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SOURCES AND DISPERSAL OF HEAVY METALS IN SURFACE SEDIMENTS ALONG THE EASTERN AEGEAN SHELF

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Summary. A total of 46 surface sediment samples from the Turkish coasts of the eastern Aegean Sea was subjected to petrographic and chemical analyses, which together with the land geology, were used to study the principal controlling factors on heavy metal dispersal and provenance. The heavy metal data show considerable similarity in composition to average sedimentary rocks worldwide. Exceptions to regional trends reflect unusual geology in the source areas, postdepositional mobility of the metal within the sediment, and perhaps to some extent, anthropogenic effects. The latter appears to be significant off the Meriç River mouth and inner Izmir Bay, where the concentrations of Cu and Zn are somewhat higher than the average. The levels of Fe off the mouths of the Menderes and Gediz rivers are rather high, presumably resulting from the metamorphic rocks of the Menderes Massif and related ore deposits. Exceptionally high Mn, and to lesser degree, Co concentrations in the sediments around Marmaris peninsula may be due to a combination of substantial input from the terrigenous sources together with diagenetic enrichment in the sediment. The distribution of Cr and Ni concentrations is largely controlled by the contribution from ultramafic rocks and related economic chromite deposits on land. From the relationships among the geochemical variables, it is concluded that the greater portions of the metals studied are associated with the Fe, Mn, clay, and to lesser extent, organic fractions of the sediments.

Overall, the distributions of the heavy metals in the surface sediments of the eastern Aegean Sea can largely be explained in terms of variations in depositional environment and provenance.

Riassunto. Le analisi petrografiche e chimiche effettuate su 46 campioni di sedimento superficiale prelevati lungo le coste turche del Mar Egeo orientale sono state utilizzate, unitamente alla conoscenza della geologia terrestre della regione, per studiare i principali fattori che controllano la provenienza e la dispersione dei metalli pesanti.

I risultati delle analisi geochimiche hanno evidenziato una considerevole similitudine con la composizione media mondiale delle rocce sedimentarie. Le eccezioni all'andamento regionale riflettono particolari caratteristiche geologiche delle aree di origine del sedimento, mobilità postdeposizionale dei metalli nello stesso e, in una certa misura, azione antropogenica. Quest'ultimo fattore appare significativo nei pressi della foce del fiume Meriç e nella Baia di Izmir, dove le concentrazioni di Cu e Zn sono più elevate del tenore medio. I tenori di Fe alle foci dei fiumi Menderes e Gediz risultano relativamente elevati, probabilmente a causa delle rocce metamorfiche del Massiccio di Menderes e dei relativi giacimenti minerari che costituiscono la zona di provenienza del sedimento.

L'elevato tenore di Mn e, in minor misura, di Co nei sedimenti della penisola di Marmaris, può essere messo in relazione principalmente ad apporti terrigeni, cui si sommano fattori di arrichimento diagenetico nel sedimento. La distribuzione di Cr e Ni è ampiamente controllata dalle rocce ultramafiche e dai relativi giacimenti di cromite nelle zone di origine del sedimento.

Le relazioni fra le variabili geochimiche studiate hanno evidenziato che la maggior parte degli elementi sono associati a Fe, Mn e all'argilla, nonché, in minor misura, alla frazione organica del sedimento. Per concludere, la distribuzione dei metalli pesanti nei sedimenti superficiali del Mar Egeo orientale può essere ampiamente spiegata in termini di variazioni degli ambienti di deposizione e dei luoghi di provenienza.

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1. Introduction

Knowledge of the geochemical anomalies in coastal and shelf sediments is important for understanding the extent of various natural and anthropogenic processes in a given region. For instance, in many coastal regions adjacent to industrial and urban areas where metals from both geological and man-made sources accumulate together, it can be difficult to determine the proportion of anthropogenic inputs. Apart from this, the nature, grain-size distribution, and provenance of the sedimentary materials are the most important factors controlling the metal variability within the sediment.

Much has been written on the sedimentology and geochemistry of surficial bottom deposits in the Aegean Sea (Emelyanov, 1972; Venkatarathnam et al., 1972; Smith and Cronan, 1975; Lykousis et al., 1981; Voutsinou-Taliadouri and Satsmadjis, 1982; Bartole et al., 1983; Conispoliatis and Lykousis, 1986; Aksu et al., 1987a and 1987b; Perissoratis et al., 1987; Saccani, 1987; Yemenicioglu et al., 1988; Balci et al., 1990; Ergin et al., 1990). However, no detailed information was available from the eastern Aegean margin, along the Turkish coasts. Thus, the aim of this paper is to gain a better understanding of the natural variability of the heavy metals in this largely unknown part of the Aegean Sea by an investigation of the land-geology, sediment texture and composition.

2. Study area

The study area extends from the Meriç River mouth in the north to the Bodrum-Marmaris peninsulae in the south, and is bordered to the east by the irregular (toothed) coastlines of western Anatolia (Fig.1). Its coastal physiography is dominated by the NE-SW-to ENE-WSW-trending four main gulfs (Edremit, Izmir, Menderes and Bodrum) which appear to be the offshore extensions of large, elongated Neogene grabens or other valley-like depressions (Mascle and Martin, 1990). Geologically speaking, these features belong to the Late Tertiary fault systems (mainly Miocene) which must have resulted from the westward motion of the Anatolian Plate with respect to the Black Sea and African/Arabian Plates (Mc Kenzie,1978; Dewey and Sengör,1979; Boer,1989). Since then, the Aegean Sea has been a region of active earth movements (Flemming,1972; Papadopoulos et al.,1986; Eyidogan,1988). The geology of the land areas to the east of the studied maritime region (Fig.2) is characterized by the occurrence of various metallogenic ore/mineral deposits of economic importance.

The main suppliers of fluvial detritus into the east Aegean Sea are the rivers of the Meriç (Ergene), Madra, Bakirçay, Gediz, K. Menderes, B. Menderes, and Dalaman delta complexes (Evans, 1971; Eisma, 1978; Aksu et al., 1990) (Fig.1). The climate shows a clearly "Mediterranean" regime; it is mild in winter (7-9°C) and hot in summer (>25°C). The average annual precipitation is between 400 and 800 mm/yr at sea level, rising to more than 1000 mm/yr in the mountains, and shows a pronounced maximum on the southwestern Turkish mainland (Dewdney, 1971; Henry, 1977).

The oceanography of the Aegean Sea is largely determined by the northerly inflow of Black Sea waters and southerly inflow of Mediterranean waters, the former being cooler and brackish and the latter warmer and saline in character (Miller, 1983). The temperature-salinity characteristics of the Aegean Sea normally appear to change towards the north. In the eastern Aegean Sea, the water masses display a temperature 11 to 26°C, salinity of 35 to 39 ppt, and oxygen content of between 5.5 and 9.2 ml/l (Artüz, 1970; Benli and Küçüksezgin, 1988). Typical salinity, temperature and oxygen profiles obtained during the sediment sampling in the study area have been selected and shown in Fig.3. The tides are small along the eastern Aegean coast (max. 30-50 cm; Erol, 1990). However, the mean tidal range during storm conditions may be as much as 122 cm in the Gulf of Izmir (Aykulu, 1952; in: Erol, 1990).

