Sediment Quality Assessment in an industrialized Greek coastal marine area (West Saronikos Gulf)

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Abstract. Eight sediment cores from the coastal marine area of West Saronikos Gulf have been analyzed for their grain size and geochemistry. The concentrations of eight metals (Al, Fe, Mn, Cu, Cr, Ni, Pb and Zn) along with total organic carbon (TOC) and carbonate content were measured. In cores taken at the deeper stations (above 100m) the analyses were performed only in the prevailing fine fraction (f < 63μm) while in cores from shallow stations (below 100m) the analyses were performed separately in both fractions fine and coarse (63μm < f < 1mm). The cores are fairly homogeneous, in terms of carbonates and the down-core variability of % TOC, is characterized by high surficial values that decrease with depth. Metals from both geological origin (Al, Mn, Cr, Ni) and anthropogenic origin (Cu, Pb, Zn), are higher at the silt and clay fraction of sediments than the sand fraction. The spatial distribution of Al, Fe, Mn, Cu, Pb and Zn in surface sediments presents increasing concentrations from the northeast to the southwest part of the study area, from the shallow to the deeper parts in contrast to Cr and Ni which are increased in the northern nearshore stations. Based on the vertical distributions, the metal to Al ratios of Cu, Pb and Zn show a constant decrease over depth along most cores, indicating the anthropogenic effects to surface sediments, while Fe/Al is constant. Spearman's correlation analysis performed among the fine grain metal contents, demonstrated a strong positive correlation ($r > 0.5$, $p < 0.05$) between Fe, Mn, Cu and Cu, Pb, Zn. Moreover, increased enrichment factors were determined at the fine fraction (f < 63μm) of some sediments. The concentrations of Cr at most surface sediments are higher than the ERL value (81 mg Kg^{-1}) but below the ERM value (370 mg Kg^{-1}) and the concentrations of Ni are higher than the ERM value (51.6 mg Kg^{-1}). Moreover, the concentrations of Cu, Pb, Zn, at most surface sediments, are below ERL values. The mean effects range medium quotients (mERMq) of surface sediments, based on the overall metal concentrations indicated that the surface sediments of most cores, are moderately toxic. The levels of Cr, Ni, Mn and Zn at most stations are decreased in 2017, but the concentrations of Pb and Cu are increased in 2017, compared to a previous study of 2007. The concentrations of Cu, Pb and Zn in the surface sediments of West Saronikos Gulf are lower than levels reported for Inner Saronikos Gulf and Elefsis Gulf, owing to the smaller industrial zone at the western coast, compared to the numerous polluting activities at the east coast of Saronikos.

1 Introduction

Sediment cores are one of the most easily accessed natural archives, used to evaluate and reconstruct historical pollution trends in aquatic environments. The cores provide data to characterize sediment physical properties and their geochemistry and composition. Vertical profiles of heavy metals can present sedimentation rate, changes in diagenetic processes and effects of human pressures. Metals released into aquatic systems, undergo several processes, such as adsorption, photolysis, chemical oxidation and microbial degredation. Sedimentation depends on the contaminant physicochemical properties, the sediment physical properties, the adsorption capabilities and the partitioning constant at the water-sediment interface. Trace metals removed from the water column are adsorbed on particulate matter and eventually deposited on bottom sediments (Bigus et al, 2014).

Sediments are repositories for metals such as chromium, lead, copper, nickel, zinc and manganese that present as discrete compounds, ions held by cation-exchanging clays, bound to hydrated oxides of iron and manganese, or chelated by insoluble humic substances. Solubilization of metals from sedimentary or suspended matter depends on the presence of complexing agents. Metals that are held by suspended particles and sediments are less available than those in true solution (Manahan, 2011).

The Saronikos Gulf is situated at the central Aegean Sea (north east Mediterranean) between $37^0$30'N-$38^0$00'N and $24^0$01' E-$23^0$00' E. The length of its coastline is 270 km, the surface is 2.866 km^2 and the mean water depth 100 m. To the north, a shallow (30 m depth) embayment is formed, known as Elefsis bay. The islands of Salamina and Aigina and the plateau between them, divide the gulf into two basins: the western basin (Western Saronikos Gulf) with maximum depths of 220 m in the north and 440 m in the south (Kontoyiannis, 2010) and the eastern basin which has a smooth bathymetry with depths of 50-70 m to the north (inner Saronikos Gulf) reaching 200 m to the southeast, from where the gulf opens to the Aegean Sea (outer Saronikos Gulf). To the west, the narrow Isthmus of Corinth connects Korinthiakos Gulf ~~in the Ionian Sea~~ with Saronikos Gulf in the Aegean Sea.

The gulf is subjected to a strong seasonal cycle of heating and cooling, with air temperatures between 0 - 40 ^{o} C, which causes the formation of a seasonal pycnocline from May to November. In winter, the water column is homogenized down to 120 m. However, in the western part, vertical mixing never reached the sea bottom (440 m) in the years after 1992 and dissolved oxygen concentration has approached nearly anoxic conditions (D.O. < 1mL/L) (Paraskevopoulou et al., 2014).

The gulf is subjected to intense anthropogenic pressure, as it is the marine border of the cities of Athens and Piraeus with 3-4 million inhabitants. Moreover, several point and non-point pollution sources are present. One of the most important point sources is the Athens/Pireaus wastewater treatment plant (WWTP) on the small island of Psittalia, one of the largest in Europe, with a population equivalent (p.e.) coverage of 5.6 million p.e. Other point sources along the coasts include marinas, touristic facilities, fish farms and the effluents of smaller towns and settlements (Paraskevopoulou et al., 2014).

The coastal marine area of the north part of West Saronikos Gulf is affected by a few types of industries established there during the 1970's, that include an oil refinery unit at the center of Susaki area, a cable manufacturer, soya mills and sulfur, fertilizers manufacturing for agricultural use and the activate wastewater treatment plant of Aghioi Theodoroi. Moreover, the increased touristic activities in the nearby coastal villages, especially during the summer months (Kelepertsis et al., 2001; Paraskevopoulou, 2009) are important point sources.

The Susaki area, which extends parallel to the northern coast of West Saronikos for about 8 Km, is known for its volcanic activity which took place during Pliocene-Quaternary. Most of the volcanic materials were transported by fluvial processes and deposited in the alluvial plains and coastal regions. The formations observed are peridotites and serpentinites, neogene deposits and Quaternary deposits. As a result, elevated values of Cr, Ni, Co, Mn, Fe in the soils and sediments of this area can be explained by the existence of the ultrabasic rocks (Kelepertsis et al., 2001).

The main aim of this work is to assess the levels and the distribution of several heavy metals (Al, Fe, Mn, Pb, Zn, Ni, Cr, Cu) in the sediment cores of West Saronikos, in order to discern ~~between geological and anthropogenic origin of heavy metals~~ and to identify the major sources of metal pollution. The second aim is to determine the evolution of marine pollution in the area by comparing the results with those of a similar study ten years ago, conducted at the Laboratory of Environmental Chemistry of the Department of Chemistry of the National and Kapodistrian University of Athens. The last aim of this work is to assess the differences between the concentrations of heavy metals in the surface sediments of the West Saronikos Gulf and the east part of the gulf.

2 Materials and methods

Eight sediment cores (12-32 cm) were obtained at corresponding stations with varying depths (50-420 m) in the area of West Saronikos Gulf ~~using~~ a box corer. The sampling ~~took place~~ in 18 October 2017 with the Greek Oceanographic vessel RV *Aegaeo*. The ~~location of~~ West Saronikos Gulf study area and the specific ~~station~~ of stations are presented in Fig. 1.

Figure 1: Location of Saronikos Gulf and sampling stations. Stations MOT13A, MOT16A, UN5, MOT16, UN6, UN6A and UN4 locate at the northwest part of Saronikos Gulf and station UN11 at the southwest part.

Stations MOT13A, MOT16A, UN5, MOT16, UN6 (near the Susaki area) and UN4 (Megara basin), at the northwestern part, are affected by the coastal industrial zone, urbanization and touristic activities. The offshore station UN6A, at the middle of Megara basin, is probably less ~~affected~~ by anthropogenic activities. Finally, station UN11 locates at the southwest part of the gulf, at Epidavros basin and is ~~affected~~ by trawling and aquaculture.

The cores ~~were stored frozen until analysis. Subsequently, they were~~ cut in layers of 1-2cm for the top 10cm and of 2cm below 10 cm ~~and they~~ were stored frozen until analysis. The separated layers were then freeze-dried. The grain size ~~treatment~~ included dry sieving for the separation of the ~~silt and clay~~ fraction (<63 μm) from the sand fraction (> 63μm) ~~(Tsoutsia et al., 2013),~~ using Retsch stainless steel '~~Test~~ Sieves'~~. The~~ percentage of both fractions (sand and ~~silt-clay) was~~

calculated. The percentage of total organic carbon and carbonates and the concentrations of heavy metals were determined in both sand and fine sediment, when the fraction percentage was more than 10 % of the total sediment. Table 1 presents the coordinates, the depth and the core length of sampling stations.

Table 1. The location and depth of sampling stations and the length of each core.

Station	Latitude N (dec.minutes)	Longtitude E (dec.minutes)	Depth (m)	Length of Cores (cm)
MOT13A	37^0 54.602	23^0 03.184	50	12
MOT16A	37^0 53.995	23^0 03.080	100	32
UN5	37^0 53.459	23^0 04.393	140	32
MOT16	37^0 54.179	23^0 05. 312	85	20
UN6	37^0 53.455	23^0 10. 857	193	26
UN6A	37^0 51.610	23^0 15.932	165	24
UN4	37^0 57.057	23^0 20.331	79	22
UN11	37^0 38.800	23^0 15.338	420	32

The total organic carbon (TOC) content was measured using the standard Walkey method (Walkley, 1947) as modified by Jackson (Jackson, 1958) and Loring and Rantala (Loring and 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) 6 M (exothermic reaction followed by HCl gas and CO_2 emission), a method modified from Loring and Rantala (Loring and Rantala, 1992).

The total metal contents were extracted via complete dissolution of sediment samples with an acid mixture of HNO_3-$HClO_4$-HF (ISO-14869-1:2000) (Peña-Icart et al., 2011). Then, the total metal concentrations were determined by Flame Atomic Absorption Spectroscopy (FAAS-Varian SpectrAA-200) (Skoog et al., 1998). In order to evaluate the precision and accuracy of the method for total metal analysis certified reference materials (ISE 921, 80MS, PACS-3) 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 show that all recoveries are between the recommended US EPA ranges (75-125 %). Moreover, the ranges of % RSD for each metal at the collected cores are presented at Fig. A1 – A15 (Appendix A).

All statistical treatment of data was performed by Microsoft Excel 2010. Moreover, the graphs with the vertical distributions were plotted with Microsoft EXCEL 2010 and the horizontal distributions of metals were visualized with the software package Ocean Data View (ODV) 2017. A Spearman correlation analysis that was performed with the statistical software IBM-SPSS Statistics 2020 was used to identify the significant relationship between different heavy metals, total organic carbon and carbonates.

3 Results

3.1 Geochemical results

Table 2 summarizes the main findings from the determination of geochemical parameters. The grain size in cores from stations MOT16A, UN5, UN6, UN6A, UN11, is dominated by clay and silt (f < 63μm), while the percentage of sand fraction (63μm < f < 1mm) is lower than 10 %, which can be attributed to the depth of these stations (above 100 m). On the other hand, the grain size in cores MOT13A, MOT16, UN4 is dominated by sand, which can be explained by the shallow depth of these stations (depth below 100 m) and their proximity to the northwestern coast. However, the percentages of ~~clay and silt~~ in cores MOT13A, MOT16, UN4 are not negligible (above 10 %).

As a result, the percentages of total organic carbon (TOC) and carbonates and the concentrations of heavy metals were determined in the fine fraction (f < 63μm) of sediments in cores MOT16A, UN5, UN6, UN6A and UN11 and both in sand and ~~fine fraction of sediments~~ in cores MOT13A, MOT16 and UN4.

Table 2. Summary statistics of variables measured along the collected cores.

Station	% sand		% silt and clay		% TOC		% CO_3^{2-}	
	Min	Max	Min	Max	Min	Max	Min	Max
MOT13A	51	66	15	38	0.45	0.92	26	28
MOT16A	1	23	77	99	0.10	0.93	22	23
UN5	1	14	86	99	0.44	1.12	20	23
MOT16	47	65	29	45	0.33	1.28	20	22
UN6	1	32	68	99	0.57	2.44	19	23
UN6A	1	22	78	99	0.33	1.32	22	25
UN4	39	60	20	50	0.51	0.75	29	33
UN11	0	15	74	100	0.77	2.35	15	19

Apart from small variations, the cores are fairly homogeneous, in terms of carbonates. The high percentages of % CO_3^{2-} in cores MOT13A and UN4 are associated with the coarse- grained samples and the presence of shell fragments. Moreover, the down-core variability of % TOC at the collected cores, is characterized by high surficial values that decrease with depth. Figure 2 presents the vertical distribution of % TOC in selected cores. The distribution at core UN4 refers to the fine sediment fraction (~~f~~ < 63 μm).

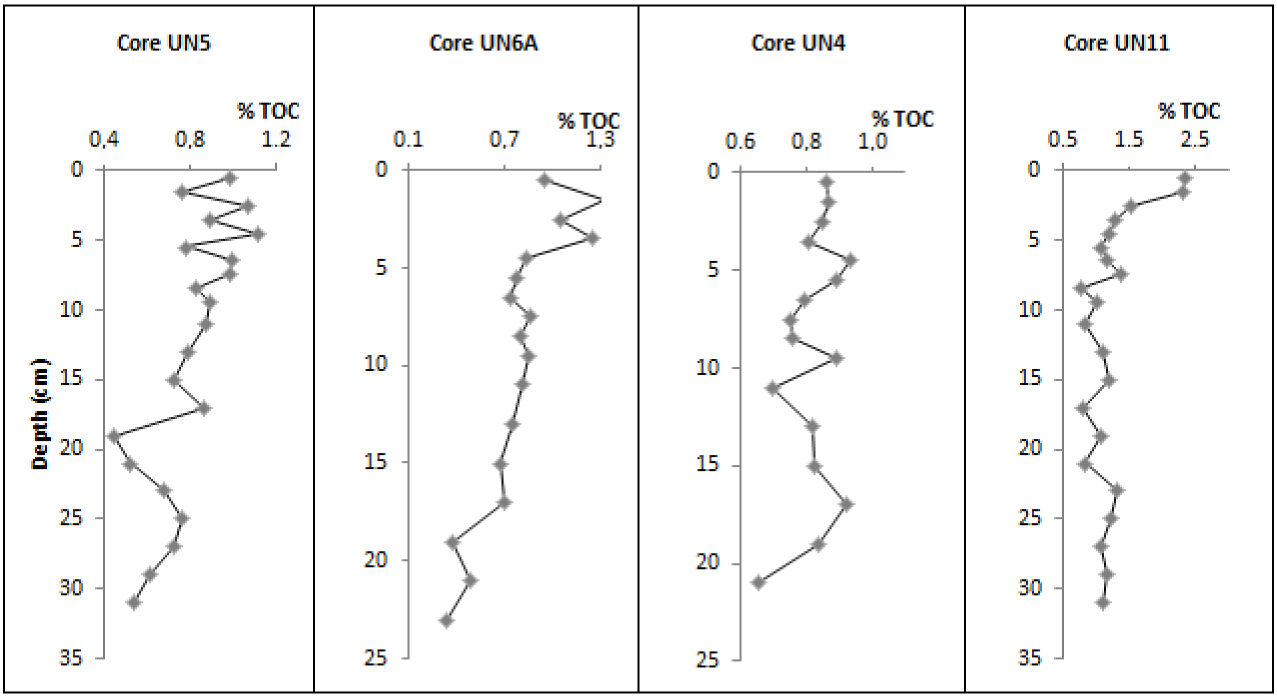

Figure 2: Vertical distribution of % TOC at cores UN5, UN6A, UN4, UN11. The distribution at core UN4 refers to the fine sediment fraction (f < 63 μm).

