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Geochemical characteristics of the recent sediments from the Sea of Marmara

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Abstract

Six box-cores, one boomerang core and one hundred sixty-six surface sediment samples recovered in the Sea of Marmara were analyzed in an attempt to establish the main controls on distribution and origin of trace metals within the oxic to suboxic basin of this sea.

Surface and downcore data indicate that the abundance and distribution of the total metal concentrations for Fe, Ni, Zn, Cr, Co, Cu and Pb can largely be explained by the variable admixtures of terrigenous components in response to textural variations and biogenic calcareous components poor in metal contents. The distribution of Cr and Ni seems to be controlled, in part, by a contribution from the weathering of basic/ultrabasic sources on the coastal hinterland. A small but significant amount of Cu, Zn and Pb in sediments from the northeastern Sea of Marmara probably suggests a pollution effect from the northerly located Golden Horn Estuary that is known as one of the most polluted coastal regions of Turkey.

Looking at the data, it seems that the Mn concentrations are unusually high in the deep-water sediments (4498–9127 ppm, carbonate free), along the east–west-trending Marmara Trough but low in sediments from the adjacent shallow waters (307–2059 ppm, carbonate free). The Mn enrichment in deep-water relative to shallow-water Marmara sediments is further indicated by the Fe/Mn ratios being, on average, 11–23 in deep waters and 34–69 in shallow waters. The contents of other metals (Fe, Ni, Zn, Cr, Co, Cu, Pb) in both shallow- and deep-water sediments fall nearly within the same range as those found in average crustal and sedimentary rocks, suggesting no significant enrichment of these metals in the deep Marmara basins.

The downcore changes in the color, from reddish-brown at the surface (top 2–5 cm) to greenish-gray in the subsurface (>5 cm), together with the occurrence of high Mn concentrations in the surface sediment layers in cores can be attributed, at least in part, to the diagenetic Mn enrichment within the sediment column. The usually low organic carbon contents and biogenic components present in sediments reflect that the well-known biogenic mechanism for the enrichment of Mn seems to be of minor importance in the deep Marmara waters. The generally low Mn concentrations contained in the surface (grab) and core sediments from the Black Sea and Aegean Sea approaching those of the Sea of Marmara do not provide any conclusion to support significant Mn contribution from these two adjacent seas, particularly from the so-called "manganese pump" zones in the shallow Black Sea waters. Comparison with other deep-sea sediments which have been deposited under the influences of hydrothermal activities, worldwide, suggests Mn enrichment in deep-water relative to shallow-water sediments of the Sea of Marmara, mainly as a result of hydrothermal contributions from this seismically active marine region. Based on the average Fe/Mn ratios obtained in cores, which tend to increase gradually from ~11 in the deep Central Basin to ~67–69 in the northeastern and southwestern shelves, the Central Basin of Marmara Trough can be considered as a possible, potential source for hydrothermal solutions leading to the enrichment of Mn in the deep Marmara waters. However, this remains to be further investigated.

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1. Introduction

The Sea of Marmara, with a surface area of ~ 11,500 km² and a volume of 3,378 km³, forms an almost totally enclosed depression between the Black Sea in the north-northeast and the Aegean or Mediterranean Sea in the south-southwest (Fig. 1). It is connected to these adjacent seas through the two narrow and shallow straits (Bosphorus and Dardanelles, respectively).

Previous studies in the Sea of Marmara have documented mostly the types and modes of distribution of surficial sediments in response to various oceanographic factors prevailing in this sea (e.g., Stanley and Blanpied, 1980; Algan and Akbulut, 1985; Ergin and Yörük, 1990; Ergin et al., 1990, 1991a, b, 1993a). However, the geochemical characteristics of the sediments in this sea have been poorly studied and the present

knowledge is limited only to the eastern deep basin of this sea (Ergin and Evans, 1988; Evans et al., 1989). In particular, trace-metal enrichments are first reported for Mn in the deep-sea sediments in the eastern Marmara Basin (Evans et al., 1989) and recently confirmed by the results from other deep-sea parts of this sea (Ergin and Bodur, 1992). Besides, trace-metal enrichments are also known to occur in surface sediments from the northeastern part of this sea, mainly as a result of the pollution influences (Ergin et al., 1991b).

The primary objective of this study was to examine the geochemical characteristics of some trace metals in the surficial bottom sediments and to discuss the results in relation to various oceanographic factors prevailing in the Sea of Marmara. These data aim to predict the mode of occurrence of some trace metals and their possible sources and associations in a transitional marine environment, the Sea of Marmara.
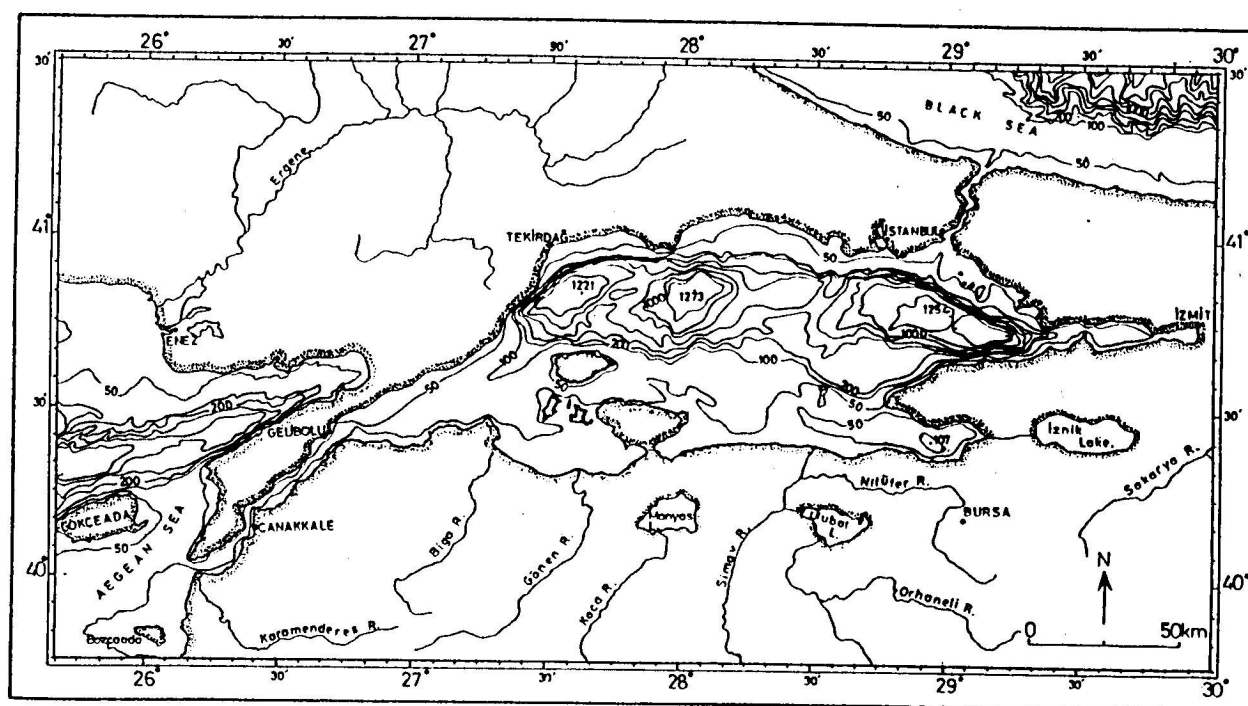

Fig. 1. The study area, the Sea of Marmara and its surroundings. Depth in meters.

2. Hydrographic and geologic setting

The hydrography of the Sea of Marmara is characterized by a two-layer flow model consisting of low-salinity (18–22 ppt) surface waters inflowing from the Black Sea and high-salinity (38.5 ppt) subsurface waters inflowing from the Aegean and Mediterranean seas (e.g., Miller, 1983; Ünlüata et al., 1990). Consequently, a permanent pycnocline exists between this stratified two-layer flow which usually occurs between 20- and 25-m water depths (50 m at the Black Sea entrance and 10 m at the Aegean exit (Ünlüata et al., 1990) and the water exchange between the Black and Aegean seas is controlled by the Dardanelles and Bosphorus straits (Stanley and Blanpied, 1980). Due to its stratified character, subhalocline water masses of the Sea of Marmara are continuously depleted in dissolved oxygen (Bastürk et al., 1990) and thus, these subhalocline waters can practically be regarded as aerobic (>1 ml l^{-1} O_2) to dysaerobic (1.0–0.1 ml l^{-1} O_2), according to the classification by Savrda and Bottjer (1987).

Geologically, the Marmara Basin is associated with major tectonic features. The east–west-trending Marmara Trough (Fig. 1) which separates the narrower northern shelf (2–13 km wide) from the much broader southern shelf ($\sim$30 km wide), through a number of secondary subparallel faults (Wong et al., 1990) is a prominent morphological feature of the Sea of Marmara. It is divided into three small depressions ("fault-bounded pull-apart basins") that have maximum depths from west to east of 1152 m (Tekirdağ Basin), 1265 m (Central Marmara Basin) and 1276 m (İstanbul Basin) (Wong et al., 1990). The Marmara Trough is a continuation of seismically active North Anatolian Fault (NAF) zone along which relative motions between the Anatolian and Black Sea blocks are taken up since the Middle Miocene (Sengör et al., 1985).

3. Materials and methods

One hundred sixty-six surface sediment samples (0–6 cm) were collected from the shelf and slope regions (10–855-m water depths) of the Sea of Marmara during the 1988–1990 cruises of R/V "Bilim" using a Dietz Lafonde®-type grab sampler. Additional sediment samples (0–50 cm) were obtained at six stations down to a water depth of $\sim$1226 m with a Soutar® Type Box Corer (Ocean Instruments® Mark III) during the Leg 134-13 cruises of R/V "Knorr" in the Sea of Marmara and its straits. A boomerang gravity core (0–80 cm) which was recovered during a cruise of R/V "Bilim" in the eastern Marmara Sea (İstanbul Basin) in 1984, was also kindly provided by Dr. G. Evans (London) for this work. Sampling stations for all grab and corer sediments are depicted in Fig. 2.

Sediment samples obtained were subjected to granulometric, microscopic and chemical investigations. All the cores in the laboratory are subsampled in slices of $\sim$2–3 cm. The grain-size analyses of the sand (0.063–2 mm) and gravel (>2 mm) fractions were carried out using dry-wet sieving techniques; the mud fraction (finer than 0.063 mm) was analyzed using the pipette method (Folk, 1974). For carbonate, organic carbon and metal analyses representative subsamples were dried at 50–60°C and ground in a mortar. Total carbonate content in the bulk sample was determined by a modified Gasometer system of Scheibler® (Müller, 1967). The percentage of organic carbon was estimated by using the wet oxidation method of Gaudette et al. (1974). The precision of the analytical methods, estimated using replicate samples, is ±1.6% for total carbonate and ±0.05–0.08% for total organic carbon. Concentrations of the heavy metals Fe, Mn, Ni, Zn, Cr, Co, Cu and Pb were determined by flame atomic absorption spectrometry (AAS); a Varian® Techtron AA6 Model Atomic Absorption Spectrophotometer was used. The heavy-metal analyses of the bulk sediment samples were carried out by complete digestion in a mixture of $HF-HNO_3$. The analyses of heavy metals were checked with international standard samples: light-sandy soil (CRM-142), sludge (EPA 286) and Shale-I (EPA 386), from the Community Bureau of Reference Materials (BCR). The analytical precision was ±2% for Fe, ±11% for Mn, ±0.3% for Ni, ±7% for
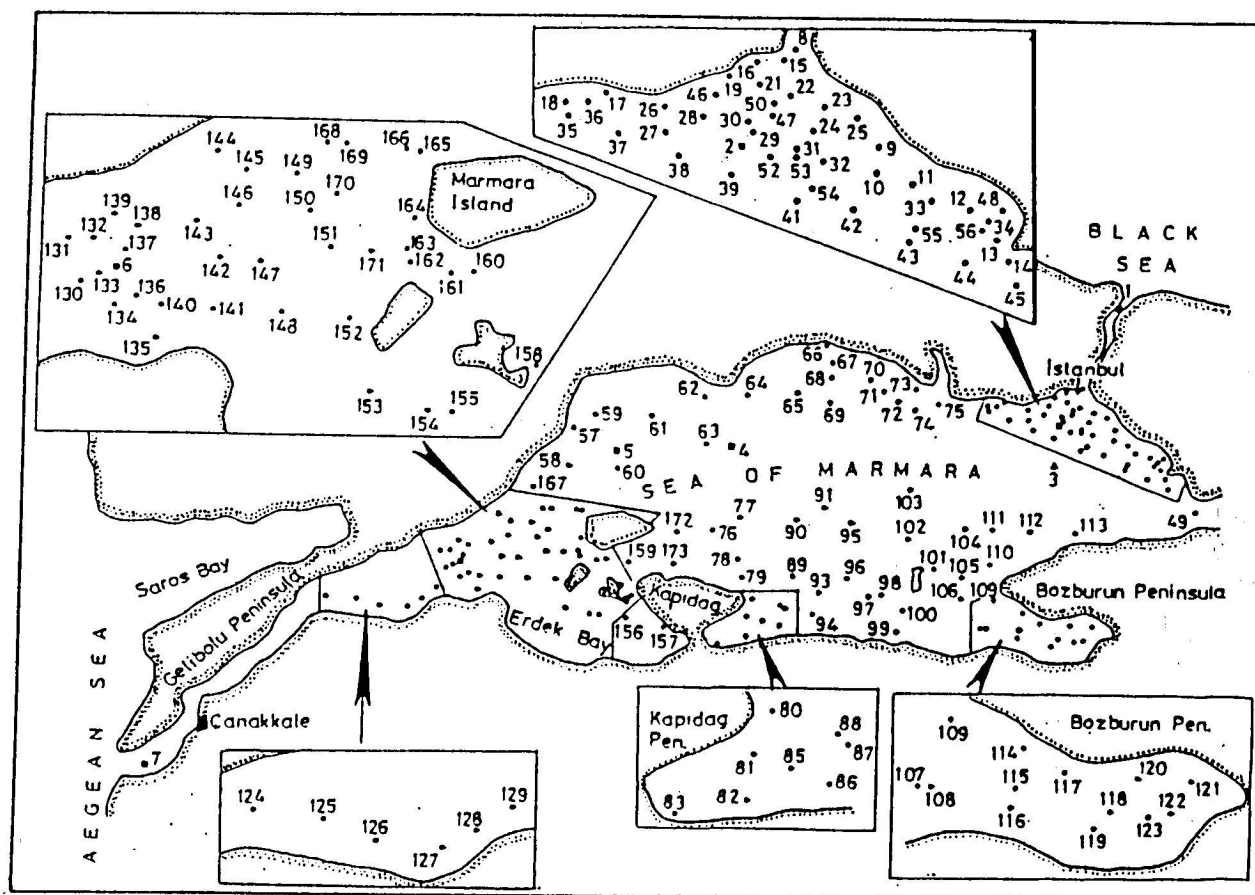
Fig. 2. Sampling stations of the studied surficial sediments in the Sea of Marmara. (Stations *1*, *2* and *4–7* are sites for box-corings while station *3* represents site of boomerang coring.)