3. Material and methods

The surface sediments were sampled at 46 locations during the R/V Bilim cruise in the eastern Aegean Sea in 1987. Samples were taken using a Dietz LaFonde Grab from depths between 12 and 640 m (Fig.1 and Table 1). The granulometric composition was investigated by standard sieving and settling procedures as described by Folk (1974) and Lewis (1984). Textural classification of the samples was based on the relative percentages of clay (<0.002 mm), silt (0.002-0.063 mm), sand (0.063-2 mm), and gravel (>2 mm), after Shepard (1954) and Folk (1974). Sand- and gravel-sized fractions of the samples were examined under the microscope to identify the principal components of the samples. Total carbonate contents (% $CaCO_3$) were determined using a gravimetric method after Müller (1967; absolute error ±0.5%). The percentages of organic carbon were determined by titration with potassium dichromate, following Gaudette et al. (1974). The accuracy of this method is ±0.25%. Concentrations of Fe, Mn, Co, Cr, Ni, Cu, and Zn were determined by atomic absorbtion spectrophotometer (Varian AA-6 Model), after total digestion in a hot HF-HNO_3-acid mixture

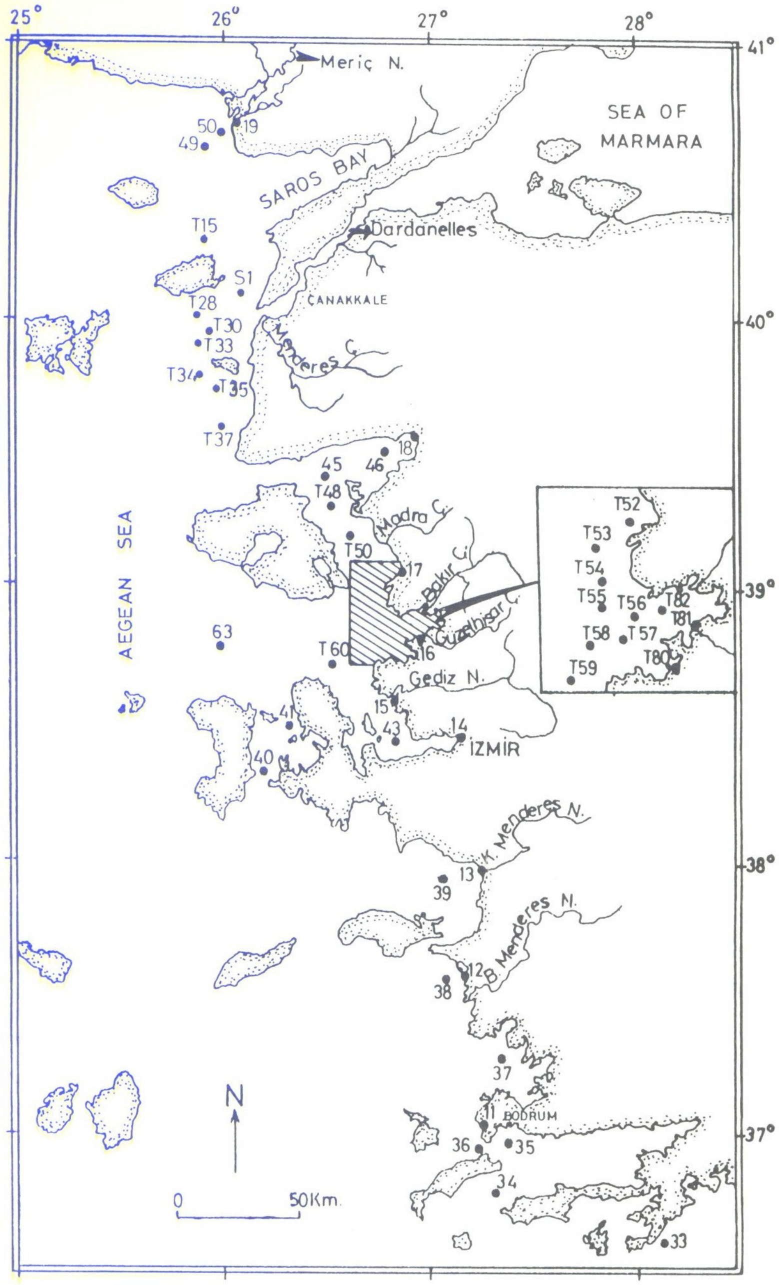


Fig. 1 - Location map of surface sediment sampling sites in the eastern Aegean Sea.

of the oven-dried (at 60° C) and grounded samples. An international standard (CRM 142 from BCR) and blanks were included in each set of samples to check the precision and accuracy of the analyses. The precision was found to be generally between 1 and 11%.

4. Results and discussion

4.1. Sediment texture

The studied bottom sediments of the eastern Aegean Sea are composed of material covering

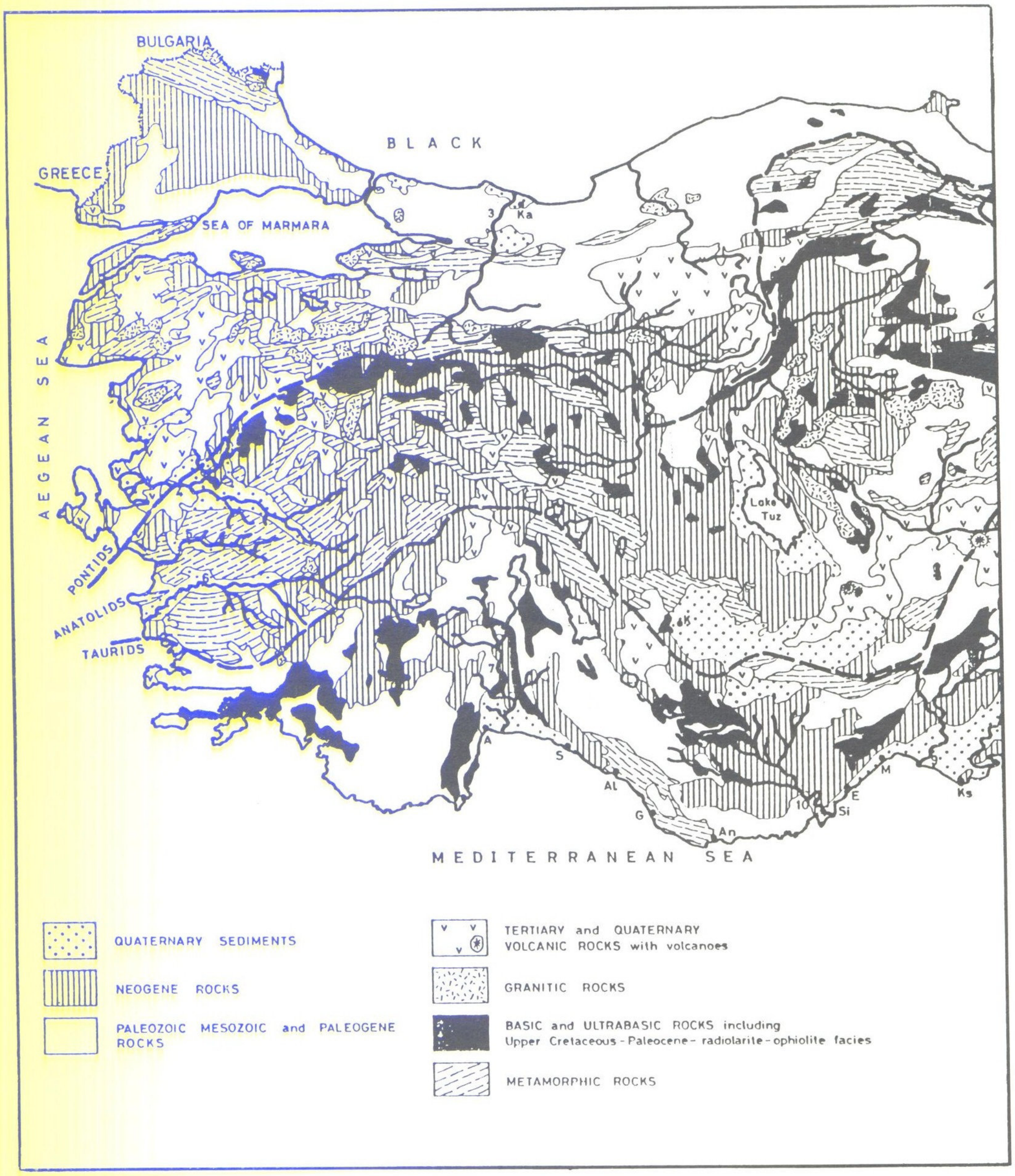


Fig. 2 - General geological map of Turkey showing the eastern Aegean surroundings (adapted from Evans, 1971: map compiled from Erentöz, 1966; Ketin, 1966; and MTA, 1961-64).