Table 3 presents TOC, carbonate and heavy metal contents in the shallow coarse-grained cores MOT13A, MOT16, UN4. It is apparent that the % TOC ~~of the silt and clay sediment fraction~~ is higher than the corresponding content of the sand fraction as anticipated. The % $CaCO_3$ content of the sand fraction is increased compared to the fine fraction in cores MOT13A, UN4 and approximately equal in the two sediment fractions of core MOT16.

The concentrations of Al, Cr, Cu, Mn, Pb, Ni and Zn are higher in the ~~silt-clay~~ sediments of MOT13A and UN4 than the corresponding in sandy sediments. The same applies to Al, Mn, Cu, and Zn in MOT16. The high content of Al at the fine fraction of sediments indicates that Al is predominantly associated with aluminosilicate minerals and occurs mostly in the clay minerals. Generally, fine sediments tend to have relatively high trace element concentrations, due to the surface adsorption and ionic attraction. Especially, the so-called anthropogenic trace metals (Cu, Pb, Zn) are normally bound within or sorbed by the clay mineral fraction of sediments (Barjy et al., 2020; Karageorgis et al., 2005). Unlike other metals the Fe content is more or less similar in both sediment fractions of cores MOT13A and UN4. The sediments of core MOT16 appear to be different with higher concentrations of Fe, Cr, Ni and Pb in the coarse-grained fraction.

Table 3. Percentage of organic and inorganic carbon and concentrations of metals in mg Kg^{-1} in coarse-grained cores (MOT13A, MOT16, UN4).

Variable/Core	MOT13A		MOT16		UN4	
	fine fraction	coarse fraction	fine fraction	coarse fraction	fine fraction	coarse fraction
% TOC	0.64-2.80	0.26-0.45	0.37-2.70	0.15-0.46	0.65-0.94	0.43-0.58
% $CaCO_3$	22-23	27-30	21-23	18-22	26-29	32-36
Al	10561-18387	6615-9226	21677-28939	10610-18538	23271-34246	10449-19765
Cr	390-651	333-486	322-374	306-517	113-133	71.6-115
Ni	293-411	220-302	314-573	424-697	139-187	78.0-140
Fe	19878-21153	17430-20643	24130-31694	32265-36080	14149-17126	13501-17931
Mn	429-476	326-386	471-530	435-484	317-366	174-238
Cu	17.1-18.8	8.9-11.8	16.7-22.6	6.7-14.8	15.1-23.6	9.7-13.4
Pb	18.0-30.7	14.8-21.0	9.1-28.0	8.3-31.9	11.2-31.2	9.3-27.3
Zn	39.3-51.8	31.0-45.6	39.8-53.7	31.5-50.9	38.9-59.2	30.3-50.3

The vertical distributions of the study metals in mg kg^{-1} along the collected cores present at Fig. A1−A15 (Appendix A). In cases of coarse cores MOT13A, MOT16, UN4, the concentrations of the total sediment (both fractions) are depicted.
Table 4 summarizes the concentrations of eight heavy metals in the surface and deeper sediment layer of the collected cores. The concentrations are measured at the fine sediment fraction (f < 63μm) of cores MOT13A, MOT16, UN4. The sediments at the deeper parts of West Saronikos (cores UN6, UN6A and UN11) present elevated concentrations of Al, Fe, Pb and Zn especially. The sediments of UN11 are also particularly enriched in Mn, which is attributed to the prevalence of the silt-clay sediment fraction and the suboxic waters at depths higher above 200 m (Kontoyiannis, 2010). The elevated values of Cr and Ni in cores MOT13A, MOT16 and MOT16A can be explained by the existence of the ultrabasic rocks of the Susaki area, in which, these metals are predominant (Kelepertsis et al., 2001).

Table 4. Concentrations in mg Kg^{-1} of the study metals in the surface and the deeper sediment layer of cores. The concentrations at coarse cores MOT13A, MOT16, UN4 are measured at the fine sediment fraction (f < 63μm).

Core	Layer (cm)	Al	Cr	Ni	Fe	Mn	Cu	Pb	Zn
MOT13A	0-1	10561	651	411	20988	476	18.2	26.1	49.6
	10-12	14673	407	383	21153	444	18.1	22.5	44.6
MOT16A	0-1	27009	280	375	23315	578	22.6	20.4	48.3
	30-32	30070	256	382	26179	562	22.1	28.1	44.1
UN5	0-1	32705	199	305	25534	635	27.4	42.7	74.5
	30-32	37885	223	320	29170	520	26.0	24.7	57.5
MOT16	0-1	21677	369	377	25816	530	22.6	28.0	53.7
	18-20	23807	348	401	29752	482	16.9	9.1	40.4
UN6	0-1	43264	142	253	27301	954	36.7	52.9	92.1
	24-26	44547	153	274	29345	707	28.5	32.5	62.4
UN6A	0-1	39314	146	187	21838	570	26.3	38.4	73.8
	22-24	41303	161	209	23827	513	25.4	38.7	58.7
UN4	0-1	34246	132	162	15762	358	23.6	26.1	52.1
	20-22	31706	113	160	17112	365	15.1	12.0	40.3
UN11	0-1	54626	142	230	32177	3925	49.7	63.9	110
	30-32	48186	163	217	31573	1459	37.3	35.1	71.4

The distribution of elements comprising the terrigenous phase of the sediments is best represented by Al, which is held almost exclusively in terrigenous aluminosilicates (Karageorgis et al., 2005). Table A1 (appendix A) presents the ratios of eight heavy metals to Al in the surface and deeper sediment layer of the collected cores. The ratios in coarse cores MOT13A, MOT16, UN4 are calculated for the fine sediment fraction. The vertical profiles of ratios along the collected cores, are given in Fig. A1−A15 (Appendix A), where the ratios in coarse cores MOT13A, MOT16, UN4 refer to the fine sediment fraction (f <63 μ).

The vertical distributions of Al (Fig. A1 (appendix A)) for the total sediment (both fractions) present minimal variation. The down-core variability of Al is lower than 10 %, in the fine sediments (cores MOT16A, UN5, UN6, UN6A and UN11) and between 10-15 % in the coarser sediments (cores MOT13A, MOT16 and UN4). In the surface layer (0-1cm) of cores MOT13A and UN5 there is a sharp decrease of Al content, while at the top 12cm of core UN11 aluminum is increased compared to the deeper layers. Similarly, the so-called lithogenic metals (Cr, Ni, Fe, Mn) present uniform vertical profiles with minimal variability (mostly below 10 %). The trend for increase of Cr, Ni, Fe and Mn in the surface sediments of MOT13A remains pronounced after normalization to Al in silt and clay fraction at the top 0-1cm. The normalized vertical profile of Cr in UN11 indicates a decrease of Cr through time in the upper sediment layers. The same trend is seen in the normalized profiles of Ni and Mn in fine sediment fraction of core UN4. The down-core variability of Mn in all stations, except UN4, is typical of shelf sediments, with high surficial Mn concentrations that diminish with depth to background values, as reducing conditions develop. These variations are largely independent of lithological or carbonate content fluctuations, being dependent solely upon the respiration of organic carbon (Karageorgis et al., 2005).

The concentrations of Cu, Pb and Zn as well as the normalized profiles (Fig. A10−A15) show a constant decrease over depth to background levels, which can be attributed to increased inputs by anthropogenic activities in recent time (Karageorgis et al., 2005). Figure 3 presents selected vertical profiles of Mn and Pb along core UN11and those of Cr, Fe, Cu, Zn at the cores UN6A, MOT16A, UN4, UN6, respectively. The concentrations were calculated at the fine fraction (f<63μm) of the sediments.

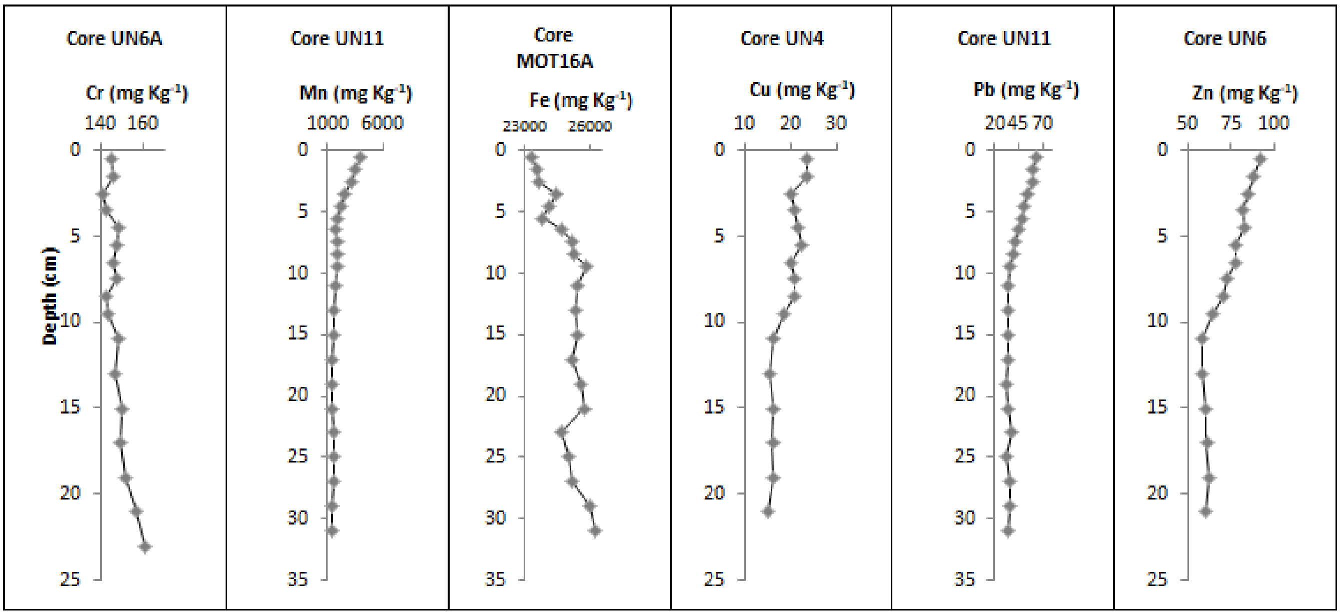

Figure 3: Vertical profiles of Cr, Fe, Cu, Zn at the fine fraction (f < 63μm) of cores UN6A, MOT16A, UN4, UN6 respectively and the vertical distributions of Mn and Pb along core UN11.

Figure 4 presents selected vertical distributions of ratios to Al at cores MOT13A, UN5, MOT16A, MOT16 and UN11 of West Saronikos Gulf. The ratios were calculated at the fine fraction (f < 63 μm) of the sediments. Based on the vertical distributions, Fe to Al ratios are constant with depth of the collected cores (Nolting et al., 1999). Ration of Cu, Pb and Zn to Al show a constant decrease over depth along the collected cores, because the surface sediments are affected much higher by anthropogenic activities than the deeper sediments (Karageorgis et al., 2005).

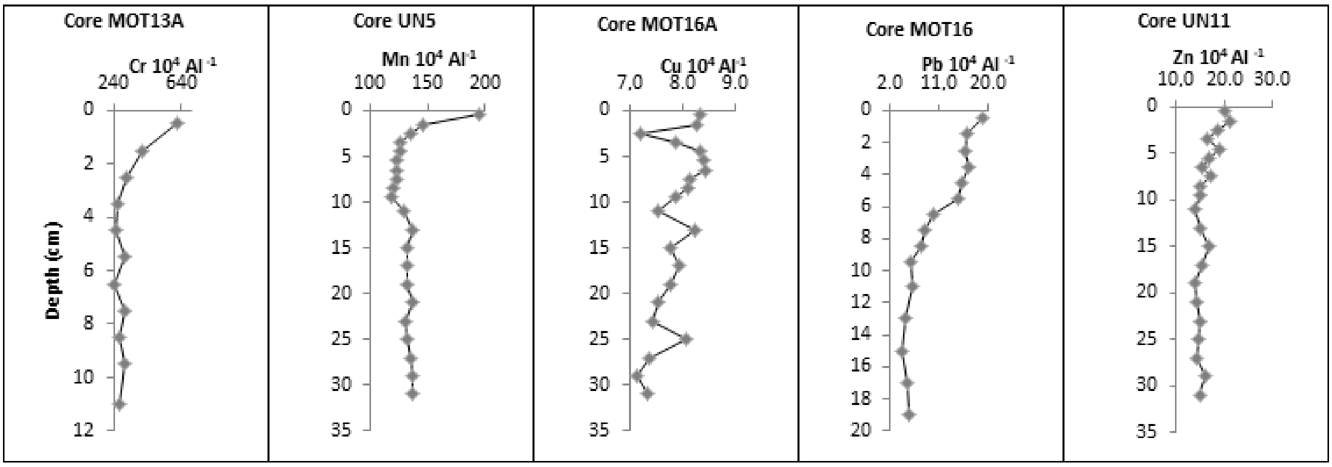

Figure 4: Vertical distributions of ratios to Al at cores MOT13A, UN5, MOT16A, MOT16 and UN11 of the northwest Saronikos Gulf. The ratios were calculated at the fine fraction (f < 63μm) of the sediments of cores MOT13A and MOT16.

3.2 Horizontal distributions

Figure 5 presents the horizontal distributions of heavy metals in the surface sediments (0-1 cm) of the study area. In cases of coarse surface sediments of MOT13A, MOT16, UN4, the concentrations of total sediment fraction (f < 1mm) were used.

The concentrations of Al, Fe, Mn, Cu, Pb and Zn are increased from the northeast to the southwest area of West Saronikos Gulf. The high content of Mn at the surface sediment of core UN11 can be explained by the prevalence of silt and clay sediment fraction and the suboxic waters at the depth of 420 m (Ozturk, 1995). The waters of West Saronikos Gulf at depths higher than 200 m, are suboxic (Kontoyiannis, 2010) and as a result, the slow diffusion of dissolved oxygen from the more oxidizing overlying waters and the upward diffusion of dissolved Mn (II) from the pore water of anoxic surface sediments to the sediment/water interface (Ozturk, 1995), cause the oxidation of dissolved Mn (II) and its precipitation as Mn (IV) oxides (Pohl and Hennings, 1999).