Zn, ±3% for Cr, ±7% for Co, ±4% for Cu and ±2% for Pb using replicate analyses of CRM 142. The reproducibility of the method was found to be normally between ±2% and ±9%, except for Pb (±14%) and Co (±17%), using some representative samples selected.

4. Results and discussion

4.1. Grain size, carbonate and organic carbon distribution

Full details of grain size, total carbonate and total organic carbon distribution in the surface sediment (grab) samples from the Sea of Mar-

mara have already been discussed by Ergin et al. (1991a, 1993a) and the bulk of the data can be obtained upon request from the authors (e.g., Bodur, 1991).

It has been shown that the surface (grab) sediments of the Sea of Marmara consisted of a wide range of grain sizes, mainly in response to bottom topography, hydrodynamic factors acting upon it and biogenic activities. Sediments rich in clay contents are mostly found in relatively deeper waters and the coastal embayments with favoured fine sedimentation whereas sediments rich in sand and gravel (except for shell and skeleton remains of the benthic organisms) are widely distributed in nearshore and shallow-water areas, where current and wave activities are

dominant. Petrographic analyses of the non-biogenic coarse-grained fractions (sand and gravel) indicate the predominance of terrigenous materials (chiefly quartz, feldspars and mica mineral grains, as well as fragments of chert, quartzite, schist and sandstone) which are well comparable with the possible weathering products from the surrounding land-based geological sources. Besides, recent X-ray bulk mineralogical studies (Shimkus and Esin, 1993) showed plagioclase (7–58%), calcite (5–37%), quartz (19–30%), illite (10–23%), potassium feldspars (<1–18%), kaolinite (5–16%), chlorite (4–14%), montmorillonite (<1–8%), aragonite (<1–7%) and dolomite (<1–7%) as the important constituents of the surface (0–5 cm) bulk sediments from the shallow waters (mainly shelf, upper slope) of the Sea of Marmara. The biogenic components observed in the sand and gravel fractions are derived mainly from the calcareous (mainly calcite) remains of various species of pelecypods, gastropods, bryzoa, echinoids, foramainifera, etc.

Grain size distribution in cores M-3, BC-3, BC-4, BC-5 and BC-6 shows that mud with slightly varying silt and clay percentages appears to be the principal sediment type throughout the cores whereas sand and gravel components are almost lacking (see Figs. 5–9). This would suggest nearly uniform and stable conditions of deposition with fine-grained sediments at the coring sites. By contrast, core sediments from the northern (BC-1) and southern (BC-2) parts of the Strait of Bosphorus contained more coarser-grained materials, with a tendency to increase down the cores (Figs. 3 and 4).

Most of the total carbonate contents of surface (grab) sediments in the Sea of Marmara fall in the range between 10% and 30% (expressed as $CaCO_3$), with the lower (down to 4%) and higher (upto 90%) values being exceptions (Ergin et al., 1993a). As aforementioned, shell remains of benthogenic organisms make up the greater part of the total carbonate contents measured. The total carbonate contents in sediments from the deep basins of Marmara Trough (cores M-3, BC-3, BC-4) and from the southwestern shelf (core BC-5) showed a rather uniform distribution throughout the cores, with values generally at

~10% (Figs. 5–8). Considerable downcore variations in carbonate contents are observed at the northeastern exit of the Sea of Marmara, at the Strait of Bosphorus (cores BC-1 and BC-2), where downward increase of carbonate contents is accompanied by coarsening of sediments (Figs. 3–4), due to the increased presence of benthogenic components. On the other hand, the downward increase in the carbonate contents in the southwestern part of the Sea of Marmara, at the Aegean exit (core BC-6; Fig. 9), seems to be resulted from the coarse-grained non-benthogenic input. It is likely related to the effects of diagenesis within sediments.

The abundance of the total organic carbon concentrations in the surface sediments of the Sea of Marmara (0.10–2.16%) appears to be controlled primarily by the variations in lithogenic and benthogenic admixtures of the sediments. Nevertheless, production and accumulation of organic matter in this sea are known to be related mainly to the influences from the two adjacent seas, the Aegean and Black seas, and to the lateral offshore transport in surface waters (Ergin et al., 1993a). In general, fine-grained sediments rich in clay or mud percentages have slightly linear trends for organic carbon ($R=0.38$ and $R=0.44$, respectively; see Table 1). The organic carbon concentrations in cores M-3, BC-3, BC-4 and BC-5 are rather uniform (~1%) throughout the cores and follow a similar distribution pattern as total carbonate contents (Figs. 5–8). Organic carbon contents in cores BC-1 (Fig. 3) and BC-6 (Fig. 9), like carbonate contents, tend to increase with depth, whereas they are slightly enriched in the surface layers of core BC-2 (Fig. 4). Apart from variations in the terrigenous and biogenous admixtures in sediments, changes in the rates and types of biogenic production and post-depositional processes are thought to cause such variations in the organic carbon contents of core sediments.

4.2. Heavy-metal distribution in surface sediments

Heavy-metal concentrations in surface (grab) sediments (including the top 6 cm of cores) from

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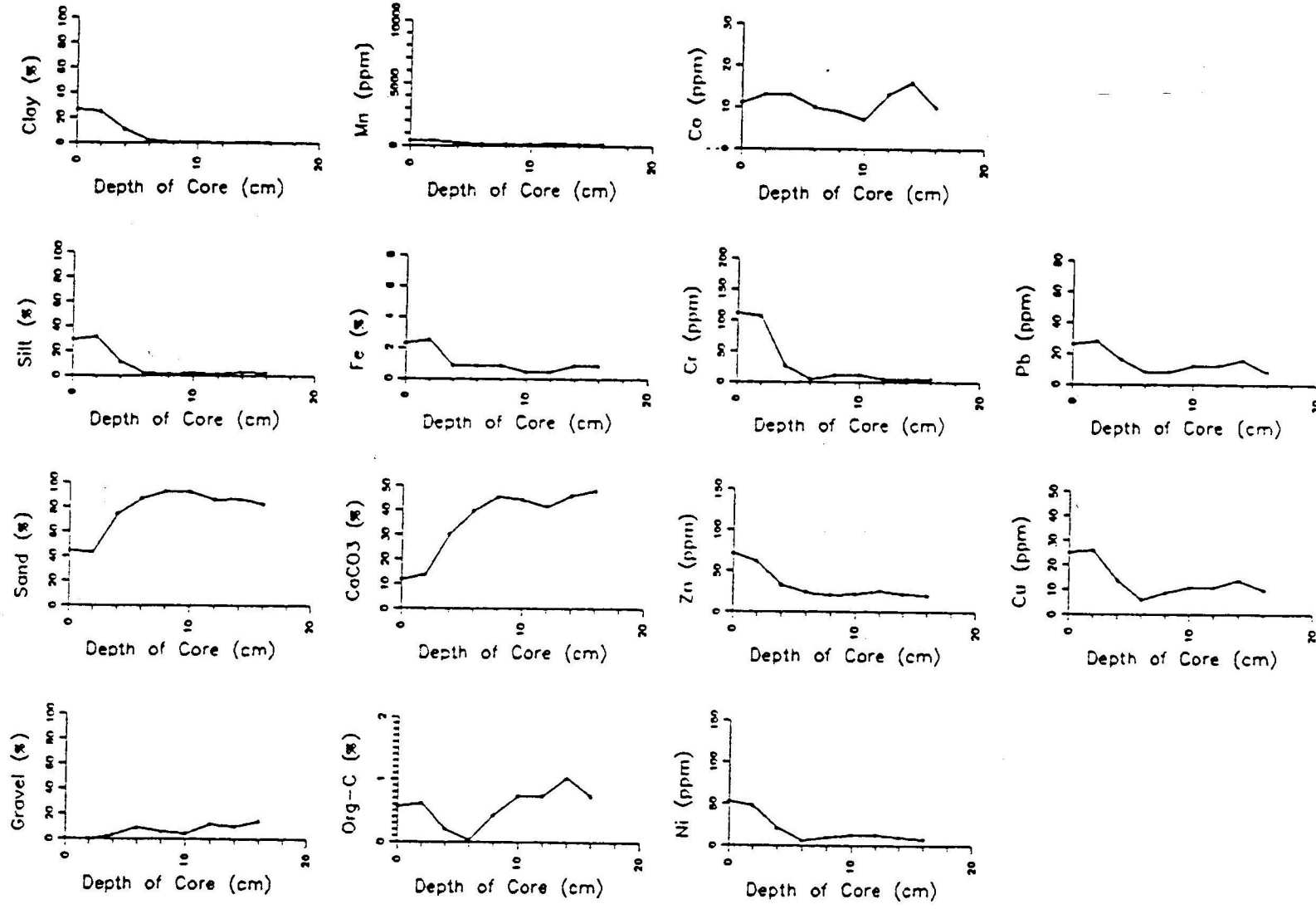
Fig. 3. Vertical distribution of some geochemical parameters in box-core (BC-1) from the Black Sea approach of the Sea of Marmara (northern exit of the Strait of Bosphorus).