a wide range of grain sizes: from silty clay to sandy gravel (Table 1). Muds (the term "mud" in this study is applied to a mixture of silt and clay) occur mainly off river mouths (areas of high terrigenous input) and in embayments (areas of low energy conditions). Embayments in which mud is prevalent are represented by stations 18 and 45 (Edremit Bay), stations 14, 43, and T60 (Izmir Bay), as well as, stations 41 and 63 from the Karaburun Peninsula-Lesbos Island-Chios Island triangle. Areas of high mud deposition due to river run-off are limited to stations 19, 50, 49 (off the Meriç River), station 15 (off the Gediz River), and station 13 (off the K.Menderes River).

The coarse-grained sediments are mainly represented by abundant sand- and gravel-size

Table 1 - Locati
organic carbon
type. Note the g
calcareous, 5-25
clay; csi: clayey
muddy sand; sg

Sampling station	Water depth
19	20
50	40
49	54
T15	125
S1	71
T28	82
T30	71
T33	40
T34	59
T35	260
T37	100
18	27
46	42
45	81
T48	50
T50	34
T52	33
17	20
T53	63
T54	84
T55	105
T56	91
T82	130
T81	380
16	21
T57	110
T58	82
T80	20
T59	215
T60	75
63	273
15	22
43	50
14	15
41	84
40	35
13	53
39	190
38	55
12	12
37	80
11	14
36	50
35	85
34	640
33	285

Table 1 - Locations and water depths of the sampling stations from the Eastern Aegean Sea together with organic carbon and carbonate contents as well as, the granulometric parameters and related sediment type. Note the genetic and granulometric components (vlc: very low calcareous, <5% $CaCO_3$; lc: low calcareous, 5-25% $CaCO_3$; c: calcareous, 25-50% $CaCO_3$; hc: high calcarous, 50-75 %$CaCO_3$; sic: silty clay; csi: clayey silt; ssi: sandy silt; si; silt; ssic: sand- silt-clay; s: sand; gm; gravelly mud; gms: gravelly-muddy sand; sg; sandy gravel).

Sampling station	Water depth	Longitude (°	"	')	Latitude (°	"	')	Org. C %	$CaCO_3$ %	Clay %	Silt %	Sand %	Gravel %	Sediment Type
19	20	26	04	00	40	43	00	1.4	4	49	46	4	1	vlc,sic
50	40	26	04	00	40	39	00	1.7	3	60	40	-	-	vlc,sic
49	54	25	52	00	40	35	00	1.1	6	50	35	14	1	lc.sic
T15	125	25	55	00	40	17	30	0.5	20	-	-		-	lc
S1	71	26	05	45	40	06	05	-	72	2	4	56	38	hc,sg
T28	82	25	53	00	40	01	00	0.3	17	8	8	82	2	ls,s
T30	71	25	26	30	39	58	00	0.2	26	4	10	62	24	c.gms
T33	40	25	53	00	39	55	00	-	-	-	-	-	-	-
T34	59	25	53	00	39	48	00	0.3	46	-	-	-	-	c
T35	260	25	57	00	39	44	00	0.3	54	9	22	59	10	hc,gms
T37	100	25	59	00	39	36	00	0.3	56	6	16	71	7	hc,gms
18	27	26	57	00	39	32	00	1.2	2	38	59	3	-	vlc,csi
46	42	26	52	00	39	31	00	0.2	13	15	25	59	1	lc,ssi
45	81	26	29	00	39	24	00	0.7	16	35	55	10	-	lc,csi
T48	50	26	30	30	39	18	30	0.3	48	-	-	-	-	c
T50	34	26	37	00	39	12	00	0.7	42	6	12	80	2	c,s
T52	33	26	45	20	39	04	00	0.4	32	2	3	93	2	c,s
17	20	26	46	00	39	10	00	2.5	27	20	47	29	4	c,ssic
T53	63	26	43	00	39	00	00	0.4	30	8	23	60	9	c,gms
T54	84	26	43	00	38	57	00	0.3	37	10	13	69	8	c,gms
T55	105	26	44	00	38	53	30	1.4	11	53	46	1	-	lc,sic
T56	91	26	51	20	38	49	30	0.4	16	21	20	57	2	lc,ssic
T82	130	26	57	30	38	52	00	0.5	12	22	23	53	2	lc,ssic
T81	380	26	57	30	38	49	30	1.0	9	21	55	23	1	lc,ssic
16	21	26	57	00	38	50	00	1.4	12	35	54	10	-	lc,csi
T57	110	26	47	00	38	47	30	1.2	13	57	42	1	-	lc,sic
T58	82	26	42	00	38	45	30	0.5	21	-	-	-	-	lc
T80	20	26	55	00	38	46	30	1.2	16	24	40	35	1	lc,ssic
T59	215	26	37	30	38	43	30	1.1	26	16	18	61	5	c,gms
T60	75	26	30	00	38	43	00	0.3	24	11	14	69	6	c,gms
63	273	26	04	00	38	44	00	0.5	45	2	81	17	-	c,si
15	22	26	47	00	38	37	00	0.4	9	51	48	1	-	lc,sic
43	50	26	49	00	38	27	00	1.3	12	40	60	-	-	lc.csi
14	15	27	08	00	38	27	00	1.9	21	40	37	14	9	lc,gm
41	84	26	22	00	38	29	00	0.3	46	9	72	17	2	c,csi
40	35	26	14	00	38	19	00	3.5	60	11	23	58	8	lc,gms
13	53	27	11	00	37	58	00	0.6	3	28	66	6	6	c,csi
39	190	27	00	00	37	55	00	0.7	29	46	49	5	-	c,csi
38	55	27	08	00	37	32	00	0.7	23	25	75	-	-	lc,si
12	12	27	08	00	37	30	00	0.9	17	12	46	42	-	lc,ssi
37	80	27	13	00	37	15	00	0.6	44	4	67	27	2	c,ssi
11	14	27	25	00	37	02	00	1.7	29	9	29	38	24	c,gm
36	50	27	20	00	36	57	00	0.7	60	9	24	66	1	hc,sis
35	85	27	19	00	36	58	00	1.1	73	15	24	37	24	hc,gm
34	640	27	19	00	36	45	00	0.9	38	48	50	2	-	c,csi
33	285	28	95	00	36	32	00	1.0	36	86	4	86	10	c,si