On the other hand, the concentrations of Fe, Cr and Ni at the north part are higher than those at the south area, which can be explained by the existence of the ultrabasic rocks in the soils of the region and the natural weathering and transport to the coastal marine environment (Kelepertsis et al., 2001).

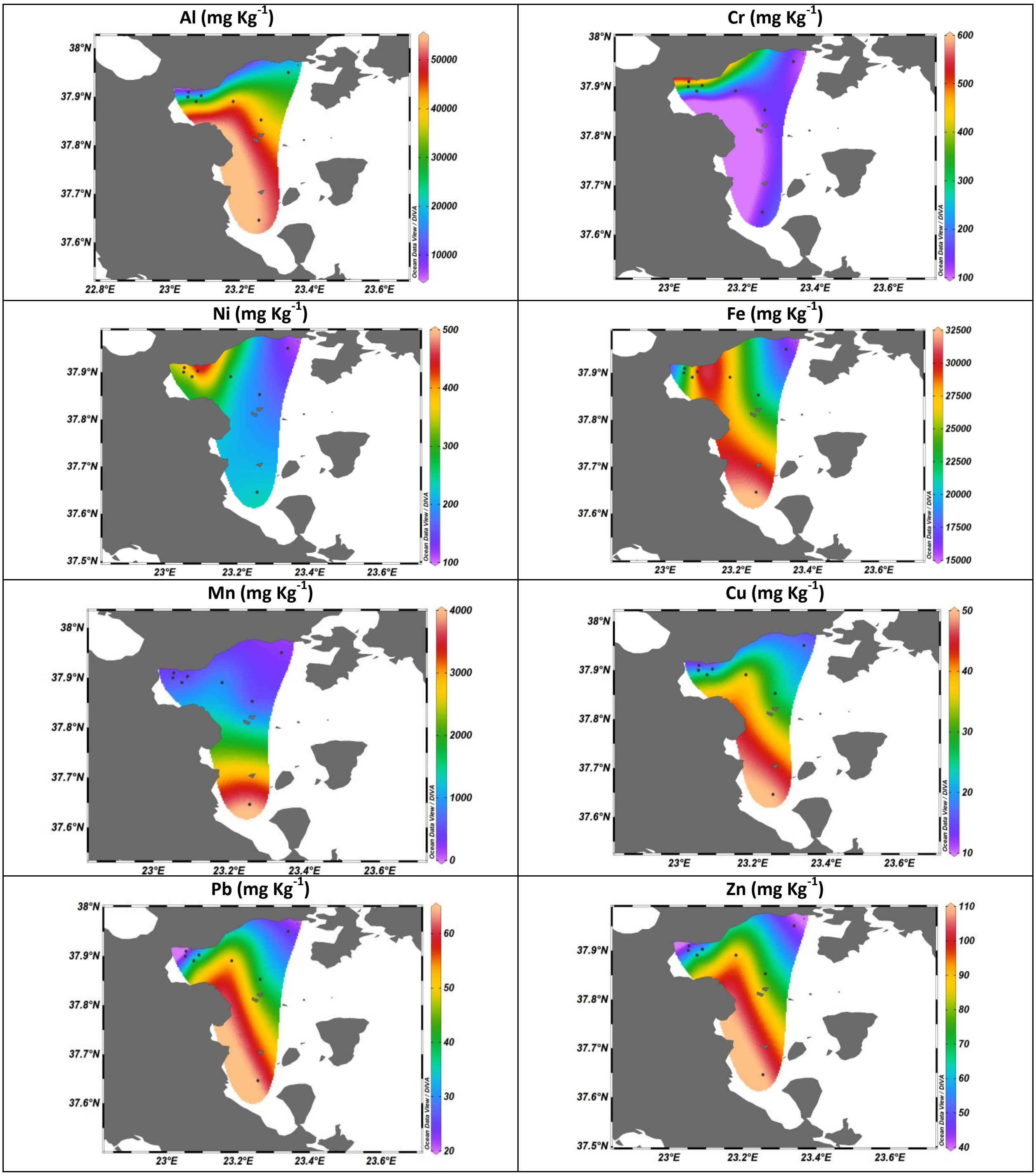

Figure 5: The horizontal distributions of heavy metals in the surface sediments of West Saronikos Gulf. In cases of coarse surface sediments of stations MOT13A, MOT16, UN4, the concentrations of the total sediment fraction (f<1mm) were used.

4 Discussion

4.1 Element interrelations

Spearman's correlation analysis was carried out to determine the relationships between heavy metals and percentages of total organic carbon (TOC) and carbonates in sediments of the collected cores. The concentrations of metals and the percentages of organic and inorganic carbon refer to the fine fraction of core sediments MOT13A, MOT16, UN4. Spearman's correlation coefficients are presented in Table A2 (appendix A) and Fig. A16 (appendix A).

Al is highly correlated ($r > 0.5$, $p < 0.05$) with Fe, Mn, Cu, Pb and Zn, which probably indicates an association between these metals in the form of metal-clay complexes of continental origin (Barjy et al., 2020). On the other hand, there is a negative correlation of Al with Cr and Ni.

Cr is highly correlated with Ni, but both of them show negative correlation with Cu, Pb and Zn, which can be attributed to their different origin (Barjy et al., 2020) and poor correlation with Mn. Cr shows bad correlation with Fe, too. The strong correlation between Cr and Ni can be observed at sediments of the northwest part, too.

Fe, Mn, Cu, Pb and Zn show positive correlation with each other. Cu, Pb and Zn are high correlated with each other ($r > 0.5$, $p < 0.05$), which can be observed at sediments of the northwest part, too, suggesting that they have a common origin and identical behaviour during transport in the marine environment (Barjy et al., 2020). Zn is highly correlated with Cu and Pb also at sediments of core UN11 at the south area.

The % TOC content presents moderate correlation with Al, Cu, Pb and Zn and negative correlation with Cr, Ni and the % carbonates. Moreover, it shows poor correlation with Fe and Mn. Finally, the percentage of carbonates content presents negative correlation with all metals.

4.2 Enrichment Factors

The Enrichment Factors (EF) are used to distinguish between metals originating from anthropogenic activities and from natural processes, assessing the degree of anthropogenic effect. Equation (1) was used for the calculations of EFs, where C_x is the concentration of the analyzed metal and C_{EN} is the concentration of the normalizing element. Al was used as the reference element.

$$EF = (C_x/C_{EN})_{sample}/(C_x/C_{EN})_{background} \quad (1)$$

In Table 5, the categories of contamination according to the Enrichment Factor are presented (Diamantopoulou et al., 2019; Sutherland, 2000). In general, EFs use concentrations normalized to Al to account for the heterogeneity of the samples due to differences in texture and organic content (Gredilla et al., 2015).

Table 5. The categories of infection according to the Enrichment Factor.

EF	Contamination Degree
< 2	Depletion to minimal enrichment- no or minimal pollution
2 to 5	Moderate enrichment- moderate pollution
5 to 20	Significant enrichment- significant pollution
20 to 40	Very high enrichment- very strong pollution
>40	Extreme enrichment- extreme pollution

Table 6 shows the Enrichment Factors of the surface sediments (0-1 cm) of the study area that were calculated according to the concentrations of heavy metals. The EFs were calculated at the fine fraction ($f < 63\mu m$) of sediments of cores MOT13A, MOT16, UN4. Most metals present minimal to moderate enrichment in almost all the cores analysed. Moderate enrichment is found for Cr, Ni, Mn and Pb in core MOT13A, Mn in UN11, and finally for Pb in UN5 and MOT16.

Table 6. Enrichment Factors of the surface sediments (0-1cm) of the study area. In cases of stations MOT13, MOT16, UN4, the EFs were calculated at the fine surface sediment fraction ($f < 63\mu m$).

Core	EF Cr	EF Ni	EF Fe	EF Mn	EF Cu	EF Pb	EF Zn
MOT 13 A	3.09	2.07	1.92	2.07	1.94	2.24	2.14
MOT 16A	1.36	1.22	1.10	1.27	1.27	0.90	1.36
UN 5	1.20	1.28	1.17	1.64	1.42	2.32	1.74
MOT 16	1.28	1.14	1.05	1.33	1.61	3.71	1.60
UN6	0.98	0.98	0.99	1.43	1.36	1.73	1.57
UN 6A	1.00	0.99	1.01	1.23	1.15	1.09	1.39
UN 4	1.00	0.87	0.79	0.84	1.34	1.86	1.11
UN11	0.68	0.82	0.79	2.09	1.04	1.42	1.20

4.3 Sediment Quality Guidelines

Sediment Quality Guidelines (SQG) of effect range low (ERL) and effect range median (ERM) are used to assess the level of toxicity of metals in the surface sediments. Metal concentrations below the ERL value, indicate that effects on biota are rarely observed. Concentrations above the ERL but below the ERM, occasionally affect the biota and concentrations above the ERM frequently affect the biota. The ERL and ERM guideline values for trace metals (ppm, dry wt) and percent incidence of biological effects in concentrations ranges defined by the two values are presented in Table 7 (Long et al., 1995).

Table 7. ERL and ERM guideline values for trace metals (ppm, dry wt) and percent incidence of biological effects in concentration ranges defined by the two values.

Metal	ERL (mg kg $^{-1}$)	ERM (mg kg $^{-1}$)	Percent incidence of effects		
			<ERL	ERL-ERM	>ERM
Cr	81	370	2.9	21.1	95.0
Cu	34	270	9.4	29.1	83.7
Pb	46.7	218	8.0	35.8	90.2
Ni	20.9	51.6	1.9	16.7	16.9
Zn	150	410	6.1	47.0	69.8

In this study, the concentrations of heavy metals at the surface sediments were compared with the ERL and ERM criteria. In cases of cores MOT13A, MOT16, UN4, the concentrations of total sediment fraction (f < 1mm) were used for the comparison with ERL and ERM criteria. The concentrations of Cr in surface sediments of cores UN4, UN5, MOT16A, UN6, UN6A and UN11 are higher than the ERL value (81 mg Kg^{-1}) but below the ERM value (370 mg Kg^{-1}) (Hahladakis et al., 2012) and the values at surface sediments of MOT13A and MOT16 are higher than the ERM value. The concentrations of Ni at the surface sediments of the collected cores are higher than the ERM value (51.6 mg Kg^{-1}) and as a result, they frequently affect the biota (Hahladakis et al., 2012).

The concentrations of Cu and Pb at surface sediments of stations MOT13A, MOT16A, UN4, UN5, MOT16 and UN6A, are below the ERL values (34 mg Kg^{-1} for Cu and 46.7 mg Kg^{-1} for Pb), which indicates that effects on biota are rarely observed. On the other hand, the concentrations at surface sediments of cores UN6 and UN11 are higher than the ERL values but below the ERM values (270 mg Kg^{-1} for Cu and 218 mg Kg^{-1} for Pb), which means that they can occasionally affect the biota (Hahladakis et al., 2012). The concentrations of Zn are below the ERL (150 mg Kg^{-1}) value and the ERM value (410 mg Kg^{-1}), which indicates that effects on biota are rarely observed (Hahladakis et al., 2012).

4.4 Mean effects range medium quotients

The mean effects range medium quotient (mERMq) is an index that is used to evaluate the possible biological effects of the coupled toxicity of all heavy metals in the surface sediments (Gredilla et al., 2015). Briefly, mERMq's were calculated by dividing the average concentration of each metal at the top 9cm, by its respective ERM (effects range median), to obtain the corresponding sediment quality guideline quotient (ERMq). Following this, mERMq's for each core were obtained as the average of ERMqs previously calculated. ERMqs indicates the pollutant concentration above which effects are expected to be frequent and have been only defined for very toxic elements (Gredilla et al., 2015).

In this study, Cr, Ni, Cu, Pb and Zn were considered in our calculations and the results are depicted in Table 8. In cases of cores MOT13A, MOT16, UN4, the concentrations of total sediment fraction (f < 1mm) were used for the calculation of mERMq. Values of mERMq in the ranges of 0.0-0.1, 0.1-0.5, 0.5-1.5 and >1.5 correspond to the following probabilities of toxicity: 9 % (non-toxic), 21 % (slightly toxic), 49 % (moderately toxic) and 76 % (highly toxic), respectively (Gredilla et al., 2015). The mERMq values obtained for the sediments varied from 0.62 to 2.00, which means that the sediments are moderately or highly toxic.

The concentrations of Cr, Ni, Cu, Pb, Zn in sediments of cores MOT13A, UN5, UN6, UN6A, UN4 and UN11 are moderately toxic and in sediments of MOT16A and MOT16 highly toxic. The concentrations of Cu, Pb, Zn in sediments of cores MOT13A, MOT16A, MOT16, UN4 are non-toxic, with mERMq range 0.08-0.10 and those in sediments of UN5, UN6, UN6A, UN11 are slightly toxic, with mERMq range 0.16-0.21.

Table 8. MERMqs values calculated for the surface sediments (0-9 cm) of the collected cores of West Saronikos Gulf, by dividing the average concentration (mg Kg^{-1}) of each metal (Cr, Ni, Cu, Pb, Zn) by its respective ERM (mg Kg^{-1}). In cases of cores MOT13A, MOT16, UN4, the concentrations of total sediment fraction (f < 1mm) were used for the calculation of mERMq.

Core	mERMq (average)	toxicity of sediments
MOT13A	1.46	Moderately toxic
MOT16A	1.69	Highly toxic
UN5	1.46	Moderately toxic
MOT16	2.00	Highly toxic
UN6	1.21	Moderately toxic
UN6A	0.95	Moderately toxic
UN4	0.62	Moderately toxic
UN11	1.09	Moderately toxic

4.5 Evolution of marine pollution

The total concentrations of eight heavy metals in the surface sediments were compared with those of a similar study ten years ago (Paraskevopoulou, 2009). In cases of cores MOT13A, MOT16, UN4, the concentrations of total sediment fraction (f < 1mm) were used and the results are depicted in Fig.6. The levels of Cr, Ni, Mn at most sediments, are decreased in 2017, compared to the study of 2007. On the other hand, the levels of Pb and Cu are increased in 2017, compared to the study of 2007. Moreover, the levels of Zn, at most sediments, are decreased in 2017 compared to the study of 2007.