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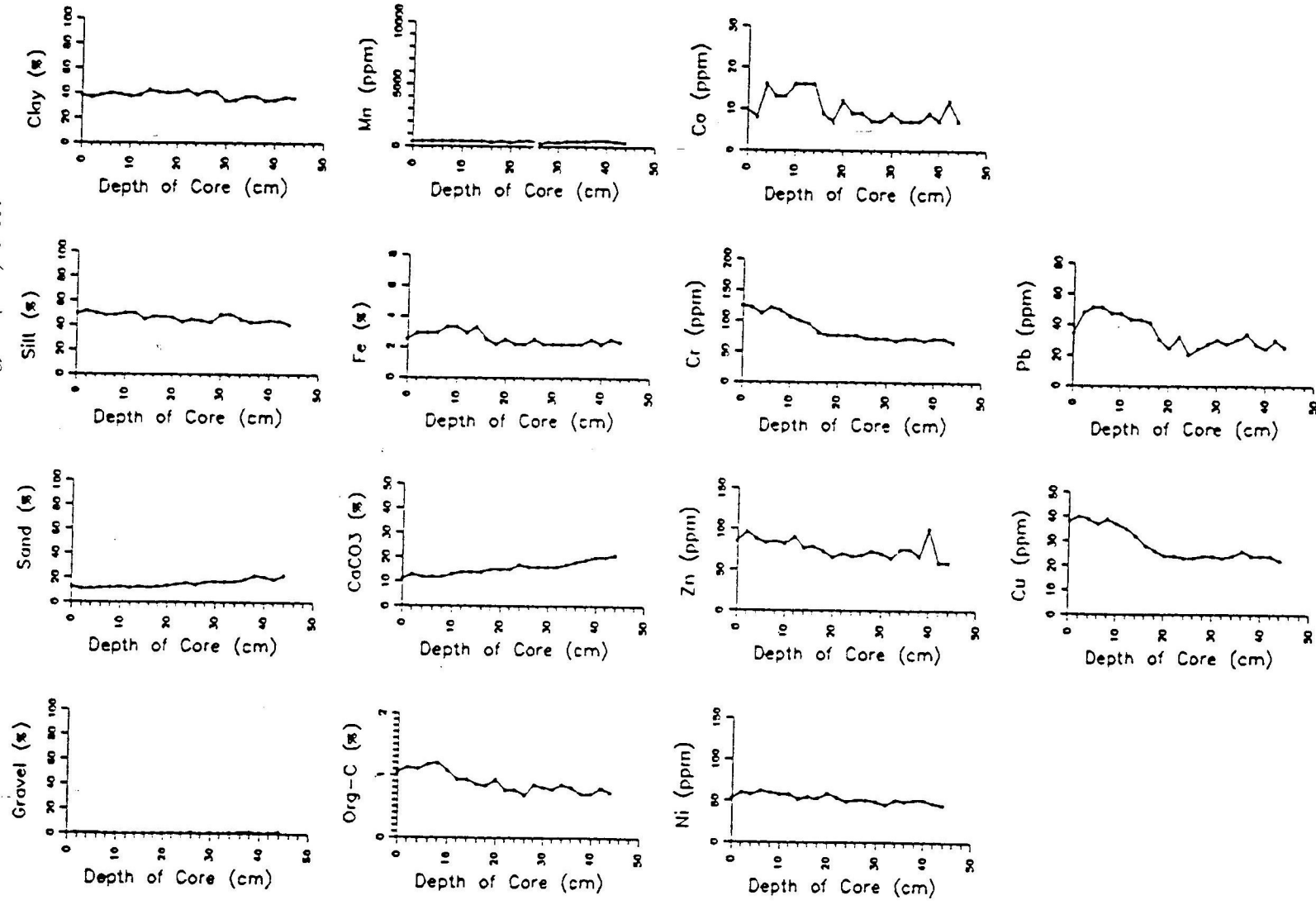
Fig. 4. Vertical distribution of some geochemical parameters in box-core (BC-2) from the northeastern Marmara shelf (southern exit of the Strait of Bosphorus or Istanbul Boğazi).
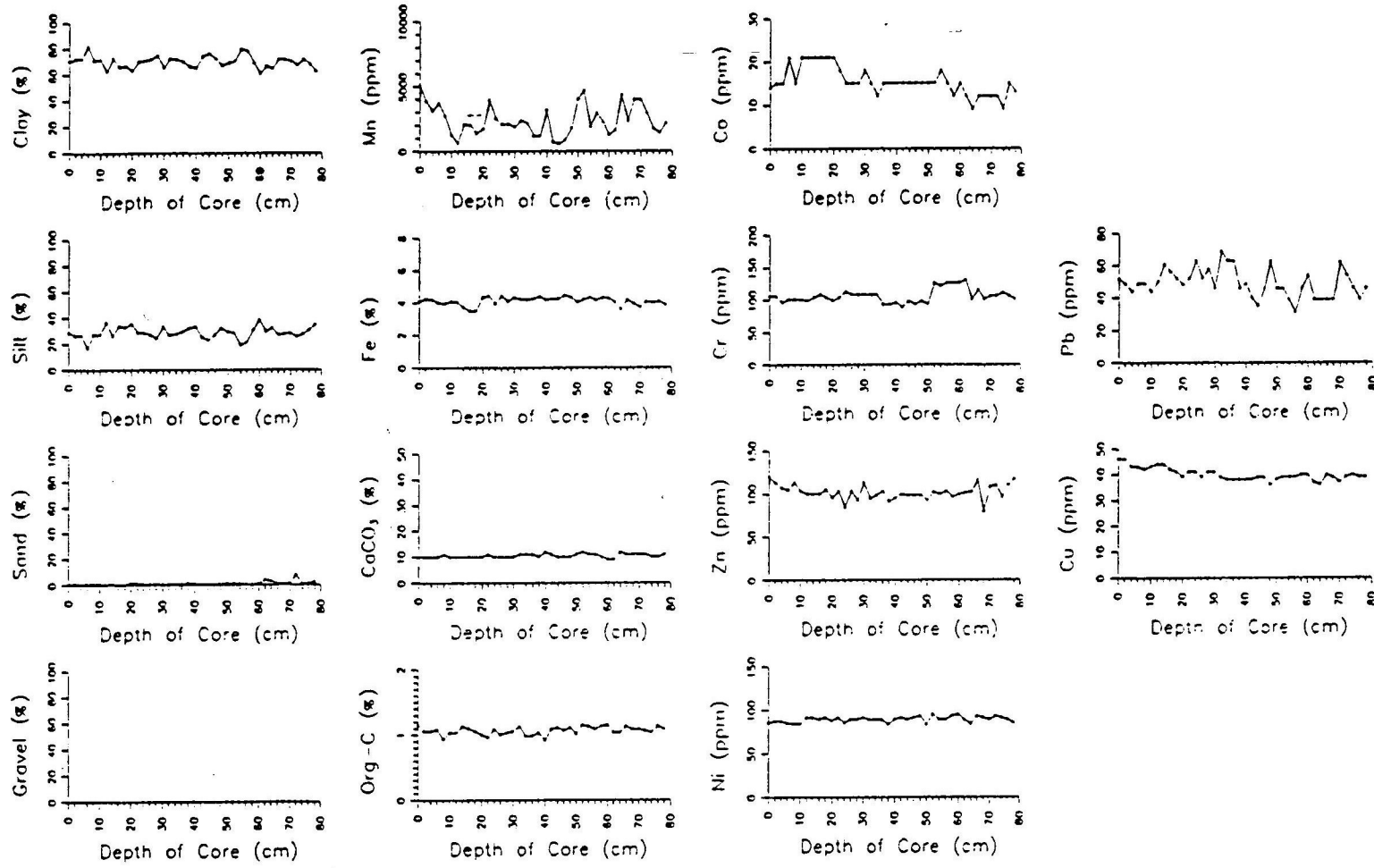
Fig. 5. Vertical distribution of some geochemical parameters in boomerang core (M-3) from the eastern Marmara Basin (İstanbul Basin).

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Fig. 6. Vertical distribution of some geochemical parameters in box-core (BC-3) from the Central Marmara Basin.

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Fig. 7. Vertical distribution of some geochemical parameters in box-core (BC-4) from the western Marmara Basin (Tekirdağ Basin).

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Fig. 8. Vertical distribution of some geochemical parameters in box-core (BC-5) from the southwestern Marmara shelf.