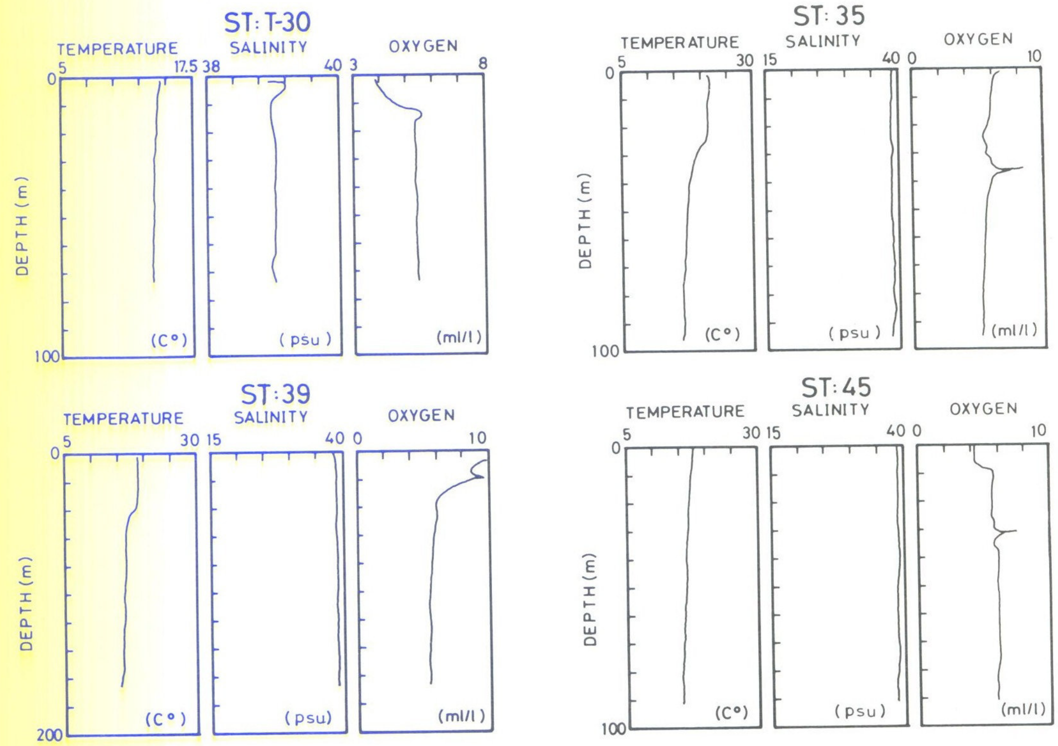
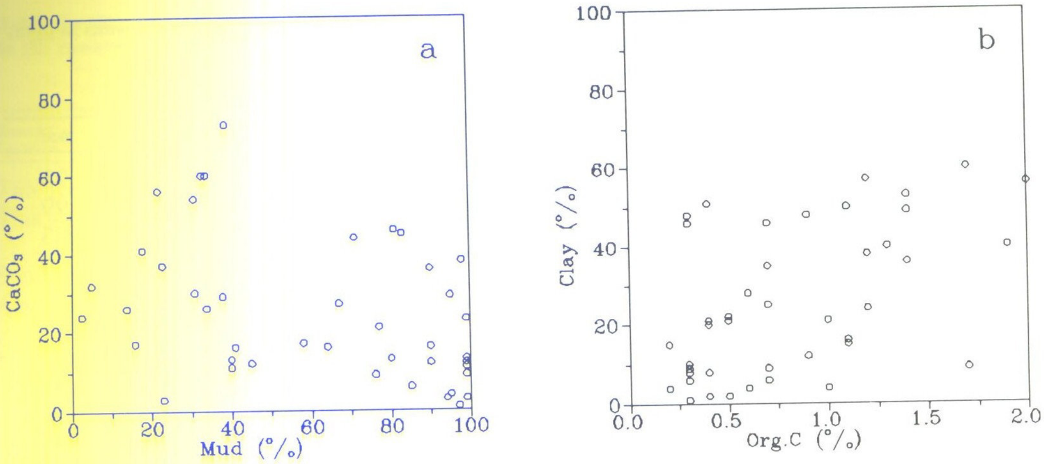


Fig. 3 - Typical temperature, salinity, and dissolved-oxygen profiles at some selected stations of the eastern Aegean Sea. Based on data from the Institute of Marine Sciences, METU (October, 1987).

fractions which are composed of both biogenic and terrigenic components. Among the sediments, those dominated by biogenic components are largely derived from the calcareous remains of various species of pelecypods, gastropods, foraminifers, ostracods, bryzoans, algae, echinoids and pterepods. The occurrence of the calcareous algae "Lithothamnium" is characteristic of sediments at stations T33, T34, and T35 (off the coasts of Bozcaada Island), and stations 35 and 36 (between Kos Island and Bodrum peninsula). The terrigenous components are generally consistent with the geological sources on land and coast.

4.2. Carbonate and organic carbon distribution

The total sediment carbonate contents ranging from 2 to 73% $CaCO_3$ by dry weight (Table 1) can generally be assumed to reflect the quantity of biogenic, and to a lesser degree, terrigenic components present in the sediments. The higher carbonate contents of marine biogenic origin were usually found, in the north, between the Island of Gökçeada and Gelibolu peninsula (st. S1: 72% $CaCO_3$), and the south off the Bozcaada Island (sts. T35 and T37: 54-56% $CaCO_3$); in the south, off the Bodrum peninsula (sts.36 and 35: 60 and 73% $CaCO_3$); and in the central part of the study area, off the Cesme peninsula (st. 40: 60% $CaCO_3$). These higher carbonate contents are probably the result mainly of the higher benthonic productivity and lower mud sedimentation prevailing in these waters. However, other areas of high carbonate contents also occur due to the presence of calcareous lithoclastics and bioclastics from the terrigenous sources, especially from adjacent land masses along the southeastern Aegean coasts. Terrigenous carbonates are represented mainly by occurrences of magnesite, dolomite, marble, marl, and limestones of various ages and formations out cropping in the drainage basins of the major rivers. Nevertheless, there is no overall significant and positive correlation between the carbonate contents and fine-sized grain fractions in the sediments (i.e.,Fig.4a). For example, very low-calcareous (<5% $CaCO_3$) to low- calcareous (5-25% $CaCO_3$) sediments were usually found at stations where the mud portions of the samples were high.



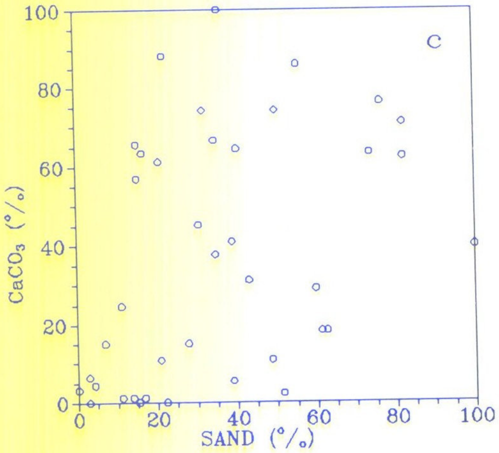


Fig. 4 - Plot of relationships between (a) mud and $CaCO_3$, (b) Corg-clay and (c) $CaCO_3$ and sand in the surface sediments.

The organic carbon contents of the sediments ranging from 0.2 to 3.5% by dry weight (Table 1) are generally high at most of the inshore stations 11-19 located at or near the river mouths (0.6-1.9% org-C), probably due to increased terrigenous input from the adjacent land masses. Obviously, the man-made activities in the vicinity of these stations must be considered as an additional source of organic matter in the sediments. It is apparent that there is a less significant trend of increasing organic carbon contents with clay-sized fractions within the sediment (Fig.4b), suggesting the importance of other enrichment mechanisms or sources in addition to the accumulation of organic matter by fine- grained sediments (Stumm and Morgan, 1981). On the other hand, the exceptionally high organic carbon (2.5 and 3.5%) occuring in sediments from stations 17 and 40 in the central part of the study area, which contained considerable amounts of sea grass and large wood and leaf fragments, possibly derived from rough sea and/or storm weather conditions. Otherwise, the greater part of the org-C values fall in the range of 0.3 to 0.7%, suggesting normal marine conditions similar to many areas elsewhere in the Mediterranean Sea (Emelyanov, 1972; Ergin et al., 1988). In comparison with the Marmara (Ergin et al., 1991;1992) and Black Sea (Shimkus and Trimonis, 1974; Yücesoy and Ergin, 1992), the organic carbon levels in the east Aegean sediments obtained here are significantly lower, most probably as a result of the primary production in the Aegean waters (Murdoch and Onuf, 1974).

