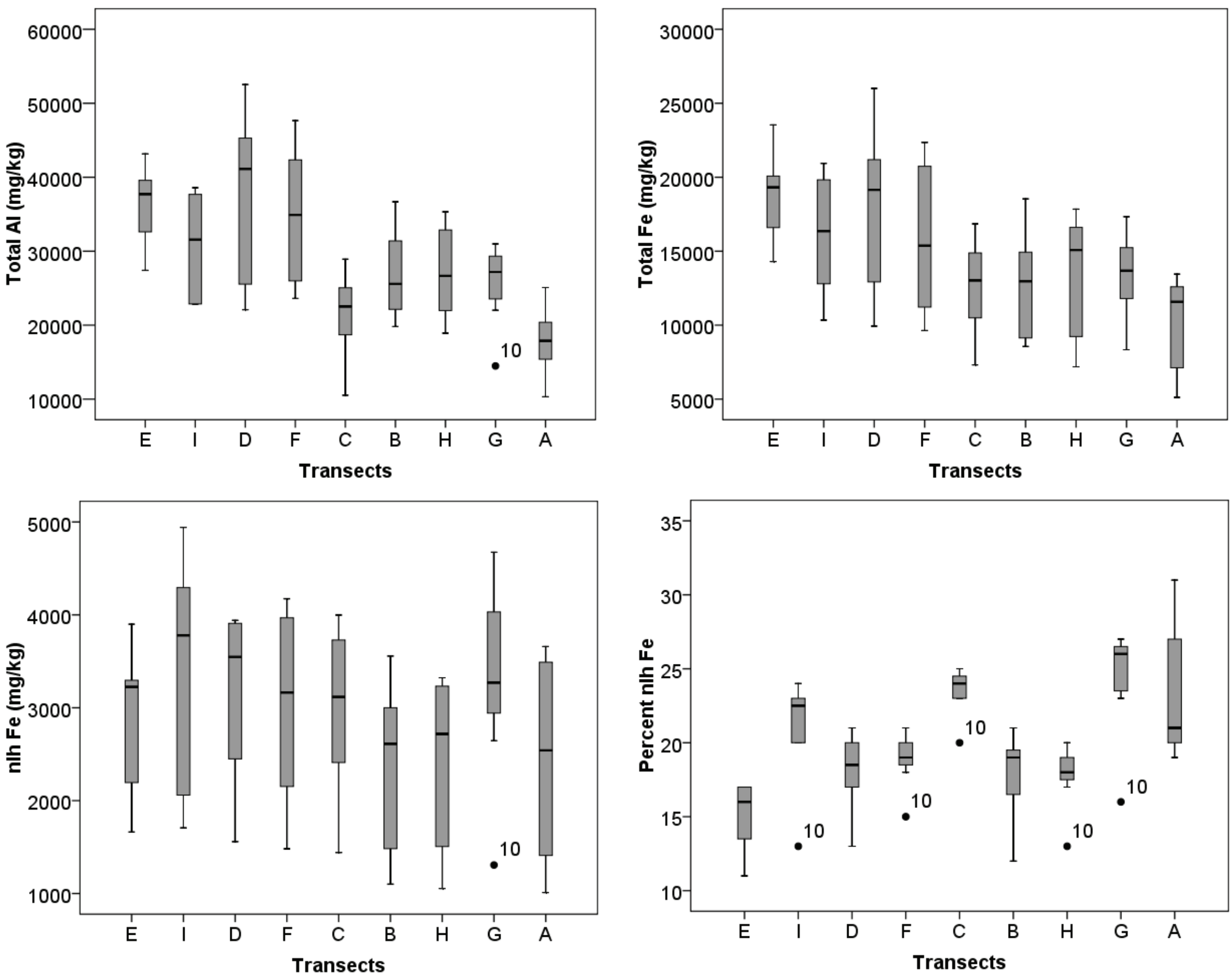

Fig. A2: Al and Fe (total, nlh and %nlh) per transect [transects are presented from west to east, (•)the outlier value symbol and numbers refer to the isobaths].