Fig. 9. Vertical distribution of some geochemical parameters in box-core (BC-6) from the Aegean Sea approach of the Sea of Marmara (southwestern exit of the Strait of Dardanelles or Çanakkale Boğazi).
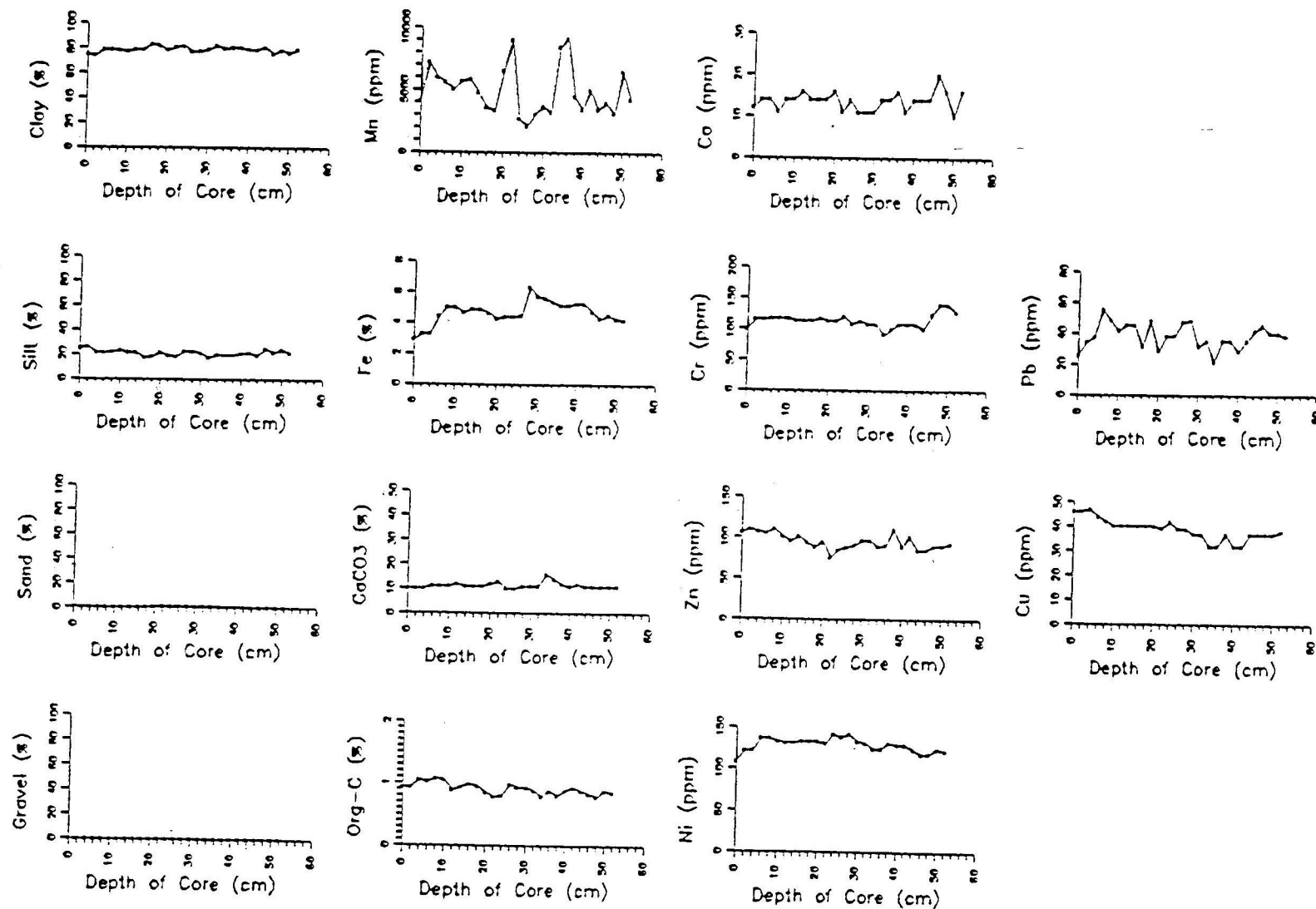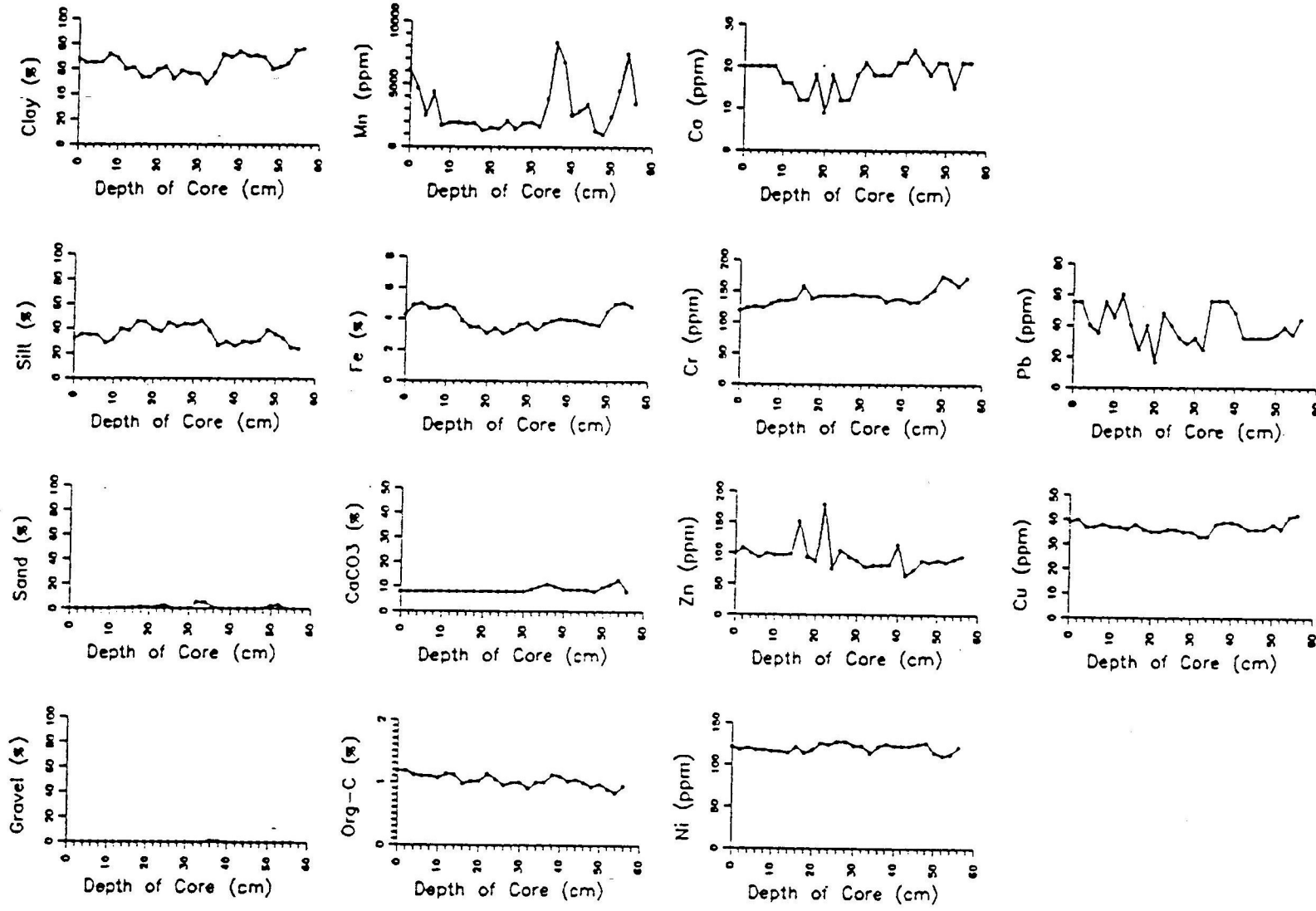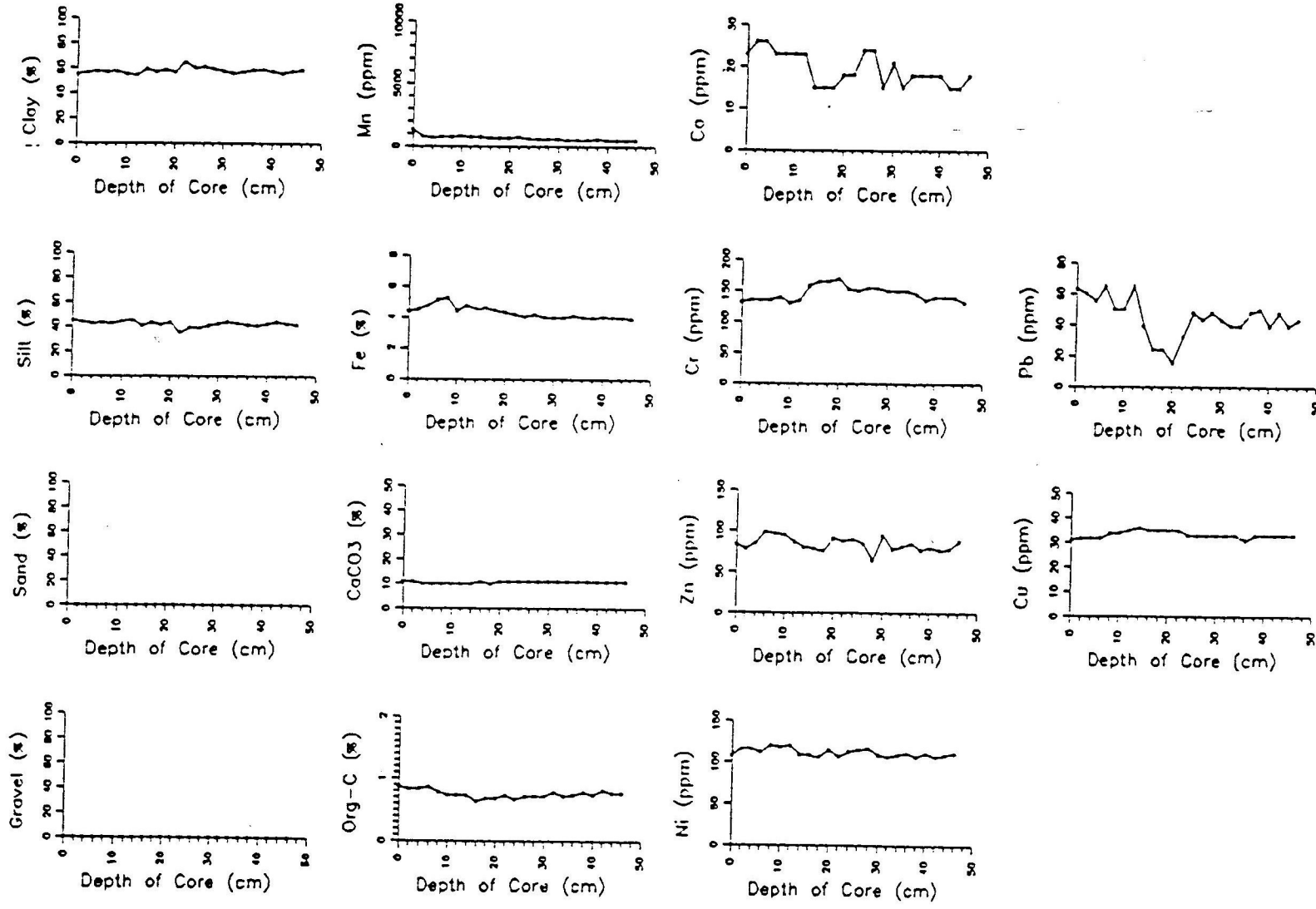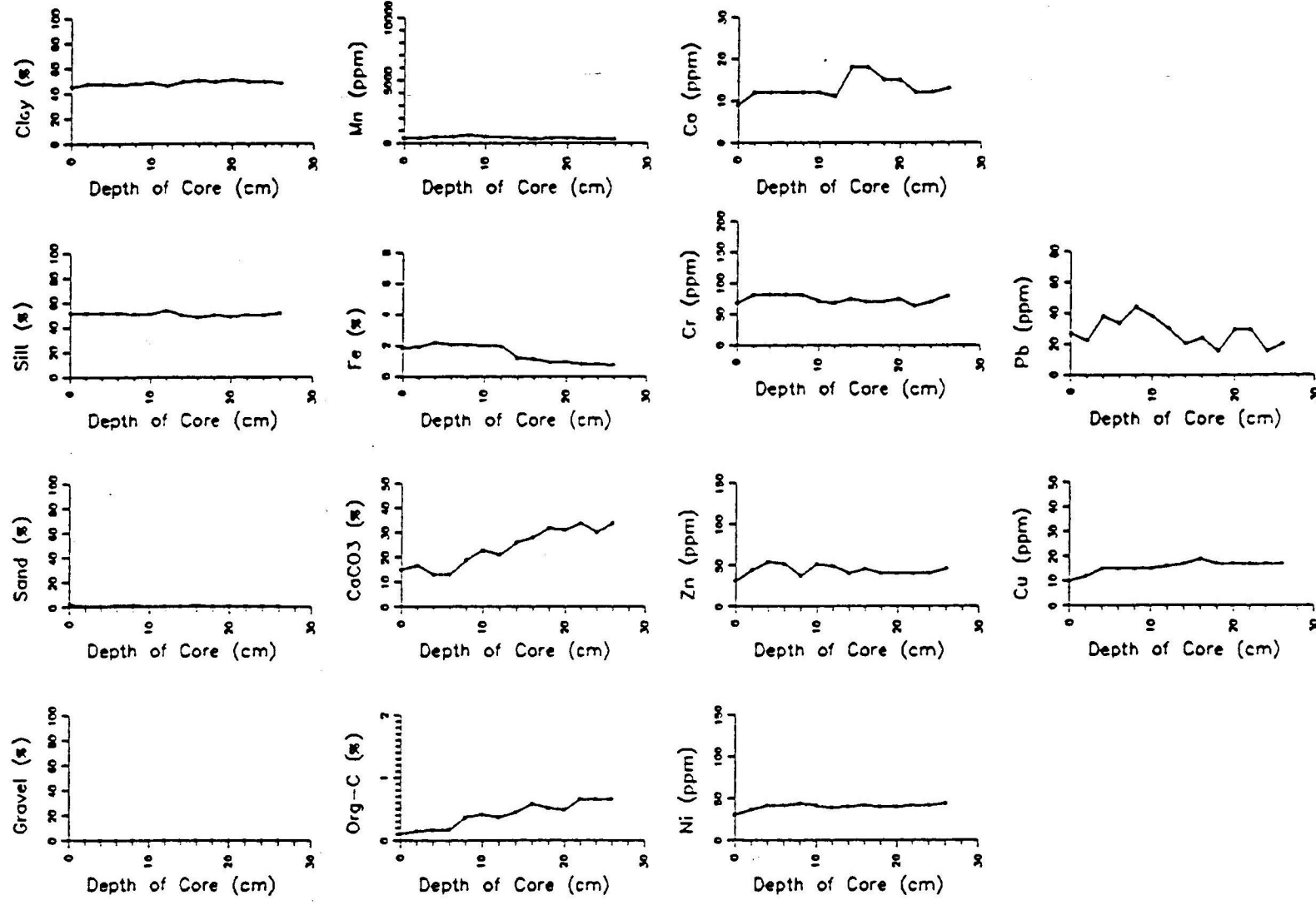
Table 1
Correlation coefficients among the textural and chemical parameters in shallow- and deep-water sediments from the Sea of Marmara

(a) Shallow-water sediments ($n = 27$)

	Mn	Co	Cr	Ni	Cu	Zn	Pb	Clay	Mud	Org. C	CaCO₃
Fe	0.58	0.83	0.82	0.81	0.19	0.64	0.40	0.77	0.90	0.40	**0.76**
Mn		0.68	0.41	0.74	0.03	0.39	0.32	0.71	0.49	0.13	**0.47**
Co			0.69	0.87	0.08	0.57	0.36	0.89	0.78	0.34	**0.63**
Cr				0.74	0.15	0.53	0.23	0.59	0.82	0.31	**0.74**
Ni					0.11	0.36	0.10	0.82	0.72	0.15	**0.65**
Cu						0.79	0.77	0.05	0.15	0.68	**0.11**
Zn							0.83	0.51	0.63	0.72	**0.55**
Pb								0.33	0.39	0.62	**0.34**
Clay									0.78	0.38	**0.59**
Mud										0.44	**0.79**
Org. C											**0.20**

(b) Deep-water sediments ($n = 96$)

	Mn	Co	Cr	Ni	Cu	Zn	Pb	Clay	Org. C	CaCO₃
Fe	0.26	0.06	0.16	0.28	0.15	0.11	0.03	0.53	0.27	**0.42**
Mn		0.10	0.03	0.38	0.06	0.15	0.11	0.44	0.33	**0.57**
Co			0.25	0.02	0.04	0.12	0.12	0.18	0.17	**0.30**
Cr				0.42	0.26	0.09	0.27	0.42	0.05	**0.47**
Ni					0.28	0.18	0.42	0.16	0.45	**0.05**
Cu						0.24	0.30	0.29	0.21	**0.01**
Zn							0.12	0.09	0.30	**0.13**
Pb								0.07	0.44	**0.03**
Clay									0.33	**0.61**
Org. C										**0.49**

Numbers in bold face indicate negative values.

the Sea of Marmara showed a wide range of values (Figs. 10 and 11; Table 2). It has been found, in general, that these variations in the metal contents of sediments reflect primarily the variations in sediment texture and carbonate contents. For example, the inverse correlations between the metal and carbonate contents in sediments show that most of the studied heavy metals, with a few exceptions, are diluted by the presence of higher carbonate concentrations; the decrease is particularly strong for Fe and Cr (−0.76 and −0.74, respectively; Table 1), but is also significant for Ni (−0.65), Co (−0.63) and Zn (−0.55). By contrast, the concentrations of the metals studied increase significantly with the clay or mud (clay plus silt) contents so that the relatively highest metal concentrations are concentrated in the fine-grained sediments. Highest r-values are found, among the others, between Fe and mud (0.90; Fig. 12a), between Co and clay (0.89; Fig. 12b), between Cr and mud and between Ni and clay (0.82) contents (Table 1). This suggests that these metals are significantly associated with the clay minerals and/or silt/clay-sized materials. It is generally accepted that the enrichment of the fine, silt/clay fraction (< 0.063 mm) of the sediments by heavy metals (e.g., Förstner and Wittmann, 1979; Farrah et al., 1980; Thorne and Nickless, 1981; Emelyanov and Shimkus, 1986; Cauwet, 1987; Ergin, 1988) is due to the large specific surface area of this fraction and to the strong adsorptive properties of alumino-phyllosilicates (mainly clay minerals and micas, i.e. cation exchange
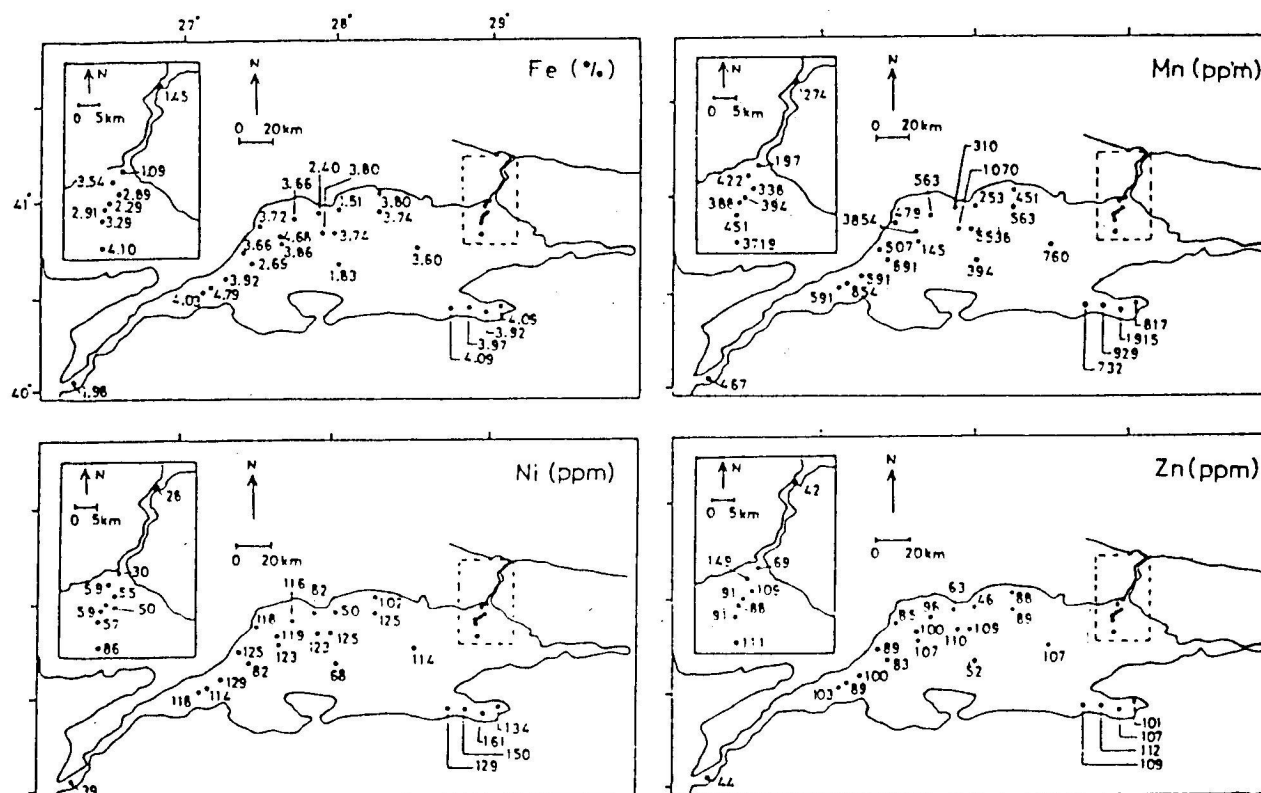
Fig. 10. Distribution of Fe, Mn, Ni and Zn contents in the studied surface sediments from the Sea of Marmara. The *numbers* refer to concentration of elements.