4.3. *Heavy metal distribution and possible source/dispersion relationships*

The concentrations of heavy metals determined in the sediments are presented in Table

Table 2 - Heavy metal concentrations in surface sediments from the eastern Aegean sea. Results in ppm, except for Fe and mud in %. In this study, "mud" is coincident with silt plus clay.

Sample	Fe	Mn	Co	Cr	Cu	Ni	Zn	Mud
19	4.17	443	14	76	77	61	156	95
50	4.63	602	17	85	62	75	114	99
49	3.81	693	12	74	33	66	64	85
T15	2.59	394	10	80	13	46	49	3
T28	1.69	266	5	56	11	30	31	16
T30	2.43	330	12	92	11	39	79	14
T34	1.18	412	41	40	11	21	22	—
T35	1.22	194	5	24	6	23	31	31
T37	1.38	437	7	24	10	70	54	22
18	4.42	416	14	76	43	57	91	97
46	3.55	414	12	65	16	46	95	40
45	3.41	409	12	92	27	70	123	90
T48	1.18	129	5	23	3	11	45	—
T50	0.85	113	7	26	8	21	33	18
17	2.62	299	10	42	45	34	87	67
T52	0.59	103	2	9	3	13	19	5
T53	1.18	172	7	32	6	30	27	31
T54	2.20	441	5	42	11	36	37	23
T55	3.07	352	9	73	34	43	81	99
T56	3.58	377	12	58	14	35	58	41
T82	3.69	343	9	74	18	52	60	45
T81	2.99	269	9	65	16	36	56	76
T80	3.16	337	12	101	21	50	93	64
T57	4.23	716	19	103	27	118	98	99
T58	2.98	704	12	161	16	70	84	—
T59	2.58	388	9	68	11	62	53	34
16	3.09	263	9	84	24	45	107	99
T60	2.31	407	7	76	10	48	49	25
63	2.31	716	12	53	22	87	43	83
15	5.35	659	21	136	43	120	96	99
43	3.50	591	21	280	19	278	104	90
14	3.98	659	127	121	59	108	162	77
41	2.08	287	7	70	14	59	37	81
40	1.00	223	5	57	16	48	27	34
13	5.74	614	24	109	51	87	122	94
39	3.83	625	21	126	25	194	83	95
12	4.49	591	21	280	19	278	65	58
38	4.59	659	26	200	33	344	102	99
37	2.29	357	7	70	11	62	51	71
11	3.07	352	9	73	34	43	72	38
36	0.89	160	2	32	8	34	36	33
35	1.12	261	5	29	13	57	25	39
34	2.33	2625	24	103	27	242	46	98
33	1.71	1306	31	312	22	406	24	90

2. To reduce the metal variability caused by the carbonates, and to compare the measured metal concentrations with other terrigenous sediments and "average shale", the bulk metal data of this study was recalculated on a $CaCO_3$-free basis (Table 3). The distribution of Fe, Mn, Cr, Ni, Cu, Co, and Zn in the samples mostly resembles that of average sedimentary rocks (Table 3), and deviations can largely be accounted for by variations in sediment texture and

s in ppm,

Mud
95
99
85
3
16
14
—
31
22
97
40
90
—
18
67
5
31
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41
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Table 3 - Comparison of metal levels in this study with literature data for surface sediments elsewhere in the eastern Mediterranean and for average sedimentary rocks. Results in ppm,except for Fe in %.

Sample/ Location	Fe	Mn	Co	Cr	Cu	Ni	Zn
This study	0.59-5.74	103-2625	2-41	9-312	3-77	11-406	19-162
This study*	0.86-5.96	151-4234	3-76	13-387	4-80	19-634	28-205
Southwest. Aegean Sea*[1]	3.53	783	—	137	37	77	93
Eastern Aegean Sea[2]	2.41	925	16	92	18	143	39
Southern Black Sea*[3]	0.32-5.29	160-1109	<1-22	18-238	22-119	14-215	61-141
Entire Marmara Sea[4]	1.09-4.79	197-5538	9-30	52-166	13-92	28-61	42-149
Eastern Marmara Sea[5]	4.00-4.30	1250-5500	22-27	105-131	37-55	80-110	79-136
East. Marmara/ Izmir Bay[6]	1.40-3.97	112-678	43-105	6-81	13-49	34-98	45-114
East. Medit./ Cilican Basin*[7]	5.72	1679	—	457	56	269	117
East. Medit/ Mersin Bay[8]	1.10-4.80	236-698	11-40	19-77	8-50	155-753	25-466
Shales[9]	4.72	850	19	90	45	68	95
Sandstones[9]	0.98	50	<1	35	10	2	16
Limestones[9]	0.38	1100	<1	11	4	20	20

Sources: *carbonate-free data; [1] Smith and Cronan, 1975; [2] Voutsinou-Taliadouri and Satsmadjis, 1982; [3] Yücesoy and Ergin, 1992; [4] Bodur, 1991; [5] Evans et al., 1989; [6] Ergin et al., 1991; [7] Shaw and Bush, 1978; [8] Bodur and Ergin, 1988; [9] Turekian and Wedepohl, 1961.

mineralogy.

The distribution of Fe is rather variable but mostly comparable with that in adjacent marine regions, as well as in average sedimentary rocks (Table 3). Low Fe concentrations (1.4-3.0%) usually occur in coarse-grade sediments which also contain high quantities of carbonates (Fig.5a), whereas high values coincide with the fine-grade, clayey (Fig.5b) and organic-rich (Fig.5c) sediments. The iron therefore appears to be associated with the clay minerals and organic matter, and is most probably present as finely divided oxides and hydroxides. Iron is quite high (5.4-5.9%) in the sediments off the mouths of the major rivers, B.Menderes, Gediz, and K.Menderes. This can be readily explained as the result of influx of iron-rich clastic sediments derived from the metamorphic rocks of the Menderes Massif and associated economically important metallic ores (Ketin, 1983; MTA, 1989).

The concentrations of Mn (151-4234 ppm; carbonate-free data) are mostly consistent with those of the other Aegean sediments and average sedimentary rocks (Table 3). Off the Marmaris peninsula, the deepest waters of the study area (285 and 640 m), sediments showed the highest