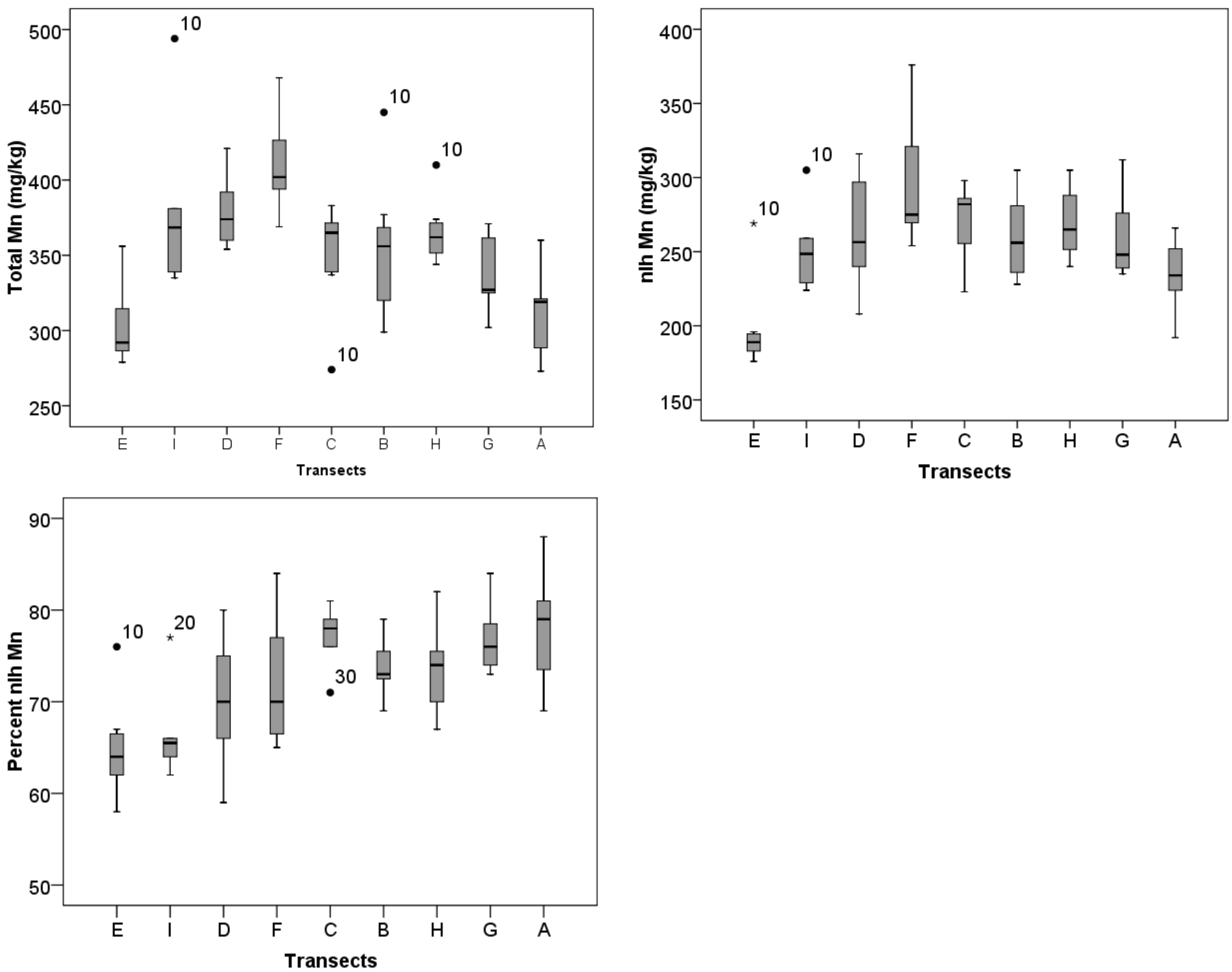

Fig. A3: Mn (total, nlh and %nlh) per transect [transects are presented from west to east, (•) the outlier value symbol and numbers refer to the isobaths].