within the crystal lattice of chlorite, smectite, illite), Fe–Mn-oxides/-hydroxides and organic materials (e.g., Calvert, 1976; Förstner et al., 1982; Loring, 1984; Salomons and Förstner, 1984; Jarvis and Higgs, 1987). For example, during the weathering and soil-forming processes, Mg in clay minerals can be substituted by Mn, Co, Ni and Zn.

Looking beyond the textural effects, the significant and positive covariances of organic carbon contents with Zn ($R=0.72$; Fig. 13a; Table 1), Cu ($R=0.68$; Fig. 13b; Table 1) and Pb ($R=0.62$) imply that strong relationships occur between these metals and the organic matter in sediments. Such associations between Zn, Pb and Cu and organic carbon in the marine sediments have often been related to the adsorption and complexation of metals by organic matter of both terrestrial and marine origin (e.g., Martin and Knauer, 1973; Loring, 1978; Salomons and För-

stner, 1984; Loder and Liss, 1985; Wangersky, 1986; Haraldsson and Westerlund, 1991). For instance, Cu and Zn are known for their high affinity for humic substances, which represent a major part of the organic matter in recent sediments (e.g., Calvert et al., 1985; Pruysers et al., 1991). Cu is also associated with the diagenesis of organic matter in sediments during its burial (e.g., Klinkhammer, 1980). The association of these metals (Cu, Zn, Pb) or their sulphides with organic matter can be either direct (i.e. within the organic matrix, or adsorbed) or indirect (e.g., adsorbed on fine-grained sediments associated with higher organic carbon contents) (Haraldsson and Westerlund, 1991). Since organic materials, like sulphide minerals, are reduced constituents of the sediments, it is difficult to distinguish their relative importance in metal association in this study.

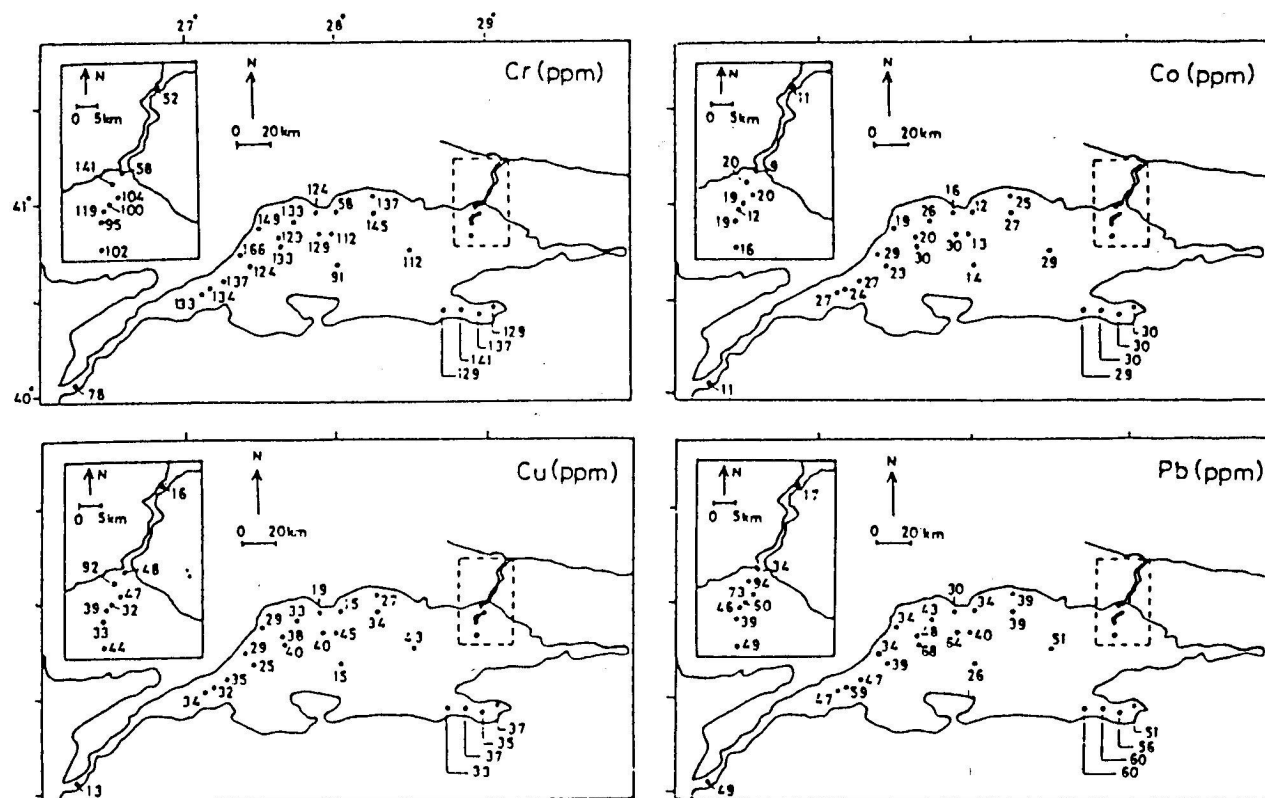The correlation analysis further revealed close

Fig. 11. Distribution of Cr, Cu, Co, and Pb contents in the studied surface sediments from the Sea of Marmara. The *numbers* refer to concentration of elements.

relationships between Fe and Co ($R = 0.83$; Fig. 14a), Fe and Cr ($R = 0.82$), Fe and Ni ($R = 0.81$), Fe and Zn ($R = 0.64$) and Fe and Mn ($R = 0.58$), as well as Mn and Co ($R = 0.68$) and Mn and Ni (0.74; Fig. 14b) concentration pairs (Table 1). These results suggest that in the surface sediments of the Sea of Marmara, Fe- and, to some extent, Mn compounds appear to be among the most effective scavengers of the other studied trace metals. This finding could be consistent with the known ability of Fe–Mn compounds (mainly oxides, hydroxides, carbonates, sulphides) to scavenge other trace metals from solution, before or during the diagenesis (e.g., Chester and Hughes, 1967; Calvert and Price, 1977; Feely et al., 1983; Loring, 1984; Salomons and Förstner, 1984). In particular, Fe- and Mn-oxyhydroxides and -sulphides, together with organic matter, are involved in redox processes associated with the enrichment of a number of trace

metals (e.g., Jarvis and Higgs, 1987; Pruysers et al., 1991). The sulphate reduction with subsequent formation of Fe-sulphides may also serve as an important sink for a number of trace metals in sediments (e.g., Volkov and Fomina, 1974; Luther et al., 1980; Emerson et al., 1983; J.N. Moore et al., 1988; Lewis and Landing, 1992) although this is not further considered in this study. Considering the usually low carbonate sedimentation and relatively oxidizing conditions prevailing in the shallow Marmara waters (on the basis of dissolved oxygen concentrations as previously discussed), we therefore expect the weakly crystalline or/and amorphous oxides/hydroxides of Fe and Mn, maybe with a small contribution of sulphides especially at near-surface layers, are to be the significant associations of most of the trace metals in the studied sediments.

The significant correlation of Mn with Co and

Table 2

Concentrations of the metals (CaCO₃-free data) analysed and total carbonate contents in surface sediments (inclusive top 6 cm of cores) of the Sea of Marmara

Sample No.	Fe	Mn	Ni	Zn	Cr	Co	Cu	Pb	CaCO₃	Fe/Mn	Mn/Fe
15	1.70	307	46	107	90	14	75	53	36	55	0.018
21	4.02	479	67	169	160	22	104	106	12	83	0.012
47	3.24	379	61	122	116	22	52	82	11	85	0.011
29	2.69	463	58	107	117	22	37	70	15	58	0.017
39	3.82	524	66	105	110	22	38	45	14	72	0.013
67	4.36	518	117	101	157	28	31	44	13	84	0.012
69	4.34	654	145	103	168	31	39	45	14	66	0.015
103	4.04	854	128	120	125	32	48	57	11	47	0.021
121	4.39	878	144	108	138	32	39	54	7	50	0.020
118	4.21	2,059	173	115	147	32	37	60	7	20	0.050
115	4.26	998	161	120	151	32	39	64	7	42	0.023
107	4.44	795	140	118	140	31	35	65	8	55	0.018
64	2.35	395	78	71	90	18	23	53	36	59	0.017
77	2.03	437	75	57	101	15	16	28	10	46	0.021
62	2.72	352	93	71	141	18	21	34	12	77	0.013
63	4.22	1,188	136	122	143	33	44	71	10	35	0.028
61	4.06	625	128	108	108	28	36	47	10	65	0.015
57	4.08	526	129	93	163	20	31	37	9	77	0.013
60	4.19	918	133	116	144	32	43	74	8	45	0.022
167	4.11	569	140	100	186	32	32	38	11	72	0.013
169	3.49	767	106	107	161	29	32	50	23	45	0.022
143	4.35	656	143	111	152	30	38	52	10	66	0.015
130	4.47	650	131	114	147	24	37	52	10	68	0.014
BC-1	2.73	461	57	77	124	13	28	31	13	59	0.017
BC-2	3.14	429	64	102	134	13	44	50	12	73	0.013
M-1*	4.05	4,900	87	102	118	24	45	52	16	8.2	0.122
M-4*	4.20	3,766	88	105	121	24	46	53	17	11.1	0.091
M-3	4.63	4,498	95	126	114	16	50	53	10	3.6	0.277
BC-3	3.45	6,355	130	120	120	14	51	35	10	1.5	0.666
BC-4	5.10	4,798	130	110	131	21	41	54	8	10	0.094
BC-5	5.10	1,040	127	92	149	28	36	66	11	49	0.020
BC-6	2.30	490	42	50	89	13	14	34	15	47	0.021

Fe and CaCO₃ contents in % and other metals in ppm. BC-1 to BC-6 indicate samples from box-cores and M-3 from boomerang core.

*Previous data from eastern Marmara Basin (İstanbul Basin, based on data of Ergin and Evans (1988) and Evans et al. (1989).

Ni (Table 1) is in good agreement with the results of, for example, Bonatti et al. (1971), Wallace et al. (1988) and Hem et al. (1989) who found Ni and Co enrichment in the Mn-rich sediment layers due to coprecipitation of these metals with Mn-oxyhydroxides as a result of varying redox conditions. Also, the strong association of Co, Cr, Ni and Zn with Fe (Table 1) is similar to that for the preferential adsorption of these metals onto surfaces of Fe-oxyhydroxides as a result of changing redox fronts in marine sedi-ments (e.g., Hem, 1977; Franklin and Morse, 1980; Balistrieri and Murray, 1986; Wallace et al., 1988).