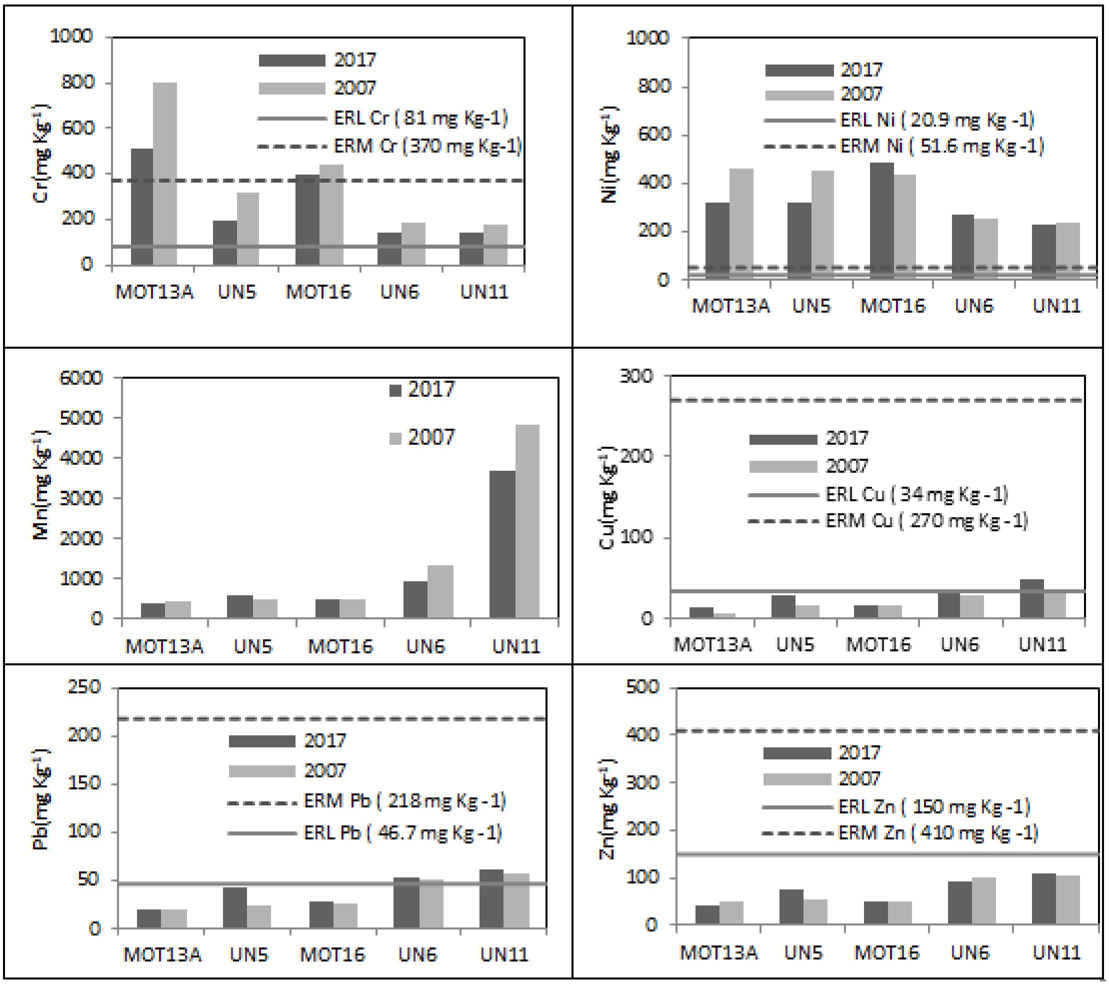

Figure 6: Levels of heavy metals in surface sediments of 2017 and 2007 and sediment quality guidelines. In cases of coarse sediments of stations MOT13A, MOT16, UN4, the concentrations of total sediment fraction (f < 1mm) were used.

4.6 Comparison of metal concentrations in West Saronikos Gulf with other areas of Saronikos Gulf

The concentrations of heavy metals in surface sediments of West Saronikos Gulf are compared with those measured at Elefsis Bay (EB), Inner Saronikos Gulf (ISG) and Outer Saronikos Gulf (OSG) from the sampling of October 2017 (Panagopoulou, 2018; Vrettou, 2019; Xarlis, 2018). Figure 7 shows the location of sampling stations.

The station at Elefsis Bay with depth of 25 m locates near the Elefsis Port and station at Inner Saronikos Gulf with depth of 75 m near the Psittalia WWTP outfall. Moreover, there are two stations at Outer Saronikos Gulf. The first one, with depth of 85 m, locates near Vouliagmeni and the last one, with depth of 189 m, northwest of Sounio. The silt and clay fraction (f < 63μm) of surface sediments northwest of Sounio and near the Psittalia is higher than the sand fraction (63μm < f <1 mm). The sand fraction of the surface sediment near Vouliagmeni is higher than the silt and clay and similar to silt and clay of surface sediment of Elefsis Gulf. The total metal contents were extracted via complete dissolution of sediment samples with an acid mixture of HNO_3-$HClO_4$-HF (ISO-14869-1:2000) (Peña-Icart et al., 2011).

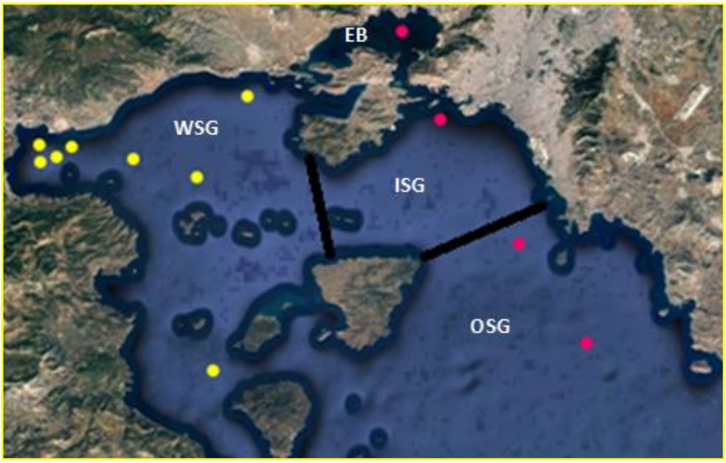

Figure 7: Map of Saronikos Gulf and the location of sediment sampling stations. The station at Elefsis Bay locates near the Elefsis Port and station at Inner Saronikos Gulf near the Psittalia WWTP outfall. Moreover, there are two stations at Outer Saronikos Gulf. The first one, locates near Vouliagmeni and the last one, northwest of Sounio.

The levels of Al of West Saronikos are comparable with those at the other areas and the low concentration of Al at station near Vouliagmeni can be explained by the coarse surface sediment. The concentrations of Ni are decreased from the northwest to the southeast part of Saronikos Gulf. High levels of Ni at the northwest area can be attributed to its geological origin (Kelepertsis et al., 2001). The levels of Fe at West Saronikos are comparable with those at the other sediments. The low content of Fe at station near Vouliagmeni may be attributed to its coarse sediment. The maximum values of Al, Fe and Mn at station UN11 can be attributed to the fine surface sediment and the hypoxic conditions at waters of West Saronikos deeper than 200m. Generally, the levels of Mn at West Saronikos are higher than those measured at Psittalia, Elefsis Gulf and station near Vouliagmeni. The highest concentrations of Mn are observed at the deepest stations (UN6 and UN11 of West Saronikos and station northwest of Sounio).

The levels of Cu, Pb, Zn at surface sediments of Psittalia and Elefsis Gulf are higher than those observed at the other sediments, which can be explained by the numerous pollution sources in the marine environment and along the coast of Inner Saronikos Gulf and Elefsis Bay (Paraskevopoulou et al., 2014). Especially the concentrations of Cu at the northwest part are comparable with those at Outer Saronikos Gulf but lower than those at the deep station UN11 and the concentrations of Pb at West Saronikos are comparable with those at Outer Saronikos. The levels of Zn at the northwest part are higher than those observed near Vouliagmeni, but lower than those at station UN11 and at the northwest area of Sounio. The results are depicted at Table 9. In cases of coarse surface sediments, the concentrations at total sediment fraction (f < 1 mm) were used.

Table 9. Comparison of heavy metals concentrations in mg Kg^{-1} measured in this study with those in other areas of Saronikos.

Station	Al	Ni	Fe	Mn	Cu	Pb	Zn	References
MOT13A	5697	344	20740	422	13.5	20.0	44.1	Present work
MOT16A	27009	375	23315	578	22.6	20.4	48.3	Present work
UN5	32705	305	25534	635	27.4	42.7	74.5	Present work
MOT16	16050	484	31191	503	16.9	30.3	52.1	Present work
UN6	43264	253	27301	954	36.7	52.9	92.1	Present work
UN6A	39314	187	21838	570	26.3	38.4	73.8	Present work
UN4	22702	123	16682	270	17.5	24.5	43.6	Present work
UN11	54626	230	32177	3925	49.7	63.9	110	Present work
Psittalia	26780	83.2	20623	239	103	102	251	Panagopoulou, 2018; Xarlis, 2018
Elefsis Gulf	44853	109	30499	394	132	141	368	Panagopoulou, 2018; Xarlis, 2018
Vouliagmeni	4424	13.4	6407	243	10.5	40.1	27.4	Vrettou, 2019
NWSounio	44902	114	27139	958	30.7	64.1	141	Vrettou, 2019

5 Conclusions

The heavy metal pollution of West Saronikos Gulf has not been sufficiently studied, despite the scientific interest of this area, in contrast to the numerous studies of the eastern coast. The distribution of metals in the sediment samples of West Saronikos indicates that the area is enriched in metals from both geological and anthropogenic origins. The concentrations of all metals (Al, Mn, Cr, Ni, Cu, Pb, Zn) of fine sediments are higher than those measured in coarse sediments. The cores are fairly homogeneous, in terms of carbonates and the down-core variability of % TOC, is characterized by high surficial values that decrease with depth.

The Cr and Ni concentrations at the northwest part of the study area are higher than those measured at the southwest area and their values are very stable with depth of most sediment cores, which can be explained by the ophiolite background (Kelepertsis et al., 2001). Al, Fe and Mn are increased from the northeast to the southwest part of the study area. The concentrations of Al and Fe are increased with depth of most cores, while the values of Mn are decreased with depth. Generally, concentrations of Fe and Mn at surface sediments are affected by oxic and hypoxic conditions.

The ~~horizontal~~ distributions of Cu, Pb and Zn present a constant decrease over depth along most cores, which can be attributed to their anthropogenic origin. Moreover, their levels at most sediments are higher than those measured ten years ago. Finally, the Cu, Pb, Zn concentrations in West Saronikos Gulf surface sediments are comparable with those at Outer Saronikos Gulf and lower than those from Inner Saronikos Gulf and Elefsis Bay, which can be attributed to the smaller industrial zone of the west coast in comparison to the numerous anthropogenic activities at the east coast.

The concentrations of metals that are measured higher than the ERL values and the indication for moderately or highly toxic sediments by the calculation of mERMq signify that more research is required, in order to investigate probable effects on the marine ecosystem. Continuous monitoring, updating of the results of the present work, metal speciation and study of bioaccumulation should be conducted, to assess the impacts of heavy metal pollution on the marine environment of West Saronikos Gulf.

6 Appendices

Appendix A

Table A1. The ratios of eight heavy metals to Al in surface sediments and sediments of the depth of the collected cores. In cases of coarse-sediment cores MOT13A, MOT16, UN4, the ratios in fine sediment fraction (f < 63 μm) are measured.

Core	Layer (cm)	Cr 10^4 Al^{-1}	Ni 10^4 Al^{-1}	Fe Al^{-1}	Mn 10^4 Al^{-1}	Cu 10^4 Al^{-1}	Pb 10^4 Al^{-1}	Zn 10^4 Al^{-1}
MOT 13 A	0-1	616	389	1.99	451	17.3	24.7	46.9
	10-12	277	261	1.44	303	12.4	15.4	30.4
MOT 16A	0-1	104	139	0.86	214	8.35	7.55	17.9
	30-32	85.0	127	0.87	187	7.35	9.35	14.7
UN 5	0-1	61.0	93.1	0.78	194	8.39	13.1	22.8
	30-32	58.9	84.5	0.77	137	6.85	6.52	15.2
MOT 16	0-1	170	174	1.19	244	10.4	12.9	24.8
	18-20	146	168	1.25	203	7.11	3.81	17.0
UN6	0-1	32.7	58.4	0.63	220	8.48	12.2	21.3
	24-26	34.2	61.6	0.66	159	6.41	7.29	14.0
UN 6A	0-1	37.0	47.5	0.56	145	6.7	9.76	18.8
	22-24	39.0	50.6	0.58	124	6.14	9.38	14.2
UN 4	0-1	38.6	47.4	0.46	104	6.9	7.63	15.2
	20-22	35.7	50.5	0.54	115	4.75	3.80	12.7
UN11	0-1	26.1	42.0	0.59	719	9.1	11.7	20.2
	30-32	33.8	45.1	0.66	303	7.75	7.29	14.8

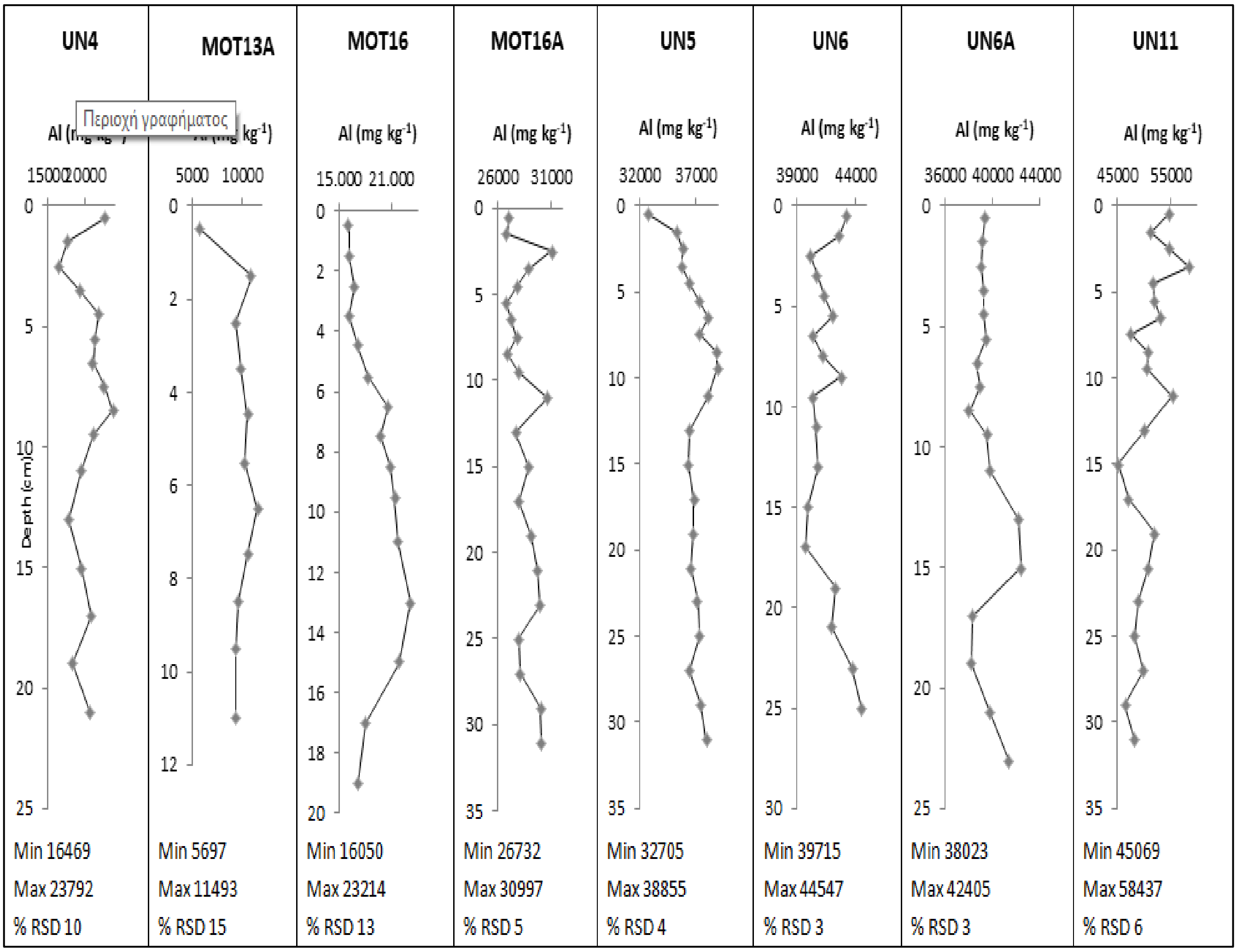

Figure A1: Vertical distributions of Al in mg kg $^{-1}$ in sediment cores. The concentrations in coarse cores MOT13A, MOT16, UN4 refer to the total sediment fraction (f < 1 mm).