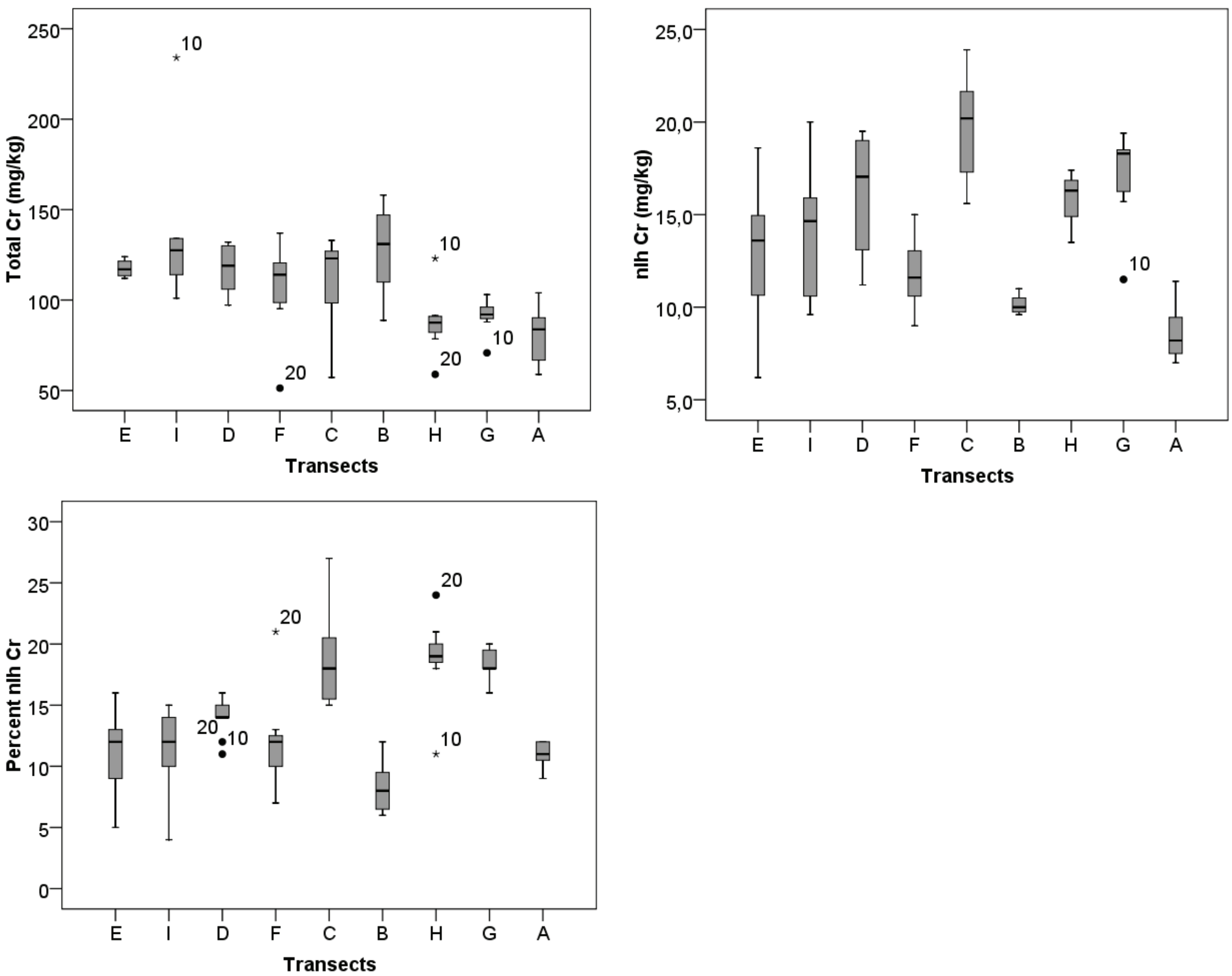

Fig. A4: Cr (total, nlh and %nlh) per transect [transects are presented from west to east, (•) the outlier value symbol and numbers refer to the isobaths].