It thus follows that the clay minerals, and fine-grained Fe- and Mn-oxides/-hydroxides and organic matter along with diagenetic modifications appear to control the abundance and distribution of most of the trace metals in surficial shallow-water sediments from the Sea of Marmara.
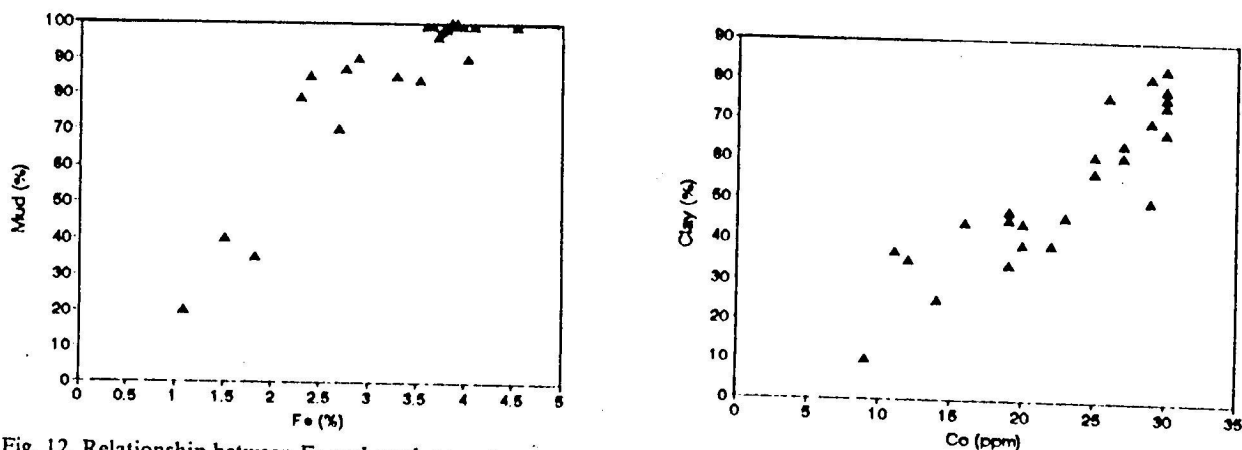
On the other hand, positive and significant

Fig. 12. Relationship between Fe and mud, as well as between Co and clay contents in the surface (shallow-water) Marmara sediments.
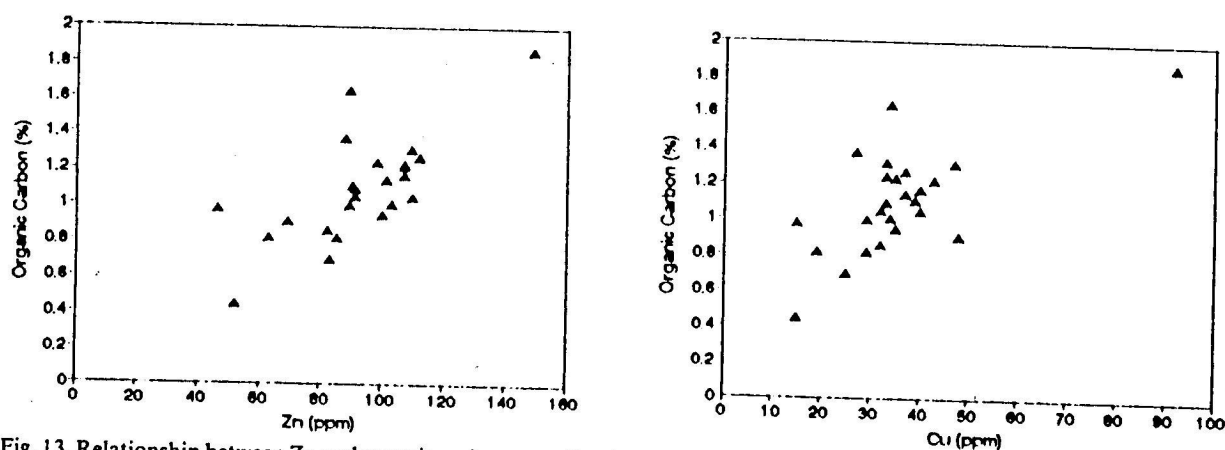

Fig. 13. Relationship between Zn and organic carbon, as well as between Cu and organic carbon contents in the surface (shallow-water) Marmara sediments.

correlations exist between Ni and Co ($R=0.87$) and Ni and Cr ($R=0.74$), as well as between Zn and Pb ($R=0.83$) and Zn and Cu ($R=0.79$) (Table 1), which would suggest either similar or common sources or/and similar enrichment mechanisms for these metal concentrations.

To compare the levels of the bulk metal concentrations measured in the sediments of this study with those from various other sources and regions, we minimised the dilution effect of carbonates by normalising (recalculating) the metal contents on a carbonate-free basis, CFB (Table 2), because the carbonate materials present in the sediment samples act as diluents for the metal contents (Table 1). Thus, Fe concentrations vary

between 1.09% and 4.79% (1.70–5.10% on CFB). Mn varies between 197 and 5538 ppm (307–6355 ppm on CFB); Co concentrations lie between 9 and 30 ppm (13–33 ppm on CFB); Ni between 28 and 161 ppm (42–173 ppm on CFB); Cr between 52 and 166 ppm (89–186 ppm on CFB); Zn between 42 and 149 ppm (50–169 ppm on CFB); Cu between 13 and 92 ppm (16–104 ppm on CFB); and Pb between 17 and 94 ppm (28–106 ppm on CFB). When compared with average crustal and sedimentary rocks (Table 3), which are taken to represent the probable source rocks in the region, the concentrations of the metals obtained in the surface sediments of this study appear to be, with some exceptions,
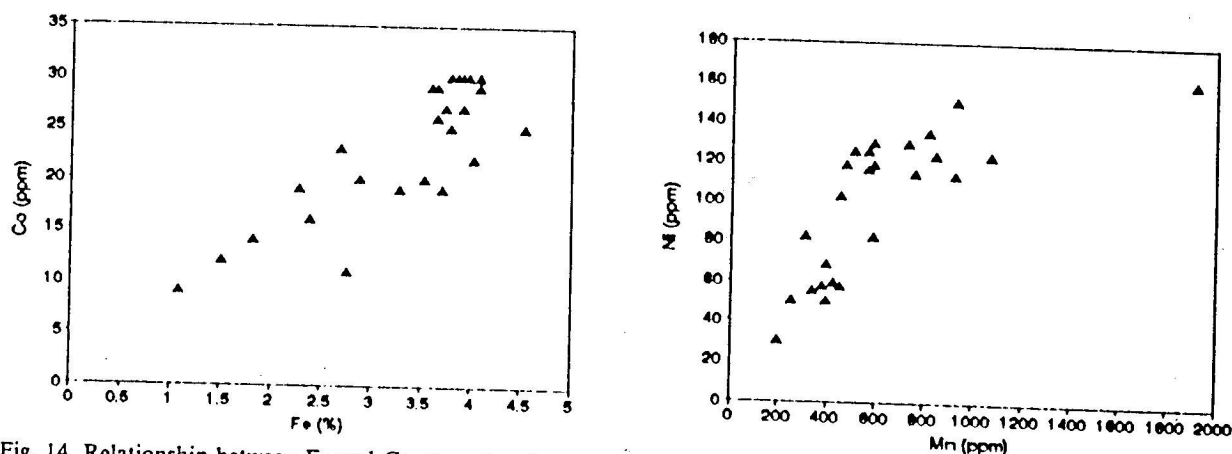
Fig. 14. Relationship between Fe and Co, as well as between Mn and Ni contents in the surface (shallow-water) Marmara sediments.

predominantly at or near the natural levels. This further indicates that the concentration values of these metals in the surface Marmara sediments must have been derived, largely, from the continental weathering and hence reflect their overwhelming terrigenous origin.

Zn, Pb, Cr and Ni are found to be noticeably high in the surface Marmara sediments compared to their possible abundances in average crustal and sedimentary rocks (Table 3). As also known from other shelf regions around Turkey (Shaw and Bush, 1978; Bodur and Ergin, 1988; Yücesoy and Ergin, 1992; Ergin et al., 1993b), particular geological sources such as weathering products from basic and ultrabasic rocks and some related economic mineral deposits which are widely distributed in the drainage basins of the coastal hinterland can provide significant amounts of Cr and Ni to the sediments. Thus, in the eastern Mediterranean Sea, especially off the Turkish coasts, the concentrations of Cr and Ni are usually found to be relatively high and are related to the input from weathering ultrabasic rocks (Emelyanov and Shimkus, 1986). Comparison of the metal data obtained in this study with reported levels from the adjoining Mediterranean, Aegean and Black seas (Table 3) also reveals a nearly good agreement among the values whereby the variations are believed to reflect differences rather in mineralogy and provenance.

Figs. 10 and 11 show that the relatively high

concentrations of Zn (149 ppm), Cu (92 ppm) and Pb (94 ppm) are found in surface sediments of station 21, from the northeastern Sea of Marmara, a sampling site that is situated very close to the highly polluted Golden Horn estuary (Ergin et al., 1991b). In this northeastern part of the Sea of Marmara, a pollution effect by increased input of Zn, Pb and Cu (due to increased metallurgical activities) was also reported in surficial core sediments (Evans et al., 1989). It is therefore expected that the enrichments of Zn, Cu and Pb in the surface sediments from the northeastern exit of the Sea of Marmara are, in part, most likely due to anthropogenic input.

More importantly, however, the only marked exception is the distribution of Mn within the Marmara Basin where unusually high Mn concentrations (4498–6355 ppm on CFB) are found in the top 6 cm of deep-sea cores whilst surface sediments from the shallower waters of this basin exhibited much lower Mn concentrations (307–2059 ppm on CFB) (Fig. 11; Table 2). Moreover, these high concentrations of Mn in surface sediments are not at or near "normal" levels in relation to their initial contributions inherited from the average crustal rocks in general and sedimentary rocks in particular (Table 3). This is further indicated by Fe/Mn ratios in sediment samples which are found to be relatively high in shallow waters (20–85; Table 3), in contrast to the lower values obtained from the deep waters

(1–11; Table 3). Regional comparisons (Table 3) also indicate that there are significant differences between the Mn concentrations in the surface sediments of the Marmara Trough (4498–6355 ppm) and the adjacent Mediterranean Sea (100–3500; avg. 1100 ppm; Emelyanov and Shimkus, 1986) and these are nearly the same as those found in clays and shales on average. It is, therefore, concluded that Mn in the deep Marmara waters, to a significant extent, originates from other than a lithogenous origin.

It is known that one of the characteristic features of deep-sea sediments is that they contain enhanced concentrations of Mn (e.g., Chester and Aston, 1976) as results of relatively low bulk sedimentation rates and limited supply by terrigenous input (e.g., Cronan, 1980), hydrothermal and volcanic influences (e.g., Bender et al., 1977; Marchig et al., 1987; Varnavas and Cronan, 1991), diagenetic and postdepositional processes (e.g., Lynn and Bonatti, 1965; Sevast'yanov and Volkov, 1967; Calvert and Price, 1970; Pruysers et al., 1991), biogenic and organic enrichments (e.g., Riley et al., 1965) and hydrogenic precipitation from normal seawater (e.g., Varentsov et al., 1991). This would therefore explain enrichments of Mn along with some other trace metals in deep-sea relative to nearshore sediments (Table 3). The behaviour of Mn to tend to increase in abundance in the deepwater sediments along the Marmara Trough relative to those of shallow waters (Fig. 10) will be discussed in the following section, together with the Mn distribution in core sediments.

Since the surficial shallow-water sediments from the northeastern (307–524 ppm Mn on CFB; Fig. 10; Table 2) and southwestern exits (490–1040 ppm Mn on CFB; Fig. 10; Table 2) of the Sea of Marmara displayed Mn contents, on average, at normal levels, it, therefore, seems that there is no reasonable evidence at this stage to support any significant Mn input from the adjacent Aegean Sea and Black Sea waters, respectively.

4.3. Heavy-metal distribution in core sediments

Total heavy-metal concentrations measured in the bulk core sediments from the Sea of Mar-

mara along with other sedimentary parameters are illustrated in Figs. 3–9.

In core BC-1 from the northeastern (Black Sea exit) of the Marmara Basin, sediments reflect marked changes in their texture and thus mineralogy and heavy-metal distribution (Fig. 3). The upper 6 cm of the core show relatively high silt and clay proportions as associated with the increasing concentrations of Fe, Ni, Zn, Cr, Cu and Pb whereas the sediments below this depth become coarser grained, and thus show decreasing metal concentrations at or near their background levels. This grain size effect on metal distribution throughout core BC-1 is seemingly less significant for Mn and Co which can probably be explained by other effects (i.e. diagenesis) rather than by textural variations. The downward increasing proportions of sand and gravel are associated with increasing contents of biogenic carbonates in the samples. Mn concentrations (461 ppm on CFB) are found to be too low to indicate any significant input from the shallow Black Sea waters which contain dominant quantities of the finely dispersed Mn particles as a result of the changing redox gradients in the water column (Kempe et al., 1991; Lewis and Landing, 1992).