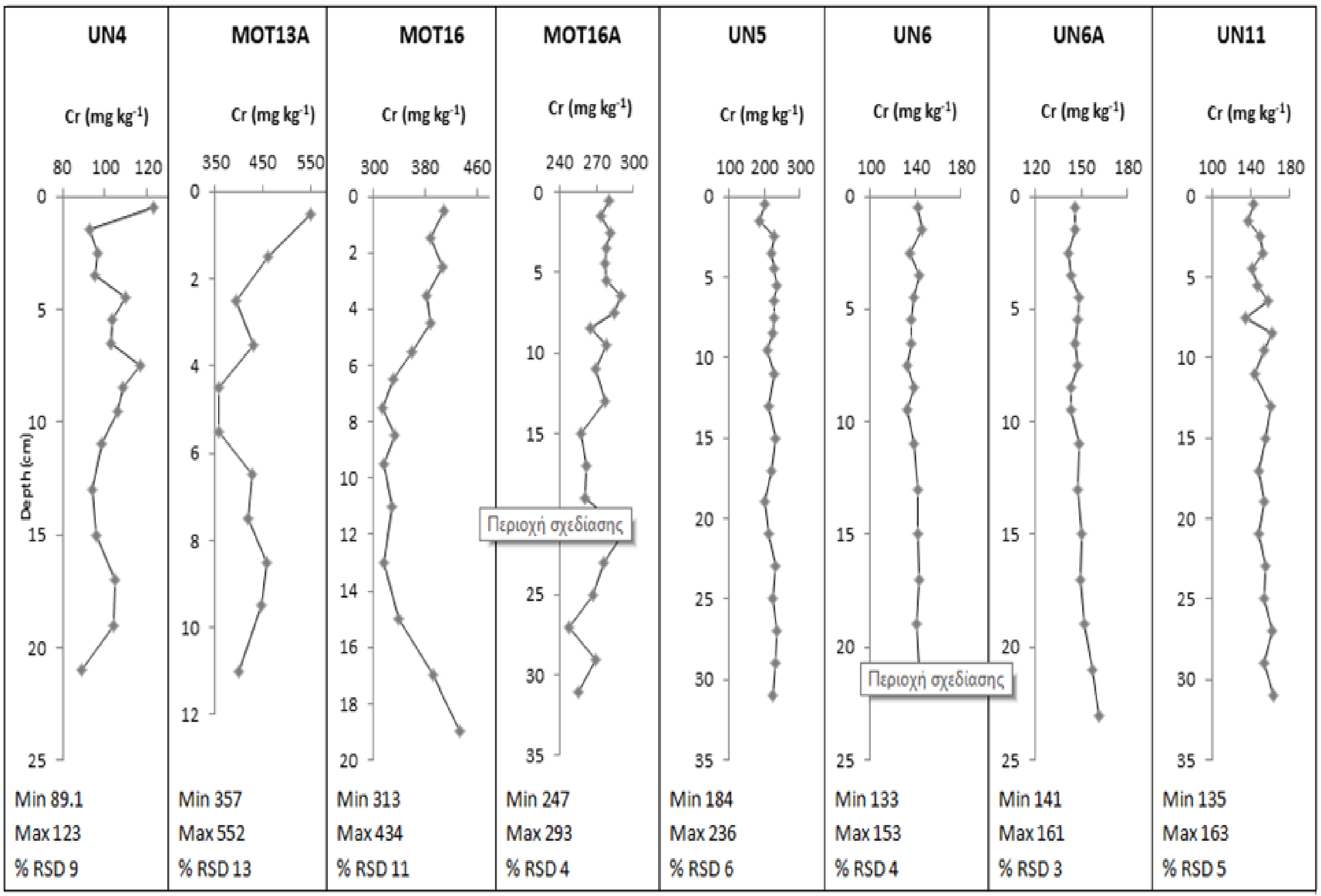

Figure A2: Vertical distributions of Cr in mg kg $^{-1}$ in sediment cores. The concentrations in coarse cores MOT13A, MOT16, UN4 refer to the total sediment fraction (f < 1 mm).

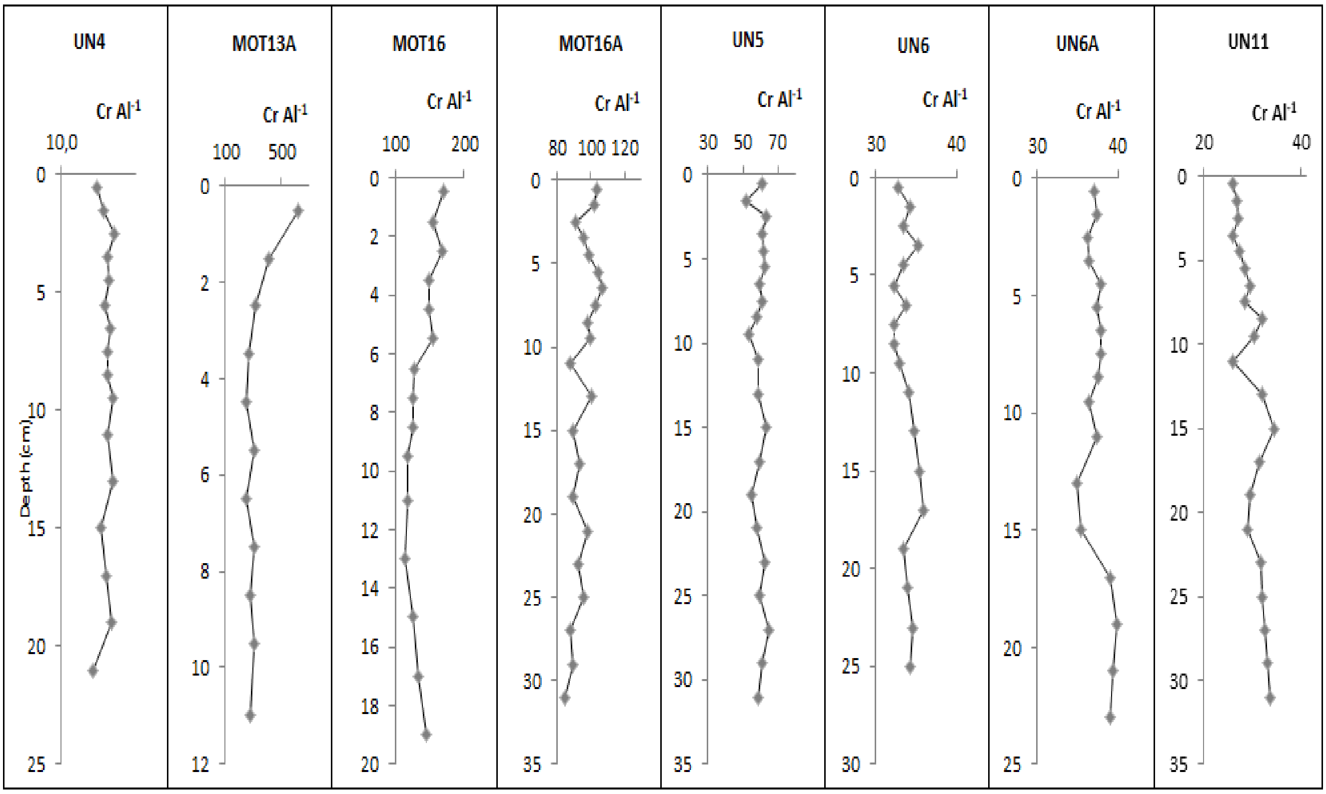

Figure A3: Vertical distributions of Cr Al $^{-1}$ (10^4) in sediment cores. The ratios in coarse cores MOT13A, MOT16, UN4 are calculated at the fine sediment fraction (f < 63 μm).

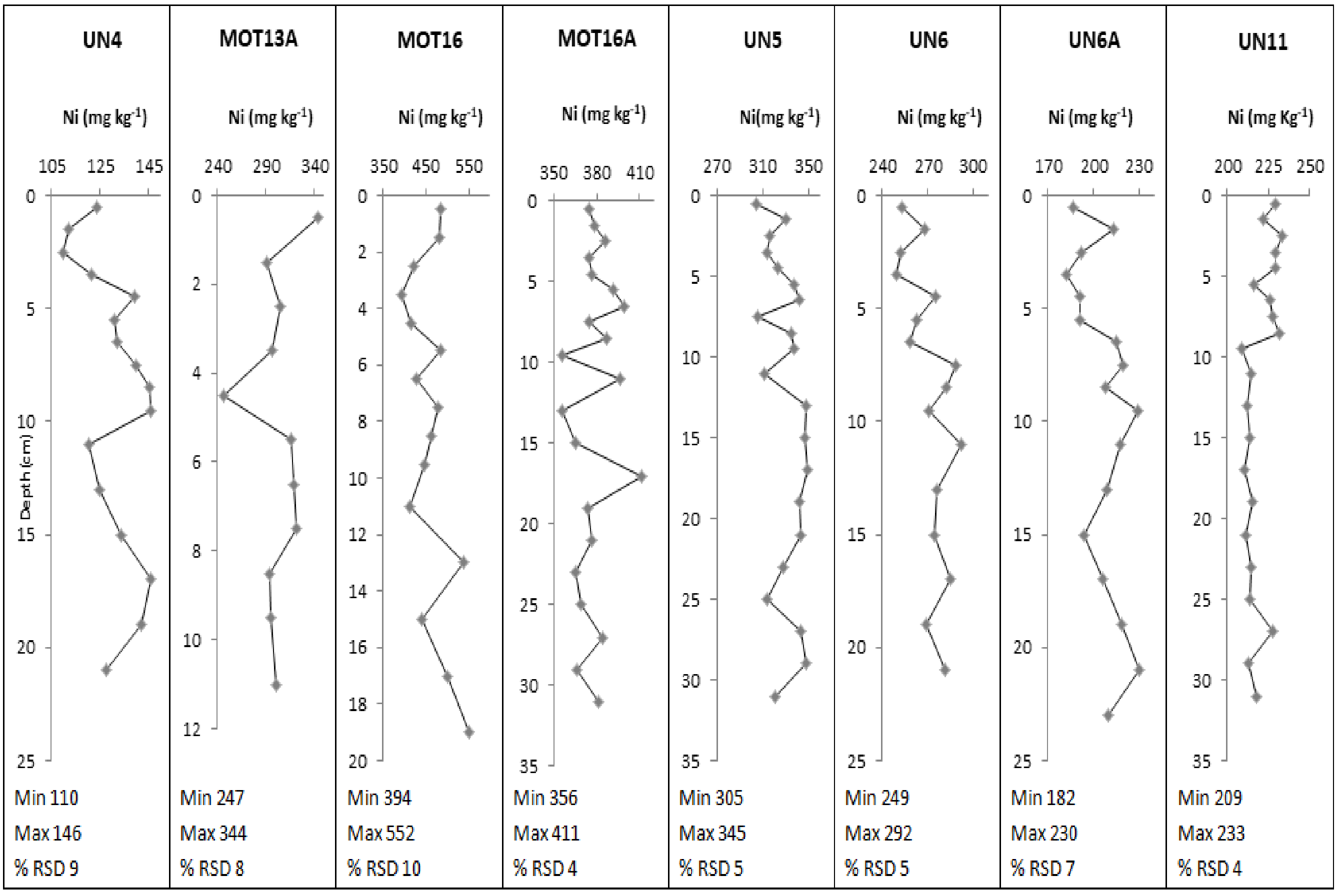

Figure A4: Vertical distributions of Ni in mg kg $^{-1}$ in sediment cores. The concentrations in coarse cores MOT13A, MOT16, UN4 refer to the total sediment fraction (f < 1 mm).

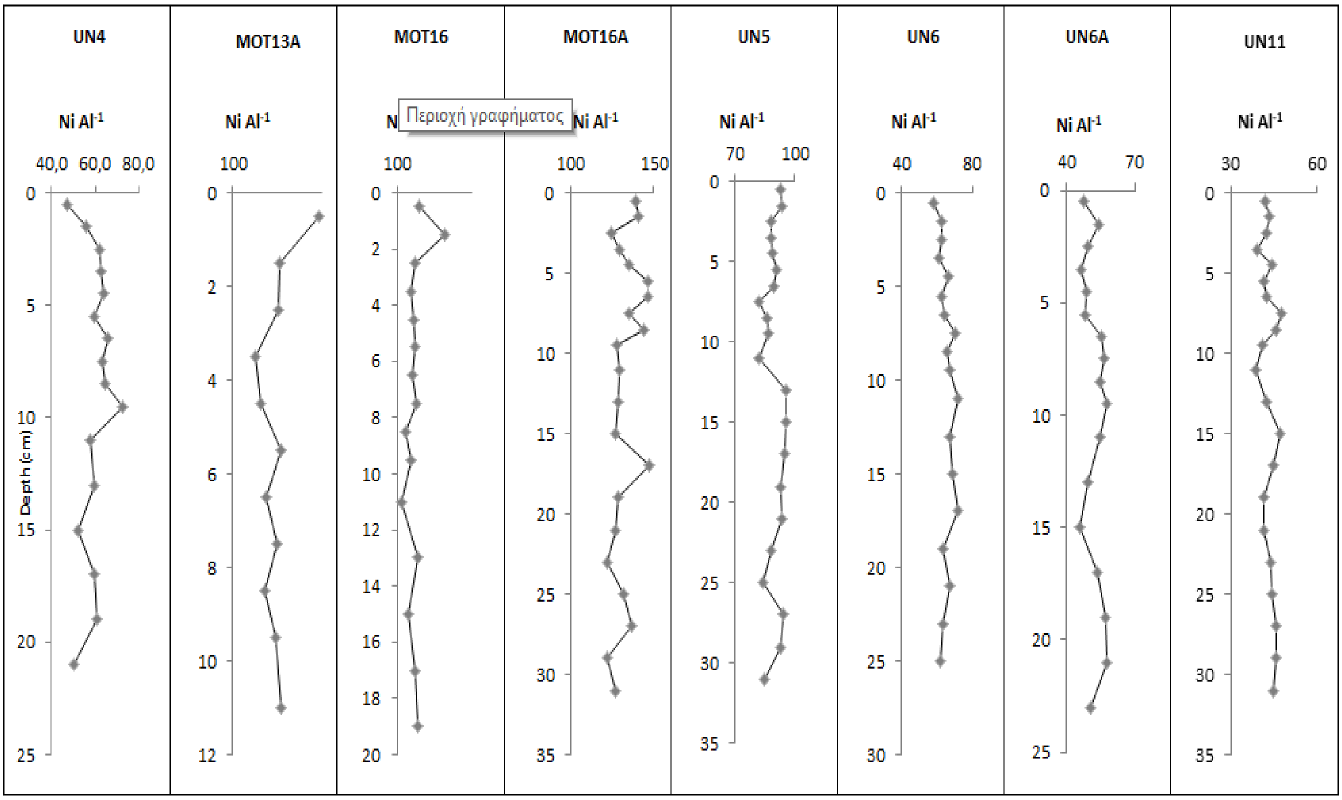

Figure A5: Vertical distributions of Ni Al^{-1} (10^4) in sediment cores. The ratios in coarse cores MOT13A, MOT16, UN4 are calculated at the fine sediment fraction (f < 63 μm).