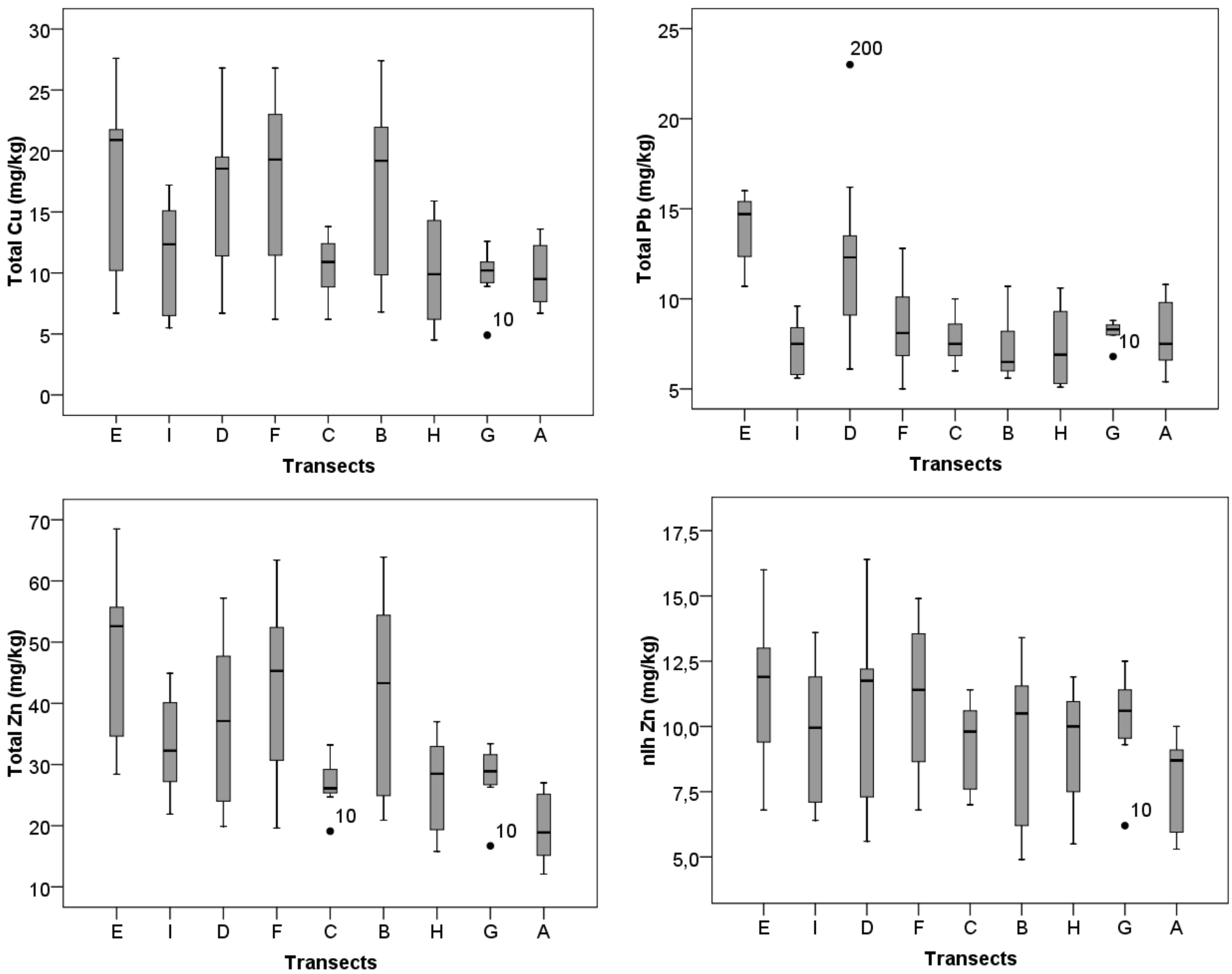

Fig. A5: Total Cu, Pb and Zn and nlhZn per transect [transects are presented from west to east, (•) the outlier value symbol and numbers refer to the isobaths].

Table A1. Sediment texture (after Folk, 1980), metals in total and non-lattice held values (in mg/kg), $CaCO_3$ and Particulate Organic Carbon (POC) content expressed in percentages [gmS: gravelly muddy Sand; S: Sand; zS: silty Sand; sZ: sandy Silt; Z:Silt; C: Clay; M: Mud (=silt+clay)].

Transect	Stations	Depth (m)	Texture	Cr tot	Cr nl	Fe tot	Fe n.l.	Mn tot	Mn n.l.	Zn tot	Zn n.l.	Al_{tot}	Cu_{tot}	Pb_{tot}	$CaCO_3$ (%)	POC(%)
A	1	10	S	59	7	5120	1010	322	266	12	5	10326	7	5	17	0.22
	2	20.6	mS	60	7	6640	1259	319	238	15	5	17887	7	6	15	0.27
	3	30.6	zS	85	10	7592	1561	273	217	16	7	16913	8	7	18	0.40
	4	40.5	sZ	104	9	12558	2541	320	231	26	9	25087	12	11	16	0.52
	5	55	sZ	95	11	13451	3419	279	192	27	9	22604	14	10	23	0.80
	6	75	sZ	84	8	12636	3659	298	234	25	10	13875	12	10	21	0.38
B	7	10	S	158	10	8937	1101	445	305	21	5	19815	7	6	15	0.21
	8	19.2	zS	89	11	8562	1350	377	298	21	6	21660	8	6	13	0.16
	9	29.3	zS	129	10	9342	1615	360	264	29	7	22617	12	6	15	0.34
	10	40	sZ	131	11	12966	2612	310	233	43	11	29274	19	6	16	0.44
	11	49.8	sZ	142	10	15633	2961	330	239	60	11	33506	23	8	14	0.61
	12	75.3	sZ	152	10	18534	3557	356	256	64	13	36691	27	11	14	0.75
C	13	12.1	gmS	57	16	7310	1441	274	223	19	7	10529	6	6	20	0.13
	14	21.5	zS	82	16	9197	2112	337	268	26	7	15728	8	6	21	0.17
	15	31.5	zS	115	24	11783	2709	341	243	25	8	21654	10	7	13	0.36
	16	42.4	zS	128	23	15368	3848	370	282	31	11	25735	13	9	12	0.52
	17	52.1	zS	123	19	13026	3117	365	289	26	10	22528	11	8	12	0.34
	18	71.1	zS	126	21	14395	3611	383	298	28	10	24362	12	7	15	0.44
D	19	10	S	106	11	9930	1558	392	313	20	6	22081	7	6	11	0.11
	20	19.5	zS	113	13	10469	2099	392	297	21	7	24260	8	8	14	0.23
	21	30	zS	97	13	12921	2449	379	285	24	7	25548	11	9	15	0.54
	22	40	zS	102	16	14524	2542	360	262	27	8	29414	14	10	17	0.58
	23	49.4	sZ	130	19	18991	3909	369	238	37	12	40983	19	14	13	0.84
	24	60	sZ	131	18	19302	3913	380	251	38	12	41267	18	14	12	0.76
	25	75.1	Z	126	19	20167	3744	366	243	40	12	43011	19	12	12	0.71
E	26	11.1	S	123	6	15249	1662	356	269	29	7	27401	7	11	13	0.18
	27	20.1	zS	120	8	14301	1783	292	196	28	8	30227	7	12	13	0.32
	28	31.5	sZ	124	13	17936	2607	286	176	41	11	35013	13	13	13	0.50
	29	41	sZ	115	15	20675	3346	279	178	53	14	37717	22	15	12	0.81
	30	50.5	sZ	112	14	19316	3225	307	193	56	12	39328	21	16	12	0.59
	31	75.1	sZ	112	15	19477	3247	287	189	56	12	39846	21	15	13	0.50