In core BC-2, from the northeastern shelf of Marmara Basin, the presence of the slight textural variations does not appear to play a significant role in determining the distribution of heavy metals throughout the core (Fig. 4). Mn and Ni contents remain rather uniform whereas Fe, Co, Zn, Cr, Cu and Pb display slight enrichment in the upper 15–20 cm of core, which cannot solely be explained by the changes in sediment texture (Fig. 4). It is most likely that a combination of diagenetic and anthropogenic effects could be responsible for the upcore enrichment of these metals. The latter contribution is based on that fact that the sampling site of core BC-2 is situated close to the highly-polluted Golden Horn estuary in the north (Ergin et al., 1991b). Whether the slightly upcore-increasing organic carbon contents associated with the decreasing carbonate contents in sediments may suggest contributions to the enrichment of these metals cannot be confirmed at this stage. It

Table 3

Heavy-metal concentrations in recent sediments of the Sea of Marmara (this study) in comparison with those from various others sources and materials

	Fe (wt%)	Mn (ppm)	Ni (ppm)	Zn (ppm)	Cr (ppm)	Co (ppm)	Cu (ppm)	Pb (ppm)	Fe/Mn	Mn/Fe
This study:										
1	0.42–6.31	152–9,127	6–161	6–180	5–174	7–30	6–92	8–94		
2	1.70–5.10	307–2,059	42–173	50–169	89–186	13–33	14–104	31–106	20.0–85.0	<0.1
3	3.45–5.10	4,498–6,355	95–130	110–126	114–131	14–21	41–51	35–54	1.0–11.0	0.1–0.6
Mediterranean area:										
4	4.00–4.30	1,250–5,500	80–110	79–136	105–131	22–27	37–55	28–59		
5	1.40–3.97	112–678	34–98	45–114	6–81	43–105	13–49	23–52		
6	3.24–6.92	271–852	35–228	7–129	12–304	21–32	24–61	7–33		
7	0.23–4.90	112–1,064	11–202	24–138	13–224	<1–20	15–82	12–66	20.5–78.1	<0.1
8	0.59–5.74	103–2,625	11–406	19–162	9–312	2–41	3–77	n.a		
9	0.91–1.83	167–369	14–39	28–98	30–64	n.a	11–17	15–120		
10	2.92–9.91	690–4,457	94–579	54–213	219–1,039	n.a.	14–122	n.a		
11	1.10–4.80	236–698	155–753	25–466	18–77	11–40	8–50	7–17		
12	1.60–3.97	600–2,100	26–71	40–107	35–96	n.a	30–56	n.a	7.6–52.8	<0.1
Diagenetic sediments:										
13	5.11	3,500	40	n.a.	46	14	30	n.a	14.6	<0.1
14	4.73	2,200	70	125	n.a.	n.a.	22	30	21.5	<0.1
Hydrothermal/hydrogenetic sediments:										
15	4.02	12,930	900	n.a.	73	190	400	<50	3.1	0.3
Hydrothermal sediments:										
16	6.76–7.75	3,100–16,400	25–94	79–143	n.a.	34–40	167–275	n.a.	3.8–25.0	<0.1–0.2
17	7.76–20.00	2,000–40,300	55–360	116–860	36–190	92–490	206–780	30–180	2.7–24.2	<0.1–0.3
18	0.15–4.13	283,200–462,400	1–177	22–194	n.a.	8–55	22–358	1–23	<0.1	9.5–265
19	4.97–6.52	2,520–91,050	108–140	105–157	106–129	44–59	119–167	34–498	0.5–24.4	<0.1–2
20	5.15	8,400	285	452	47	23	212	n.a.	6.1	0.1
21	20.29–33.92	379–3,850	30–70	800–3,400	n.a.	n.a.	3,200–14,500	132	229	<0.1
22	5.88–10.52	8,277–14,976	198–275	170–950	n.a.	n.a.	200–470	42–49	6.1	0.1
23	5.60–13.73	16,600–44,900	163–533	99–321	n.a.	26–149	325–728	71–212	3.0–4.6	0.2–0.3
Hydrothermal/volcanogenic sediments:										
24	5.00–9.90	5,600–11,400	161–324	125–404	n.a.	98–258	193–522	63–109	4.0–17.8	<0.1–0.1
25	4.37–17.54	2,300–6,900	15–38	n.a.	19–45	13–29	35–70	n.a.	16.7	<0.1
26	4.00–10.00	1,000–10,000	6–60	70–20,000	20–80	10–80	6–92	8–94	0.8–100	<0.1–0.8
27	14.30–28.00	92,000–224,000	10–15	n.a.	<5	15–30	160–420	n.a.	18.5–781	
28	2.54–18.28	234–1,457	6–198	39–134	11–122	n.a.	6–111	17–120	2.9–57.4	
29	2.09–11.79	670–17,436	5–441	10–9,062	5–583	9–128	16–230	9–1867		
Average deep-sea clays:										
30	6.50	6,700	225	165	90	74	250	80	9.7	0.1

Table 3 (continued)

	Fe (wt%)	Mn (ppm)	Ni (ppm)	Zn (ppm)	Cr (ppm)	Co (ppm)	Cu (ppm)	Pb (ppm)	Fe/Mn	Mn/Fe
Average near-shore muds:										
31	6.99	850	55	95	100	13	48	20	82	<0.1
Polluted sediments:										
32	2.60–3.80	333–565	98–167	450–8,750	242–485	17–31	333–3,900	124–702	56.0–86.0	<0.1
33	3.50–5.50	650–2,600	90–440	80–2,400	80–280	15–35	35–70	45–310		
34	0.28–2.86	n.a.	13–51	2–450	4–120	5–14	2–45	10–68		
35	3.83–4.12	468–700	31–42	125–285	31–49	8–10	28–44	62–107	56.0–83.7	<0.1
Average rocks:										
36	5.00	950	75	70	100	25	55	13	52.6	<0.1
37	4.07	850	68	95	90	19	45	20	47.8	<0.1
38	0.98	50	2	16	35	<1	10	7		
39	0.38	1,100	20	20	11	<1	4	9		

1 = bulk material, all samples; *2* = shallow-water sediments, top 0–5 cm, carbonate-free data; *3* = deep-water sediments, top 0–6 cm, carbonate-free data; *4* = deep-water sediments, E. Marmara Basin, bulk material (Evans et al., 1989); *5* = shallow-water sediments, İzmit Bay, E. Marmara Sea, bulk material, top 0–5 cm (Ergin et al., 1991b); *6* = mostly anoxic deep-sea sediments, top 0–10 cm, bulk material, entire Black Sea (Hirst, 1974); *7* = shelf/slope sediments, top 0–5 cm, bulk material, S. Black Sea (Yücesoy and Ergin, 1992); *8* = shelf/slope sediments, bulk material, E. Aegean Sea (Ergin et al., 1993b); *9* = shelf/slope sediments, bulk material, S. Aegean Sea (Smith and Cronan, 1975); *10* = shallow- and deep-water sediments, carbonate-free data, Cilicia Basin, NE Mediterranean (Shaw and Bush, 1978); *11* = nearshore sediments, bulk material, Mersin Bay, NE Mediterranean (Bodur and Ergin, 1988); *12* = shallow- and deep-water sediments, bulk material, entire Mediterranean Sea (Emelyanov and Shimkus, 1986); *13* = associated with ferromanganese deposits, bulk material, on average, Black Sea (Sevast'yanov and Volkov, 1967); *14* = associated with ferromanganese deposits, bulk material, on average, Loch Fyne, Scotland, U.K. (Calvert and Price, 1970); *15* = pale yellowish-brown mud, Krylov Seamount, E. Atlantic (Varentsov et al., 1991); *16* = carbonate-free data, Lau Basin, SW Pacific (Hodkinson and Cronan, 1991); *17* = carbonate-free data, North Fiji Basin, SW Pacific (McMurtry et al., 1991); *18* = low-temperature hydrothermal, containing submetallic layers, Kaikata Seamount, Ogasawara Arc, Pacific (Usui et al., 1989); *19* = top 0–21 cm, carbonate-free data, Eratosthenes Seamount, E. Mediterranean (Varnavas et al., 1988); *20* = carbonate-free data, average values from 0.4–32-m depths, Galápagos mounds, Pacific (Migdisov et al., 1983); *21* = mud, carbonate-free data, near the vent, Galápagos Rift Spreading Center, Pacific (Marchig et al., 1987); *22* = mud, carbonate-free data, some distance from the vent, Galápagos Rift Spreading Center, Pacific (Marchig et al., 1987); *23* = low-temperature hydrothermal, top 0–5 cm, Wilkes Fracture, E. Pacific (Varnavas, 1988); *24* = sandy–silty mud, average values from 5 cores, top 20 cm, Aitutaki Passage, SW Pacific (Forg, 1980); *25* = mud, carbonate-free data, Santorin, E. Mediterranean (Butuzova, 1969); *26* = high-temperature hydrothermal, top 0–30 cm, ranges from 12 cores, Red Sea (Hendricks et al., 1969); *27* = Stromboli, Aegean Sea (Bonatti et al., 1972); *28* = Hellenic Volcanic Arc, S. Aegean Sea (Varnavas and Cronan, 1991); *29* = carbonate-free data, Hellenic Arc Trench, S. Aegean Sea (Varnavas, 1989); *30* = Turekian and Wedepohl (1961); *31* = Wedepohl (1960); *32* = bulk material, top 0–10 cm, Golden Horn Estuary, NE Sea of Marmara (Ergin et al., 1991b); *33* = Thermaikos Gulf, Greece (Voutsinou-Taliadouri, 1982); *34* = Gulf of Venice, Italy (Donazzolo et al., 1981); *35* = mud, bulk material, Eckernförder Bay, W. Baltic Sea (Ergin, 1982, 1990); *36* = crustal average (Mason and Moore, 1982); *37* = shales (Turekian and Wedepohl, 1961); *38* = sandstones (Turekian and Wedepohl, 1961); *39* = carbonates (Turekian and Wedepohl, 1961).

should be mentioned also here, low Mn concentrations throughout the core indicate no significant input of Mn from the shallow Black Sea waters.

In cores M-3, BC-3 and BC-4, from the eastern, central and western deep basins of the Marmara Trough, respectively, the pattern of distribution and abundances of Fe, Ni, Cr, Co, Cu and Pb most closely resembles the heavy-metal composition of the shallow-water sediments. For example, the concentrations of these metals were almost in the same range as in both shallow-water and deep-water sediments of the Marmara Basin (Tables 2 and 3; Figs. 5–7, 10 and 11). When compared with the average crustal rocks in general and sedimentary rocks in particular (Table

3), it is apparent that the concentrations of Fe, Ni, Cr, Co, Cu and Pb contained in the deep-sea sediments of the Marmara Trough can largely be accounted for in terms of contributions from products of continental weathering in the region.

Unlike shallow-water sediments, the deep-water sediments of the Marmara Trough generally showed poor correlations between metal contents and textural characteristics of sediments (Table 1). Significant and positive correlation was observed only between clay and Fe contents ($R=0.53$; Fig. 15a) and, to a lesser degree, between clay and Mn contents ($R=0.44$; Fig. 15b). This indicates that the concentrations of Fe and Mn should be expected to occur mainly in the finest, clay-sized grain fractions. Otherwise, the correlations between metals and clay contents in the sediments were insignificant ($R<0.29$; Table 1) although most of the metals studied must be transported to the deeper Marmara waters from the continental weathering in the region, particularly in association with fine-grained solids (i.e. clay minerals, feldspars, discrete particles of hydrous oxides) such as observed in many other deep-sea regions (e.g., Chester and Aston, 1976). For example, in the Atlantic deep-sea sediments, only ~30% of Mn in the sediments was held in the lattice positions within continentally-derived minerals and the remainder of it was present as discrete hydrous

manganese or ferro-manganese oxides (Chester and Messia-Hanna, 1970).

Obviously, silt contents have a dilution effect on metal concentrations, particularly for Fe and Mn (Fig. 16a and b) probably because of the less abundances of clay minerals, oxyhydroxides and finest organic complexes in this fraction. In addition, there was no significant relationship between organic carbon and metal contents in the sediments (Table 1). All this may suggest that the primary composition is overprinted by a wide variety of metal associations or partitions prevailed before or/and during the burial of sediments.

With its exceptionally high concentrations along the Marmara Trough, Mn differs greatly from that observed in the surrounding shallower waters (Fig. 10). This is also evident from the Fe/Mn ratios in the cores, being considerably low in the deep waters (4–74; avg. 17 in cores M-3, BC-3, BC-4) and high in the shallow waters (21–87; avg. 53 in cores BC-1, BC-2, BC-5, BC-6). Similar low Fe/Mn ratios (7–32; recalculated from data by Ergin and Evans, 1988) are obtained in the two sediment cores previously recovered in the deep eastern Marmara Basin. It is also interesting to note that the other metals studied did not follow the same trend of enrichment (Figs. 10 and 11). This suggests enrichment of Mn within the deep basins of the Marmara Trough in which other metals appear to
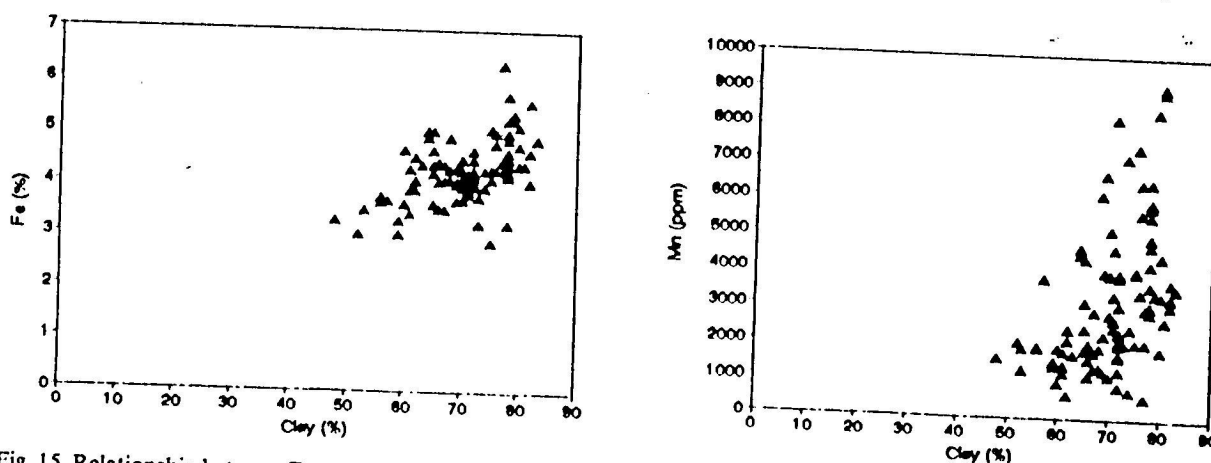