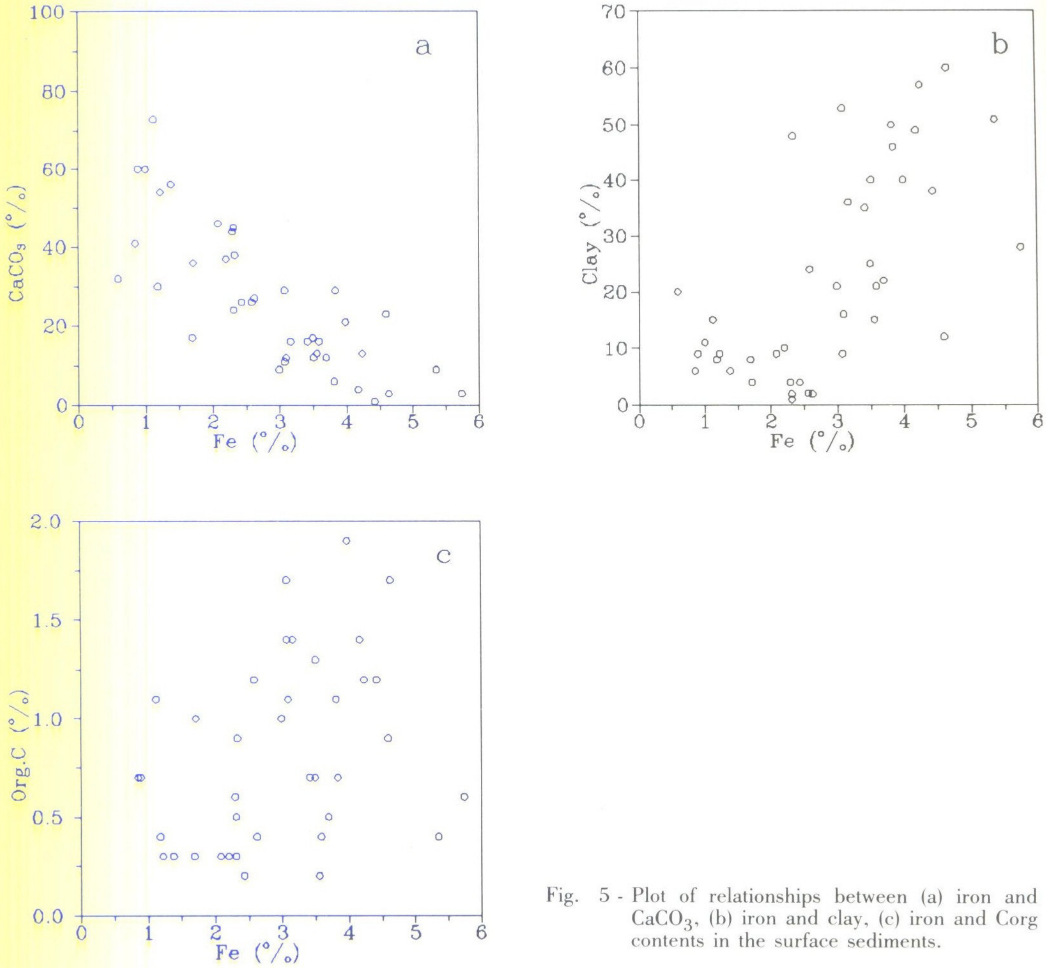


Fig. 5 - Plot of relationships between (a) iron and $CaCO_3$, (b) iron and clay, (c) iron and Corg contents in the surface sediments.

Mn content (2040 ppm and 4234 ppm, respectively), perhaps due to a combination of diagenic modification together with an influx of material from onshore mining activity. The Mn-rich deposits in the drainage basin southwest of Turkey (MTA, 1977; MTA, 1989) probably provides, in part, a ready source of terrigenous material relatively rich in Mn. On the other hand, the enrichment of Mn due to diagenesis in sediments has also been reported in other parts of the eastern Mediterranean, the Cilician Basin (Shaw and Bush, 1978), the Marmara Trough (Evans et al., 1989; Bodur, 1991), and the Black Sea (Hirst, 1974; Yücesoy and Ergin, 1992). In general, the high Mn concentrations in the samples can be correlated with the high proportion of fine-grade (clayey) material (Fig.6a) and low content of carbonate in these sediments (Fig.6b). It is very likely that the manganese, together with iron (Fig.6c) is present in the samples mainly as oxides and hydroxides, and to some degree associated with the clay minerals.

Cobalt (5-48 ppm, carbonate-free data) shows many similarities to Fe and Mn (Fig.7a,b) in its regional variation, with most of the values comparable to the average composition of sedimentary rocks and to the other Aegean sediments (Table 3). This is a reflection of the terrigenic influences in the study area. However, local enrichments of Co occur off the Menderes River mouths (sts. 33;48 ppm and 34;39 ppm) and off the Marmaris peninsula (st.38;34 ppm), suggesting significant input of Co from the particular geological sources in the hinterland, as with Fe and Mn. On the other hand, the association of Co with Fe and Mn (Fig.7a,b) could be indicative of diagenesis, most probably as a result of coprecipitation of these metals, particularly in the fine-grained fractions (Fig.7c), which has been observed in marine sediments from many parts of the world (Halbach et al., 1982; Aplin and Cronan, 1985).

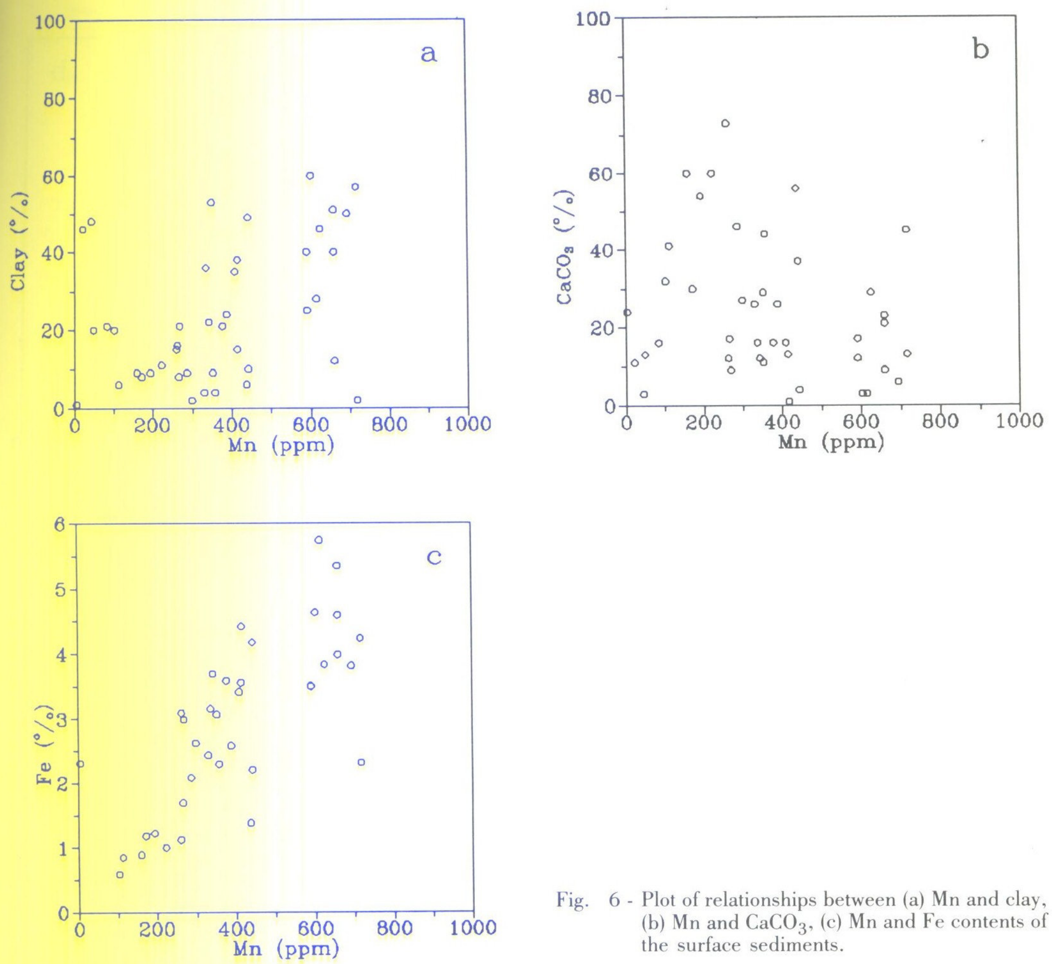


Fig. 6 - Plot of relationships between (a) Mn and clay, (b) Mn and $CaCO_3$, (c) Mn and Fe contents of the surface sediments.

The distribution of Cu concentrations (4-80 ppm carbonate-free data; Table 3) appears to indicate additional influx of material from other than the terrigenous sources, although the majority of the Cu levels in the samples would obviously reflect the effect of the land geological predominance. Off the Meriç River mouth (sts.19 and 50) and in the Izmir Bay (st.14), where the coastal waters receive significant amounts of anthropogenic effluents, sediments display the highest Cu contents (64-84 ppm). Overall, the measured Cu levels in the studied sediments are not only comparable with those of average sedimentary rocks but also with data reported elsewhere in the Aegean Sea and its surroundings (Table 3). While the distributions of the Cu, Fe, Mn, mud, and organic carbon contents of the sediments generally support the contention that there are significant associations among these variables (Figs.8a,b,c,d), by contrast, the carbonate concentrations seemingly have a dilution effect on Cu (Fig.8e).