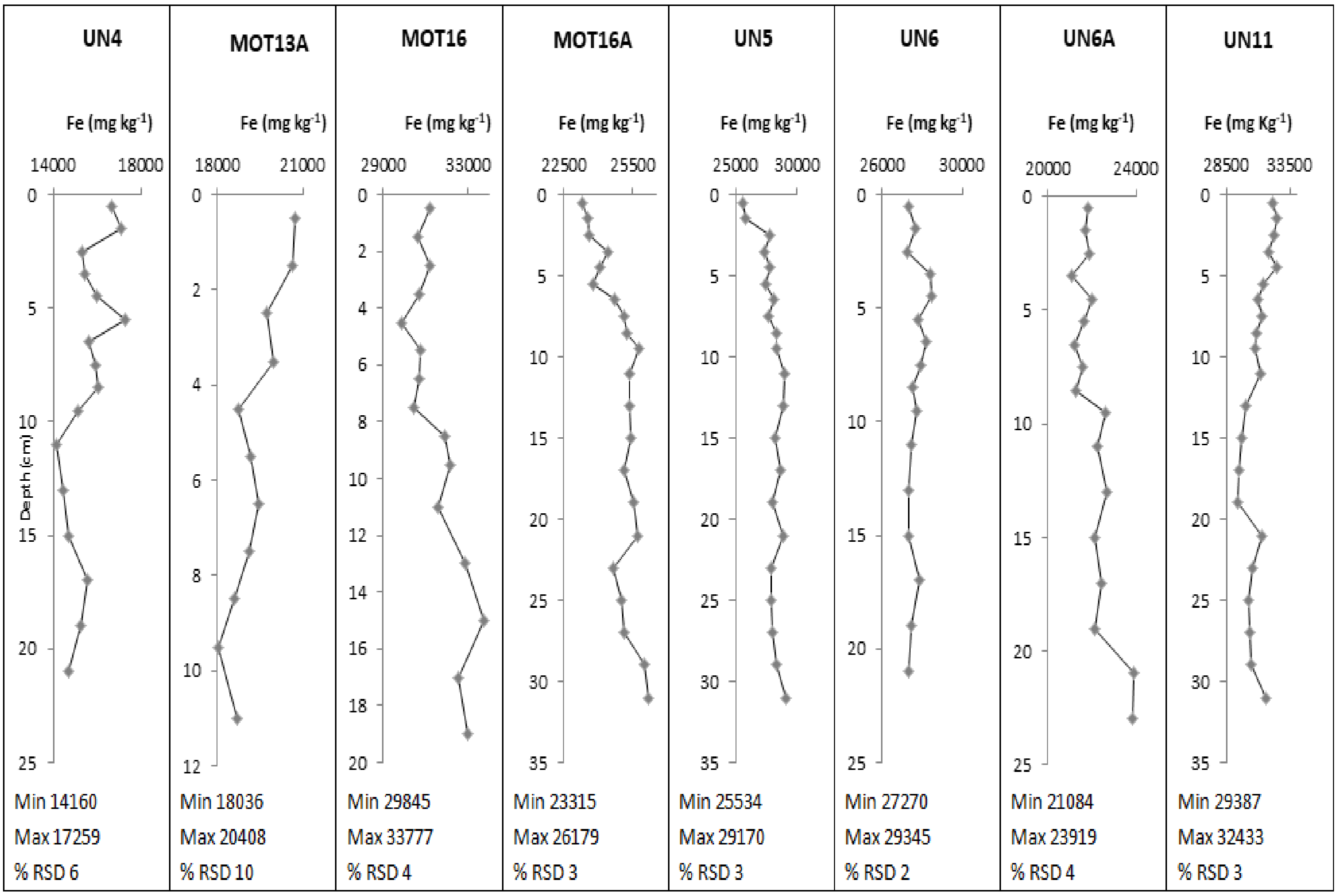

Figure A6: Vertical distributions of Fe in mg kg $^{-1}$ in sediment cores. The concentrations in coarse cores MOT13A, MOT16, UN4 refer to the total sediment fraction (f < 1 mm).

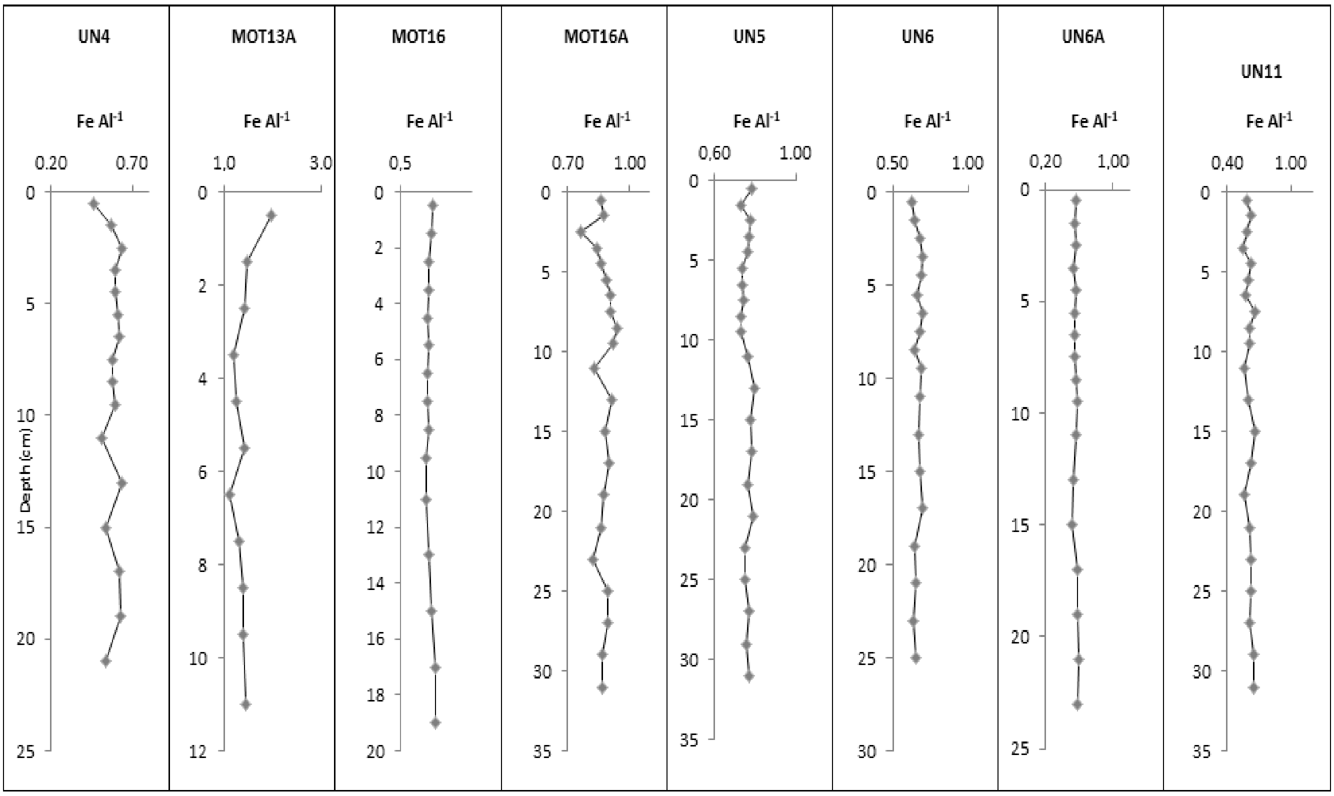

Figure A7: Vertical distributions of Fe Al^{-1} in sediment cores. The ratios in coarse cores MOT13A, MOT16, UN4 are calculated at the fine sediment fraction (f < 63 µm).

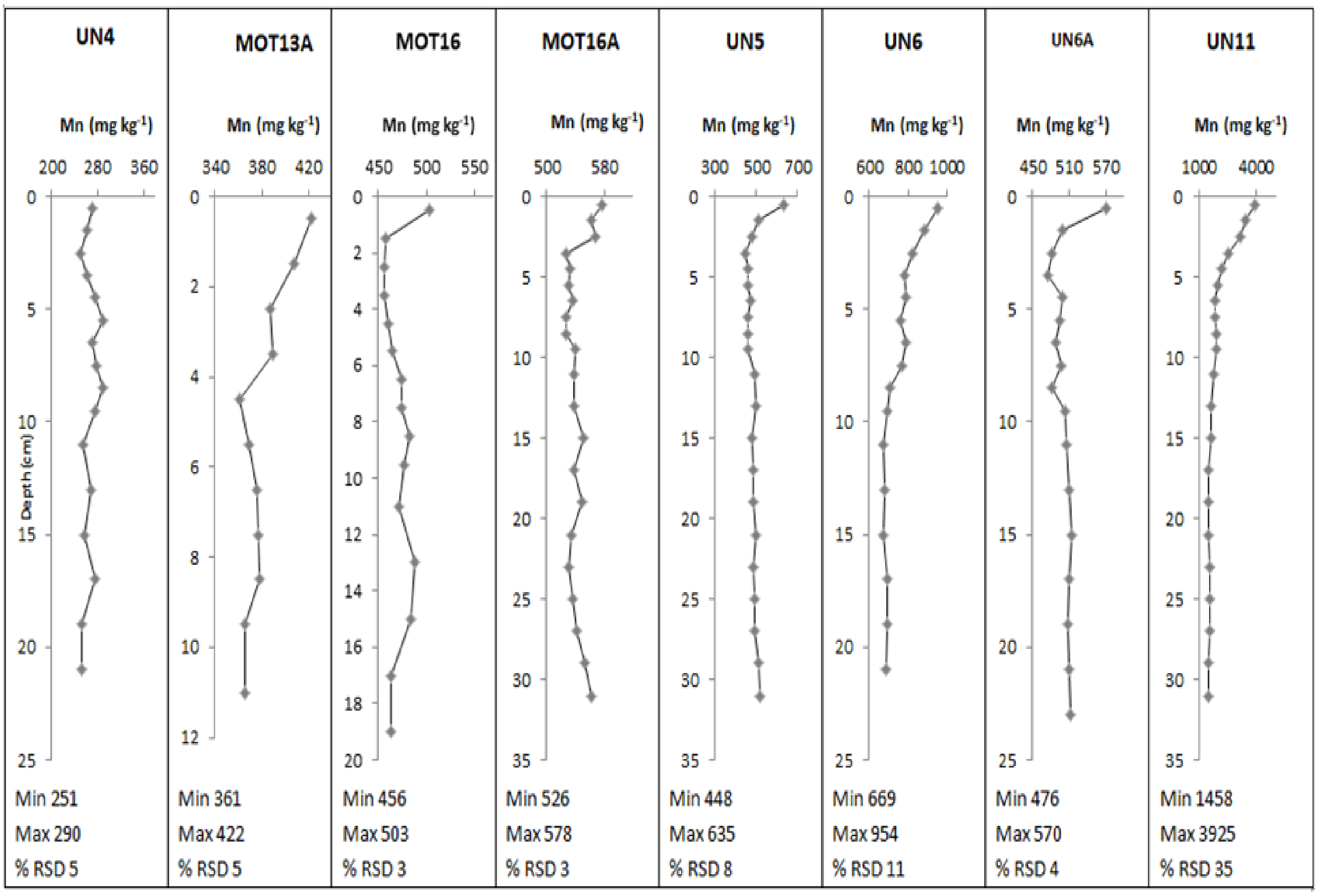

Figure A8: Vertical distributions of Mn in mg kg $^{-1}$ in sediment cores. The concentrations in coarse cores MOT13A, MOT16, UN4 refer to the total sediment fraction (f < 1 mm).

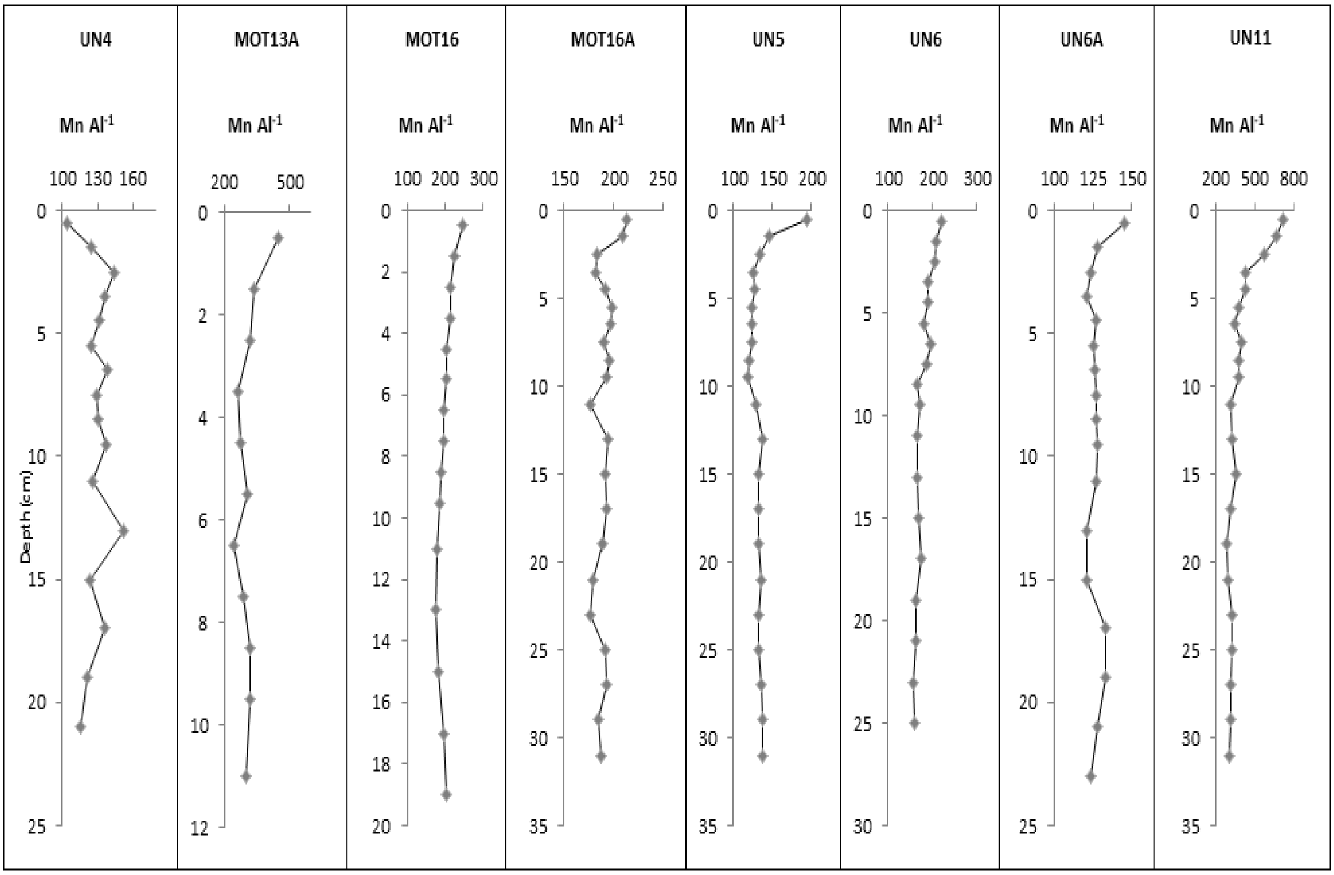

Figure A9: Vertical distributions of Mn Al^{-1} (10^4) in sediment cores. The ratios in coarse cores MOT13A, MOT16, UN4 are calculated at the fine sediment fraction (f < 63 μm).