Fig. 15. Relationship between Fe and clay, as well as between Mn and clay contents in core (deep-water) sediments from the Sea of Marmara.
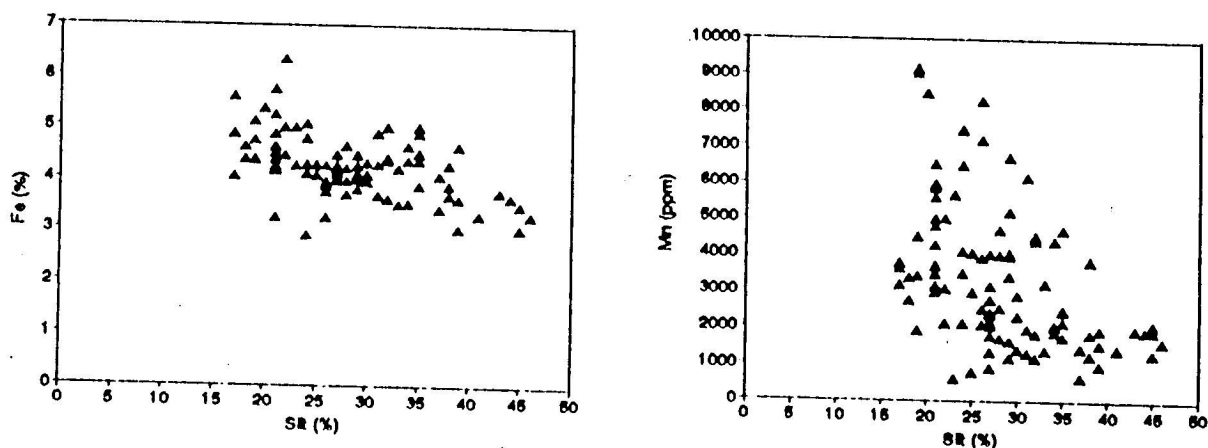
Fig. 16. Relationship between Fe and silt, as well as between Mn and silt contents in core (deep-water) sediments from the Sea of Marmara.

vary not significantly with Mn. For instance, compared with shallow-water sediments (R for Fe–Mn = 0.58; for Mn–Co = 0.68; and for Mn–Ni = 0.74; Table 1), deep-water sediments displayed rather poorly correlations between Fe and Mn (R = 0.26; Fig. 17a), Mn and Co (R = 0.10), and Mn and Ni contents (R = 0.38; Fig. 17b; Table 1).

As previously mentioned, elevated Mn concentrations in the deep-sea sediments have been commonly interpreted in terms of slow and directly precipitation from normal seawater (hydrogenetic), derivation from the underlying sediment as a consequence of postdepositional

remobilization (diagenetic), rapid and directly precipitation from the hydrothermal solutions and submarine weathering of volcanics, and biological processes (e.g., Bonatti et al., 1971; Murray and Brewer, 1977; Marchig et al., 1987; Pruysers et al., 1991; Varentsov et al., 1991).

On the basis of insignificant correlations of Mn with some other metals (i.e. Cu, Ni, Co), a hydrogenetic origin of Mn enrichment in the Marmara Trough sediments is to be excluded. Studies have demonstrated that hydrogenetic Mn deposits are usually associated with high concentrations of Cu, Ni and Co (Boström et al., 1972; Cronan et al., 1991; Varentsov et al., 1991),
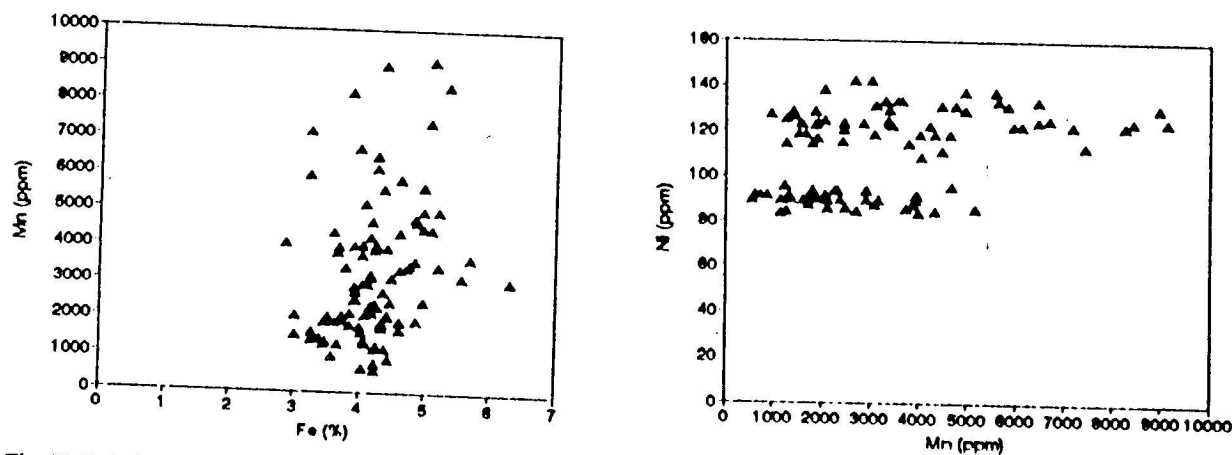

Fig. 17. Relationship between Fe and Mn, as well as between Mn and Ni contents in core (deep-water) sediments from the Sea of Marmara.

which is seemingly not comparable with the results of this study. Also, due to low organic carbon (avg. 1%) and biogenic carbonate contents (avg. 10%) present in the sediments, a biogenic Mn enrichment can also be ruled out in the Marmara Trough.

On the other hand, it was observed during the recovery of box-core samples in the Marmara Trough that the fine-grained top 2–5-cm core sections were characterized by yellowish-brown to rust-colored sediments, suggesting relatively oxidizing zones. Below this interface, sediments are characterized by dark greenish-gray colors, reflecting relatively reducing conditions. As shown by Lyle (1983), such color transition from reddish-yellowish brown to greenish-gray in marine sediments marks the depth at which the Fe(III) reduced to Fe(II) due to oxidation or reduction of Fe present in the smectite interlayers. Moreover, the upper 15–20-cm core sections often show elevated Mn concentrations compared to lower core sections, with exceptions of some fluctuations (Figs. 5–7). In addition, in the eastern Marmara Basin, close to the box-coring site of M-3, sedimentary pyrites are found to occur mostly in form of infillings and coatings with biogenic particles and showed a general tendency to increase in abundances with core depth (Ergin, 1988). This, together with the higher Mn concentrations at the surface layers within the sediment column in the eastern Marmara Basin, was mainly attributed to the effects of early diagenesis (Ergin, 1988). Such enrichments of Mn due to diagenesis (0.49% MnO in oxidizing and 0.05% MnO in the underlying reducing sediment column) were found in recent sediments from the northern Black Sea (Sevast'yanov and Volkov, 1967). Significant Mn enrichments in the surface sediment layers of diagenetic origin are also known from many other marine regions (e.g., Bonatti et al., 1971; Colley et al., 1984; Thomson et al., 1984; Ridgway and Price, 1987). Therefore, the results achieved in this study would compare well with the early-diagenetic or postdepositional Mn enrichment in the upper sections of cores M-3, BC-3 and BC-4, most probably as a result of the changing redox conditions within the sediment column, and thus reflecting

the effects of metal remobilization and precipitation processes. Similar Mn enrichments or considerable Mn fluctuations also occurred in some subsurface core sections (i.e. M-3, BC-3 and BC-4; Figs. 5–7) and these were apparently unrelated to lithogenic input and to changes in the sediment texture in order to suspect any changes in the sources or external input to the sediments. Perturbations and interruptions of the remobilization and precipitation processes as related to the varying physical, chemical, biological and sedimentological conditions in the depositional environment (Froelich et al., 1979; Colley et al., 1984) could result in such Mn enrichment in the discrete subsurface layers within the sedimentary column of Marmara cores.

Although increased Mn concentrations under the influences of diagenetic or postdepositional processes probably make up a significant portion of the total Mn present in the sediments, particularly in both surface and discrete subsurface core sections, the overall high Mn concentrations found in the deep Marmara Trough sediments cannot solely be explained by the effects of diagenesis. Also, as previously discussed, there is no evidence for neither the occurrences of particular geological Mn sources on the surrounding land nor the input from the shallow Black Sea waters which could possibly provide unusually high Mn concentrations to the sediments.

Also, petrographic studies on sedimentary grains showed that there were no important occurrences of volcaniclastic materials on the sea floor which could be indicative of possible submarine weathering processes that in turn favor an increase in the Mn concentrations (e.g., Elderfield, 1977), as found in the fine-grained sediments of the Santorin area, Mediterranean Sea (4.23–17.15% Fe and 2000–6200 ppm Mn; Butuzova, 1969).

Because the Sea of Marmara is located in the tectonically active North Anatolian Fault Zone associated with frequent seismic activities (i.e. earthquakes) and occurrences of several hot water springs and mineral-rich waters aligned along grabens and fault planes (Ternek et al., 1987), it seems likely that hydrothermal Mn contributions should also be applied to explain

the anomalies with the occurrences of Mn-rich sediments in the deep waters of the Marmara Trough. Yet, no such data are available to show the occurrences of metalliferous sediments connected with the possible hydrothermal emanations in the Marmara Trough.

Therefore, assessment of this role of submarine hydrothermal activities in controlling the deposition of high Mn concentrations in the deep Marmara sediments would require a knowledge of the heavy-metal composition and distribution in common metalliferous sediments associated with hydrothermal activities on the floor of world seas and oceans. Hydrothermal metal enrichments have been described from a considerable number of localities in many deep-sea regions (e.g., Butuzova, 1969; Cronan, 1972; W.S. Moore and Vogt, 1976; Cann et al., 1977; Grill et al., 1981; Moorby and Cronan, 1983; Glasby, 1984; Moorby et al., 1984; Varnavas et al., 1988).

Table 3 compares the heavy-metal contents of the Marmara Trough sediments with those found in other deep-sea regions where the influence of hydrothermal supply is prominent. From this comparison, it also appears that heavy-metal compositions of the Marmara Trough sediments are, to some degree, similar to those found typically for the hydrothermally-derived sediments.

It can also be seen from Table 3 that the hydrothermal activities may favor an increase in Fe and Mn concentrations, but at the same time, sediments may not be enriched in other metals and their concentrations are usually within the range of average crustal and sedimentary rocks (Table 3). For instance, Mn and Fe concentrations in some hydrothermally-derived recent sediments showed a wide range of the values between 234 and 462,400 ppm and between 0.15% and 33.92%, respectively (Table 3). These differences among the values are readily attributed, in part, to the varying influences of other factors, such as texture and mineralogy of the sediments, and the proximity to the source. More specifically, however, is the behaviour of Fe relative to Mn with increasing distance from hydrothermal sources. Hydrothermal Mn does not settle with Fe-hydroxides immediately near the outflows of sources (Emelyanov and Shimkus, 1986). As re-

ported from the Stromboli region in the Mediterranean Sea (Bonatti et al., 1972), fractionation of Mn from Fe due its higher mobility takes place during deposition, whereby Fe precipitates close to the source, while Mn has a longer residence time in solution. Similarly, surface sediments from the Galápagos Rift zone of the eastern Pacific (Marchig et al., 1987), are marked by relatively high Fe/Mn ratios (229; Table 3) close to the hydrothermal vent, which gradually decrease with some distance from the vent (6.1; Table 3). This possibility may also be considered for the Sea of Marmara on the basis of Fe/Mn ratios. Here, the average Fe/Mn ratios in the cores gradually increase from the Central Basin (11 in BC-3) to both the western (17 in BC-4) and eastern deep basins (23 in M-3, and 7-32 in M-1 and M-4 recalculated from previous data by Ergin and Evans, 1988), and further to both the northeastern (67 in BC-2) and southwestern (69 in BC-5) shelf regions. Taking these calculations into account, one might expect that the central basin of the Marmara Trough could be a possible region providing hydrothermal solutions which in turn are responsible for the Mn enrichment in the deep-sea sediments of the Marmara Trough.

5. Conclusions

On the basis of results obtained here, it can be concluded that the concentrations of Fe, Ni, Zn, Cr, Co, Cu and Pb in the recent Marmara sediments are usually within the range of those normally found in average crustal and sedimentary rocks. The differences in the metal contents seem to be controlled largely by the degree of variations in texture and lithogenic and biogenic components present in the sediments.

Anthropogenic influences are believed to be effective on the levels of Cu, Zn and Pb, particularly in sediments from the northeastern Marmara shelf. Cr and Ni, in part, show influences of weathering products from basic–ultrabasic sources.

The concentrations of Mn are unusually high and seem to be increased significantly in deep-water relative to shallow-water sediments. The

combined effects of diagenetic and hydrothermal processes are related to the enrichment of Mn in the deep-water sediments from the Sea of Marmara.

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