continued

Table A1 continued

Transect	Stations	Depth (m)	Texture	Cr		Fe		Mn		Zn		Al_{tot}	Cu_{tot}	Pb_{tot}	$CaCO_3$%	TOC%
				tot	n.l.	tot	n.l.	tot	n.l.	tot	n.l.					
	32	9.5	S	137	9	10183	1481	468	328	22	7	23613	6	6	14	0.12
	33	20.5	S	51	11	9636	1809	445	376	20	7	23654	7	5	15	0.16
F	34	30.3	zS	95	11	12267	2496	397	314	39	10	28327	16	8	13	0.37
	35	38.7	sZ	102	13	15373	3164	369	275	45	11	34901	19	8	15	0.67
	36	45.3	sZ	117	15	21071	4174	408	264	45	14	41045	21	10	14	0.86
	37	73.2	Z	124	12	20409	3856	391	254	59	13	43632	25	13	13	0.69
	38	12.4	S	71	11	8338	1307	370	312	17	6	14488	5	7	14	0.13
	39	19.9	zS	96	18	12332	3240	302	235	27	11	22024	11	8	15	0.84
G	40	31.3	zS	92	17	11257	2645	325	238	26	9	27188	9	8	16	0.40
	41	40.1	sZ	103	19	13677	3270	325	240	29	10	30231	9	8	12	0.54
	42	51	sZ	96	19	15136	3975	327	248	33	11	30994	13	8	13	0.63
	43	73.1	sZ	92	18	15349	4089	353	277	33	12	28420	11	9	14	0.40
	44	10.1	S	123	14	8423	1053	410	305	17	6	19437	5	5	16	0.25
	45	19.3	S	59	14	7190	1224	362	299	16	6	18909	5	5	15	0.25
H	46	30	zS	86	15	10036	1789	344	265	22	9	24504	7	5	15	0.40
	47	40.5	sZ	87	17	15082	2718	348	243	31	11	35323	13	7	24	0.64
	48	51.5	sZ	91	17	17061	3182	355	240	35	11	31904	15	10	16	0.72
	49	75.3	sZ	91	17	17839	3323	369	260	37	12	33831	16	11	16	0.56
	50	10.5	S	234	10	12795	1707	494	305	27	7	22862	6	6	11	0.12
	51	20.5	zS	101	11	10336	2059	335	259	22	6	22848	6	6	13	0.18
I	52	30	zS	129	14	14622	3325	339	224	28	9	29422	11	7	12	0.62
	53	40.5	sZ	126	16	18086	4234	360	229	36	11	33701	14	8	11	0.67
	54	50	Z	134	20	20932	4942	381	253	45	14	38584	17	8	10	0.67
	55	75.5	sZ	114	16	19821	4294	377	244	40	12	37686	15	10	10	0.39
Ref. Stat.		199		132	19	26004	3362	354	208	57	16	52529	27	23	12	0.62