The distribution pattern of Zn nearly follows that of Cu, with the highest Zn values, 162 and 205 ppm, occuring at the mouth of the Meriç River (st.19) and the inner Izmir Bay (st.14), respectively. These markedly higher Zn concentrations, to large extent, may be due to anthropogenic effects. The majority of the remaining Zn values shows a considerable measure of similarity in composition to average sedimentary rocks (Table 3). The somewhat high Zn levels in sediments from the Edremit Bay (st.45; 146 ppm) can be explained by the widespread Zn-Pb deposits which occur on the adjacent landmasses (MTA,1989). In most cases, Zn shows a correspondence with the Fe, Mn, and to lesser extent, clay and organic carbon contents of the sediments (Fig.9a,b,c,d). This suggests that, whatever the sources of the Zn it is closely associated with the Fe, Mn, and organic matter in the fine-grade fractions of sediments. The

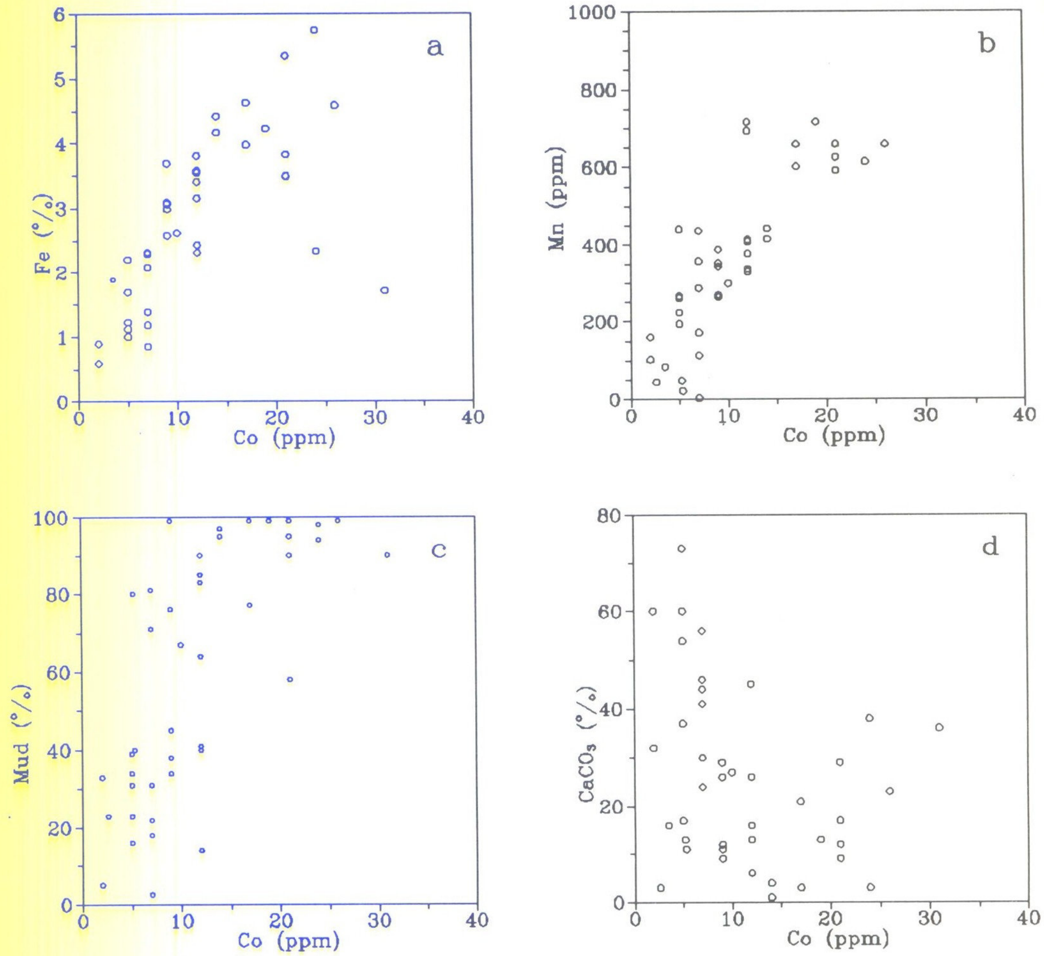
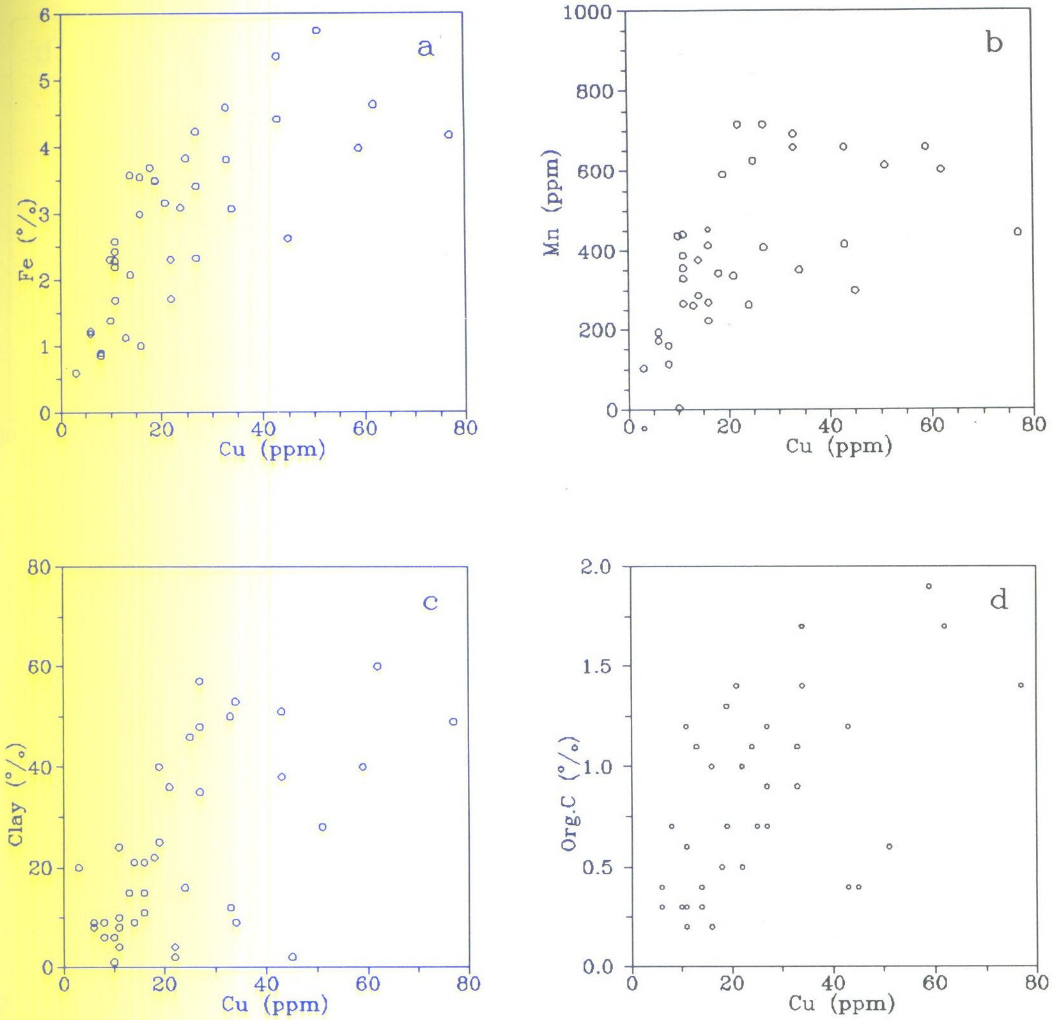


Fig. 7 - Plot of relationships between (a) Co and Fe, (b) Co and Mn, (c) Co and mud, (d) Co and $CaCO_3$ contents of the surface sediments.

presence of carbonates usually have adilution effect on Zn levels in the samples (Fig.9e).