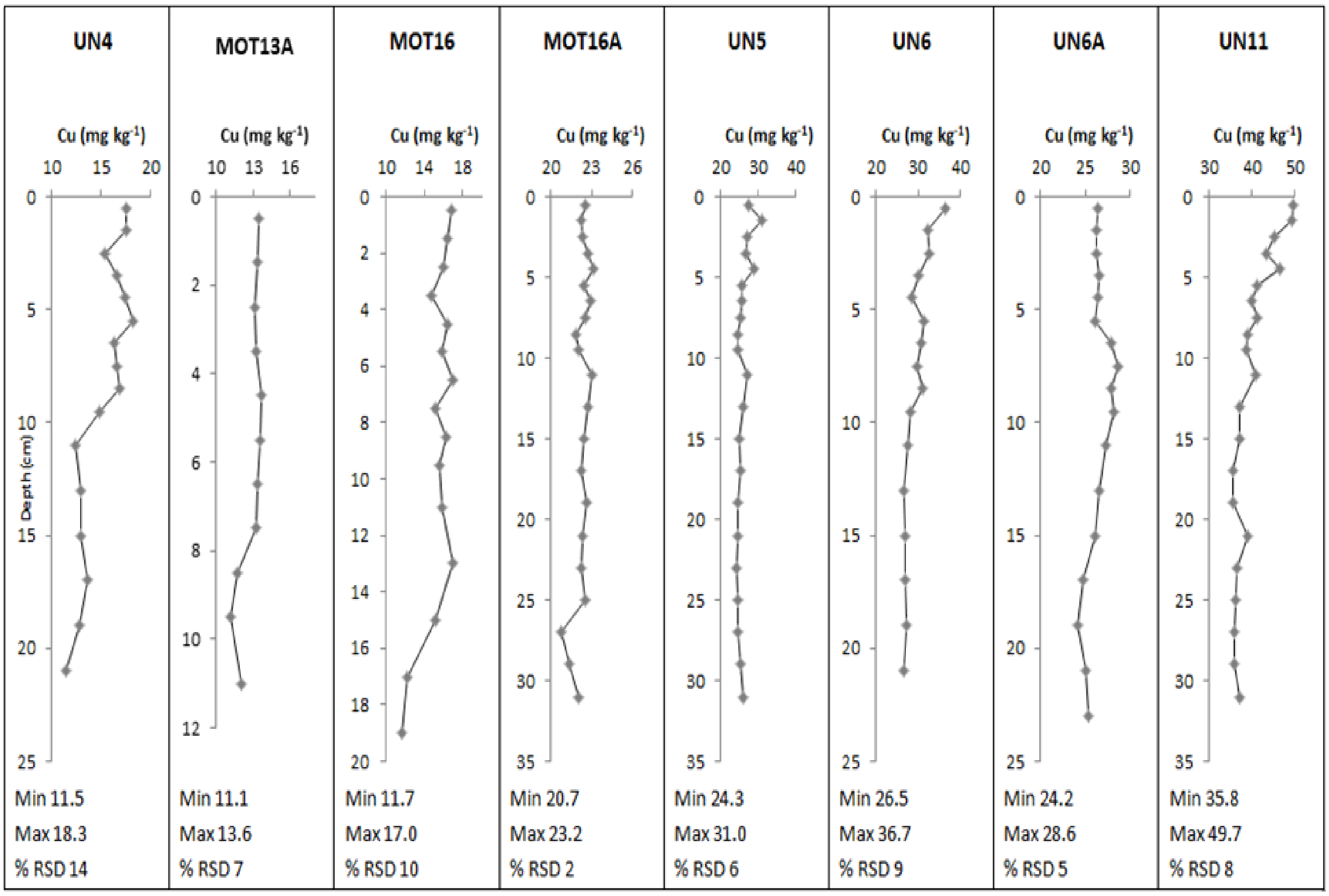

Figure A10 : Vertical distributions of Cu in mg kg $^{-1}$ in sediment cores. The concentrations in coarse cores MOT13A, MOT16, UN4 refer to the total sediment fraction (f < 1 mm).

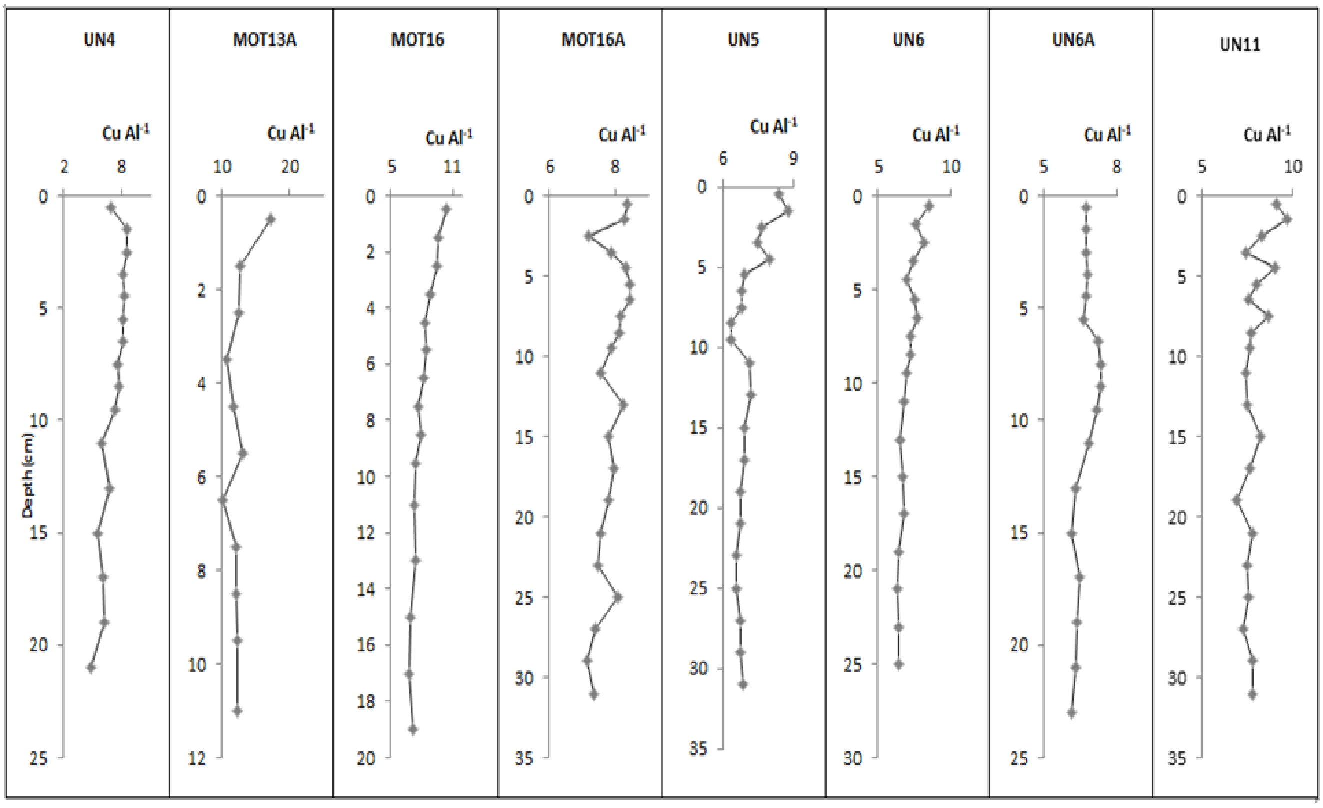

Figure A11: Vertical distributions of Cu Al^{-1} (10^4) in sediment cores. The ratios in coarse cores MOT13A, MOT16, UN4 are calculated at the fine sediment fraction (f < 63 µm).

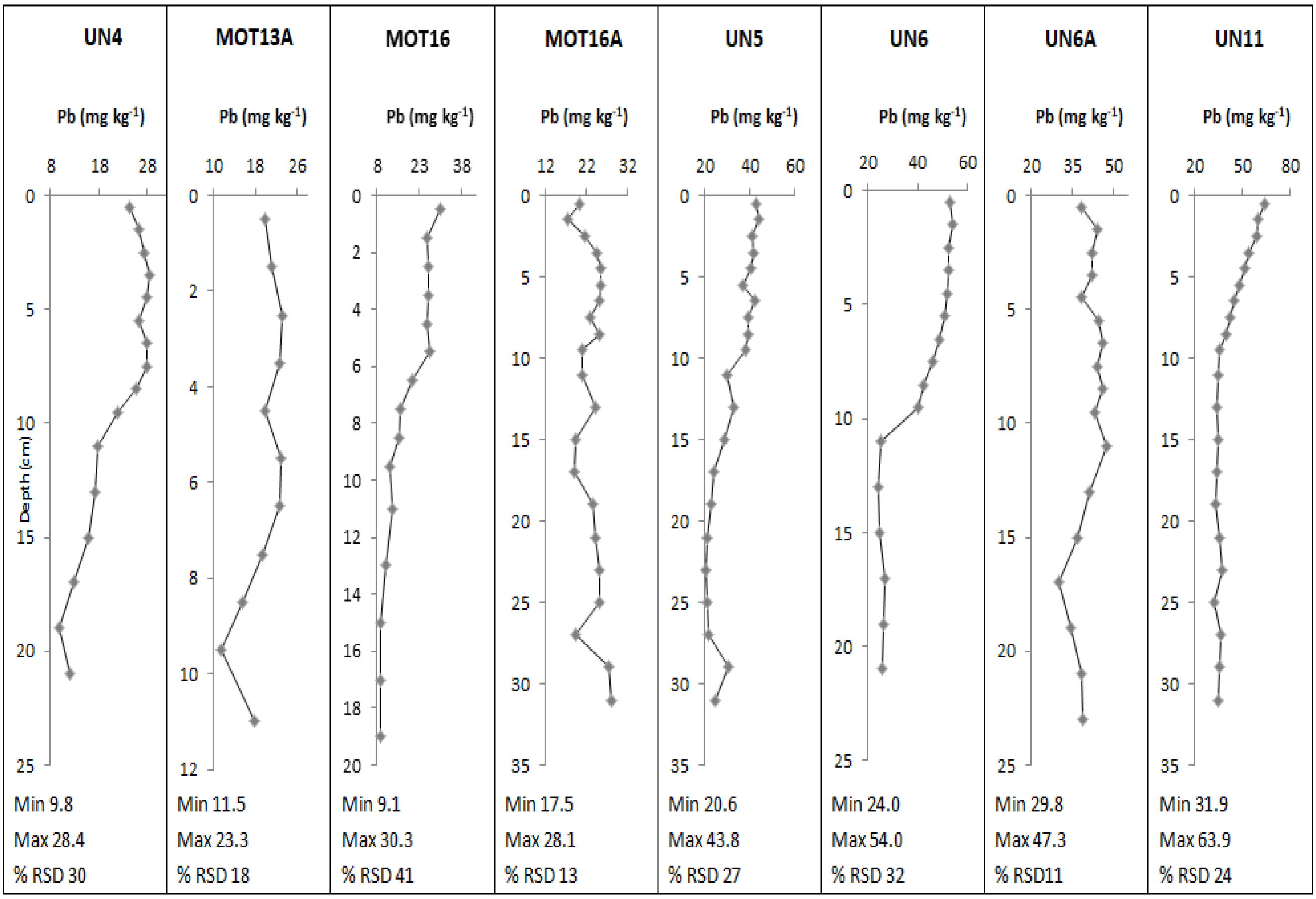

Figure A12: Vertical distributions of Pb in mg kg $^{-1}$ in sediment cores. The concentrations in coarse cores MOT13A, MOT16, UN4 refer to the total sediment fraction (f < 1 mm).

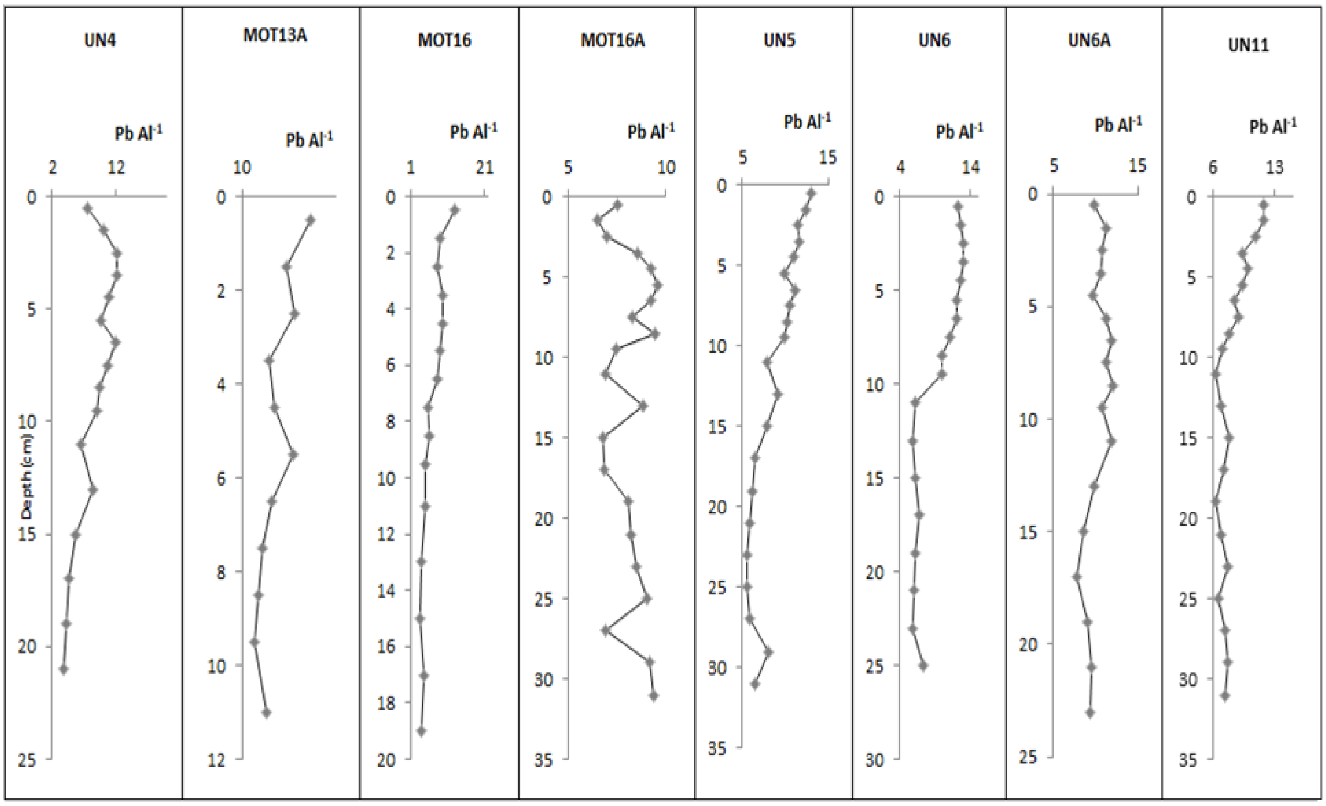

Figure A13 : Vertical distributions of Pb Al^{-1} (10^4) in sediment cores. The ratios in coarse cores MOT13A, MOT16, UN4 are calculated at the fine sediment fraction (f < 63 µm).

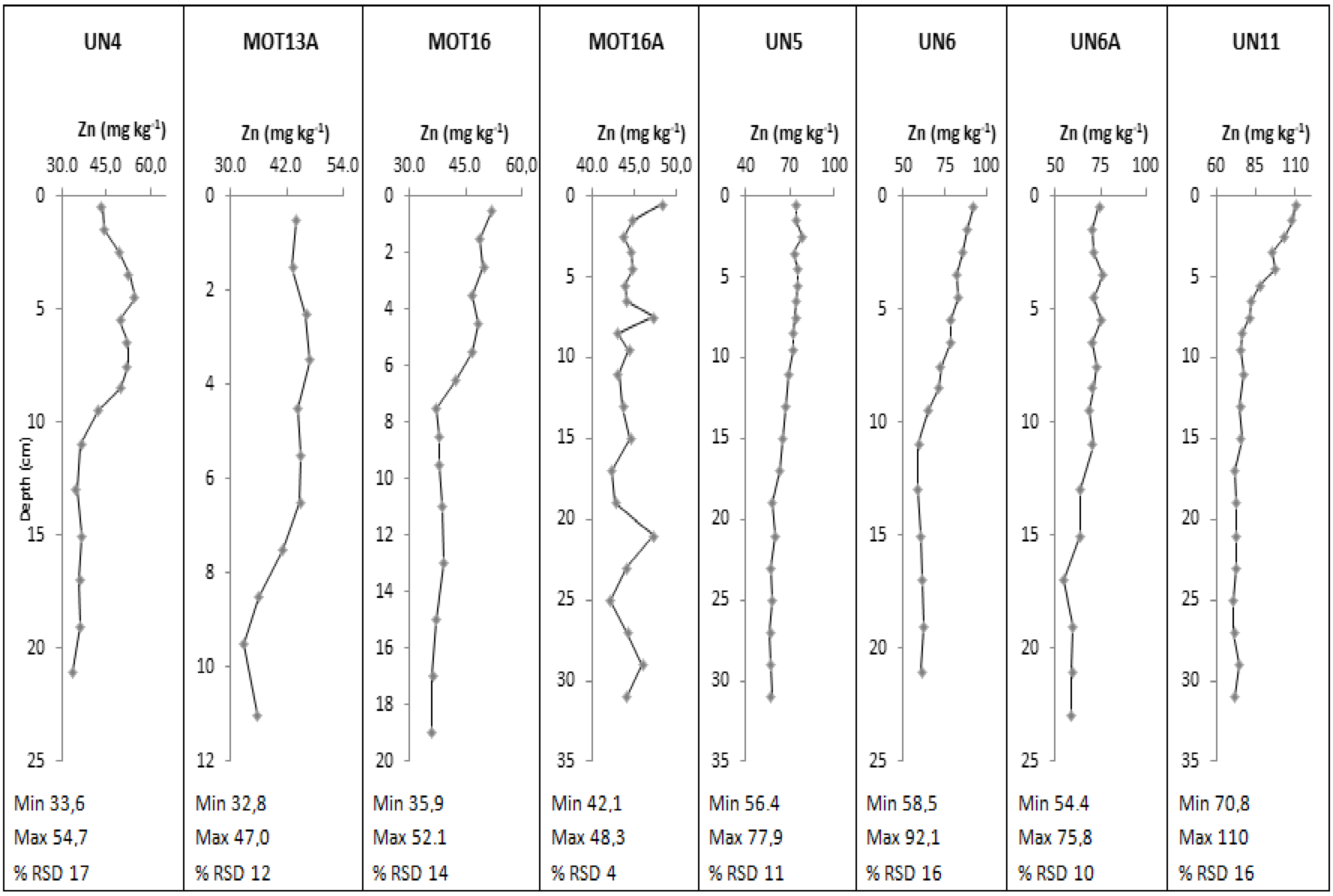

Figure A14: Vertical distributions of Zn in mg kg $^{-1}$ in sediment cores. The concentrations in coarse cores MOT13A, MOT16, UN4 refer to the total sediment fraction (f < 1 mm).

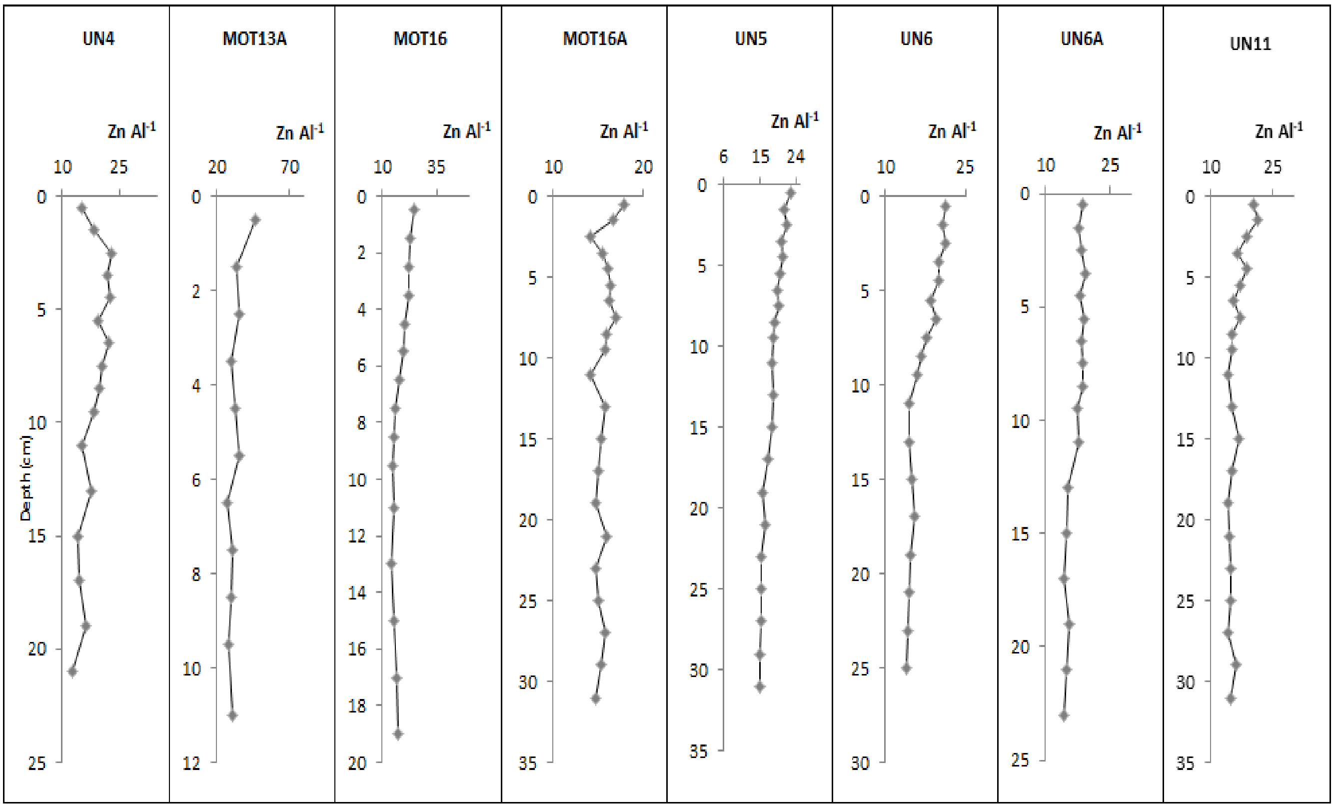

Figure A15: Vertical distributions of Zn Al^{-1} (10^4) in sediment cores. The ratios in coarse cores MOT13A, MOT16, UN4 are calculated at the fine sediment fraction (f < 63 µm).

Table A2. Spearman's correlation coefficient matrix for Al (mg Kg^{-1}), Cr (mg Kg^{-1}), Ni (mg Kg^{-1}) , Fe (mg Kg^{-1}), Mn (mg Kg^{-1}), Cu (mg Kg^{-1}), Pb (mg Kg-1), Zn (mg Kg^{-1}), TOC (% Total Organic Carbon), carbonates (% $CaCO_3$) (N=140 sediment samples).

Correlations

Spearman's rho	Al	Cr	Ni	Fe	Mn	Cu	Pb	Zn	TOC	% $CaCO_3$
Al	1.000									
Cr	-0.521**	1.000								
Ni	-0.453**	0.841**	1.000							
Fe	0.624**	0.081	0.179*	1.000						
Mn	0.735**	-0.108	0.029	0.694**	1.000					
Cu	0.924**	-0.419**	-0.342**	0.633**	0.746**	1.000				
Pb	0.676**	-0.440**	-0.433**	0.244**	0.397**	0.779**	1.000			
Zn	0.790**	-0.452**	-0.441**	0.459**	0.479**	0.882**	0.894**	1.000		
TOC	0.244**	-0.198*	-0.272**	0.096	0.155	0.351**	0.428**	0.483**	1.000	
% $CaCO_3$	-0.472**	-0.215*	-0.222**	-0.766**	-0.597**	-0.566**	-0.358**	-0.516**	-0.282**	1.000

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

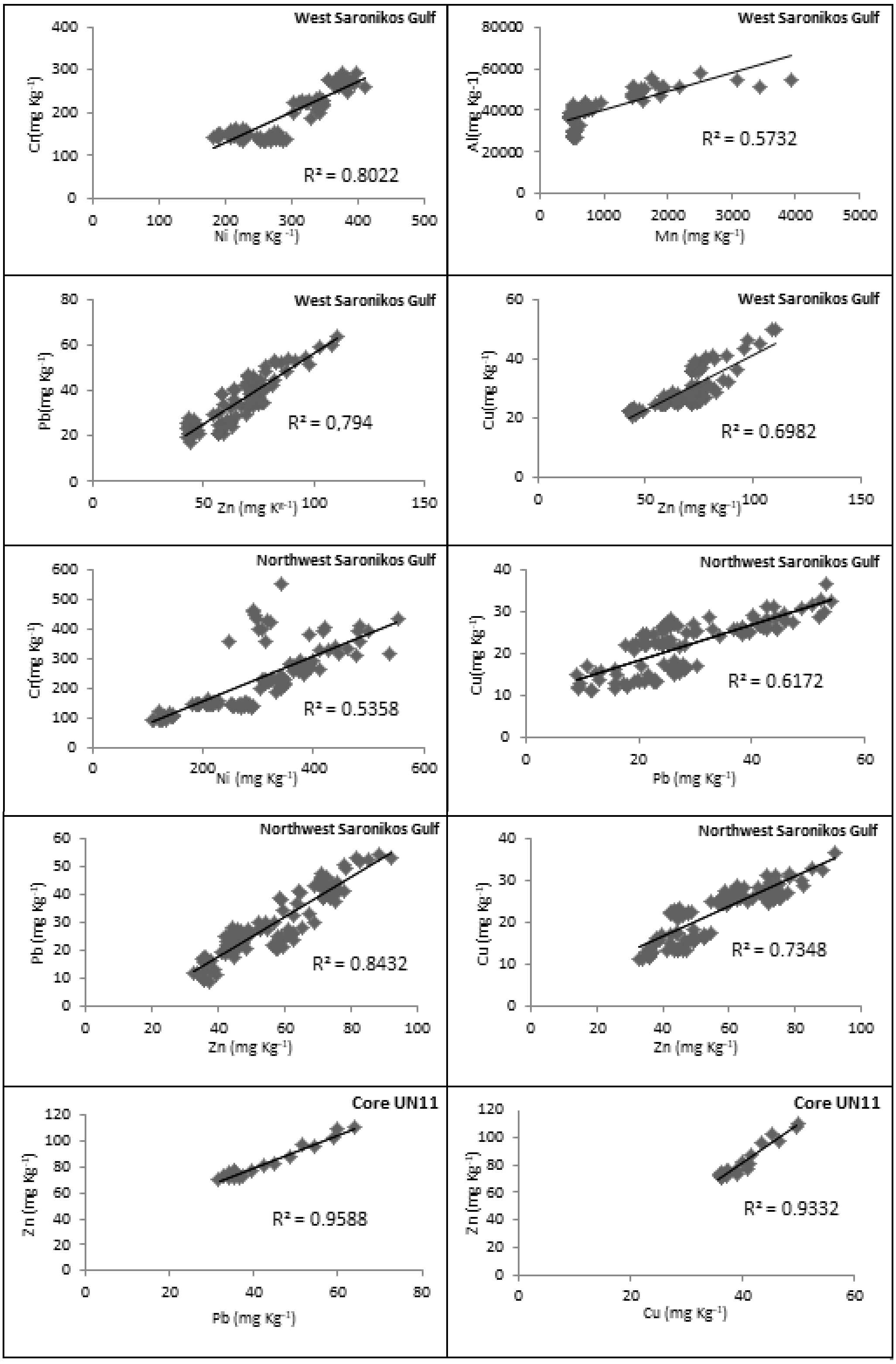

Figure A16: Correlations of heavy metals for the core samples of West Saronikos Gulf.

7 Code availability

Not applicable.

8 Data availability

Datasets and their sources are fully detailed in the manuscript.

9 Executable research compendium (ERC)

Not applicable.

10 Sample availability

Not applicable.

11 Video supplement

Not applicable.

12 Supplement link

Not applicable.

13 Team list

Not applicable.

14 Author contribution

Georgia Filippi and Vasiliki Paraskevopoulou conducted the chemical analyses in the Laboratory of Environmental Chemistry of the National and Kapodistrian University of Athens. Georgia Filippi wrote the paper, with contributions and reviews from all co-authors. Manos Dassenakis was the supervisor of the laboratory work and this article.

15 Competing interests

The authors declare that they have no conflict of interest.

16 Disclaimer

Not applicable.

17 Special issue statement

The statement on a corresponding special issue will be included by Copernicus, if applicable.

18 Acknowledgements

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