The distributions of Cr and Ni are generally similar (Fig.10), indicating an association of these metals, most probably derived from the adjacent landmasses. However, the concentrations of Cr (13-487 ppm, carbonate-free data) and Ni (19-634 ppm, carbonate-free data) in the samples appear to be significantly higher than those found in average sedimentary rocks (Table 3). In contrast to the lower Cr and Ni contents of samples from the north, greater abundances of these metals are found in the southern part of the study area, where the present land geology is characterized by numerous outcrops of basic-ultrabasic rocks and related economic chromite deposits (Ketin, 1983; MTA, 1989). As has also been observed in marine sediments from other parts of the eastern Mediterranean adjacent to the Aegean Sea (Hirst, 1974; Show and Bush, 1978; Smith and Cronan, 1975; Perissoratis et al., 1987; Bodur and Ergin, 1988; Ergin et al,. 1988; Yücesoy and Ergin, 1992; Table 3), it is clear from the land geology that the mafic and ultramafic associations are the most likely sources of Cr and Ni enrichment in the studied sediment samples. The relationships among the geochemical variables (Fig. 11) suggest that considerable amounts of Cr and Ni are associated with the Fe and Mn phases, more likely in the clay-sized fractions of sediments, whereas carbonates show an inverse relationship due to the dilution effect.



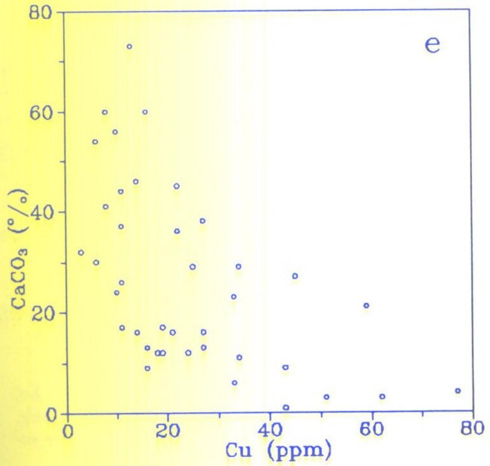


Fig. 8 - Plot of relationships between (a) Cu and Fe, (b) Cu and Mn (c) Cu and clay, (d) Cu and Corg, (e) Cu and $CaCO_3$ contents of the surface sediments.

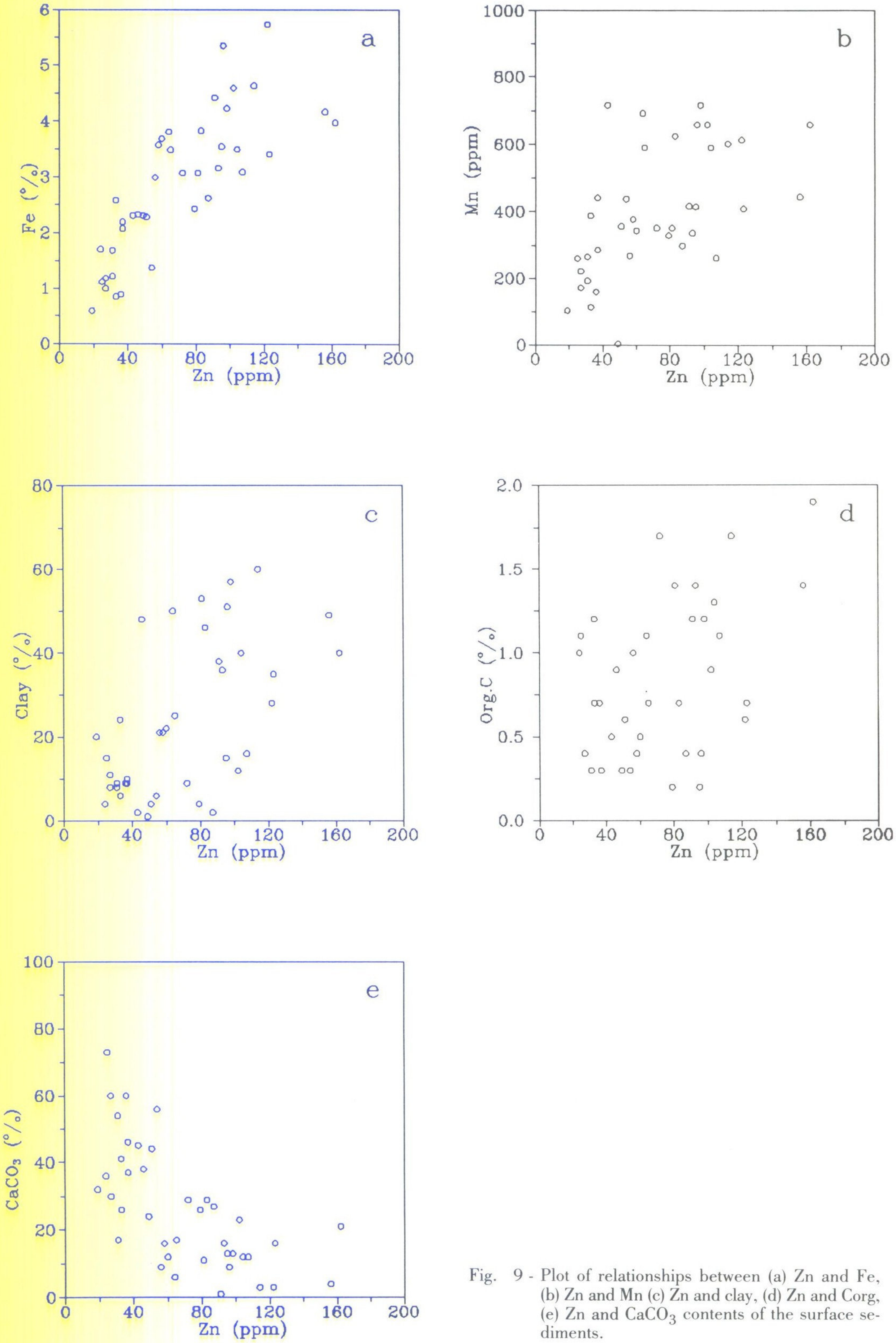


Fig. 9 - Plot of relationships between (a) Zn and Fe, (b) Zn and Mn (c) Zn and clay, (d) Zn and Corg, (e) Zn and $CaCO_3$ contents of the surface sediments.

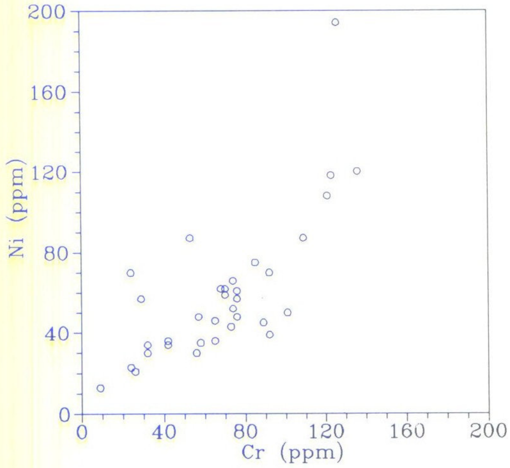


Fig. 10 - Plot of relationship between Cr and Ni contents of the surface sediments.

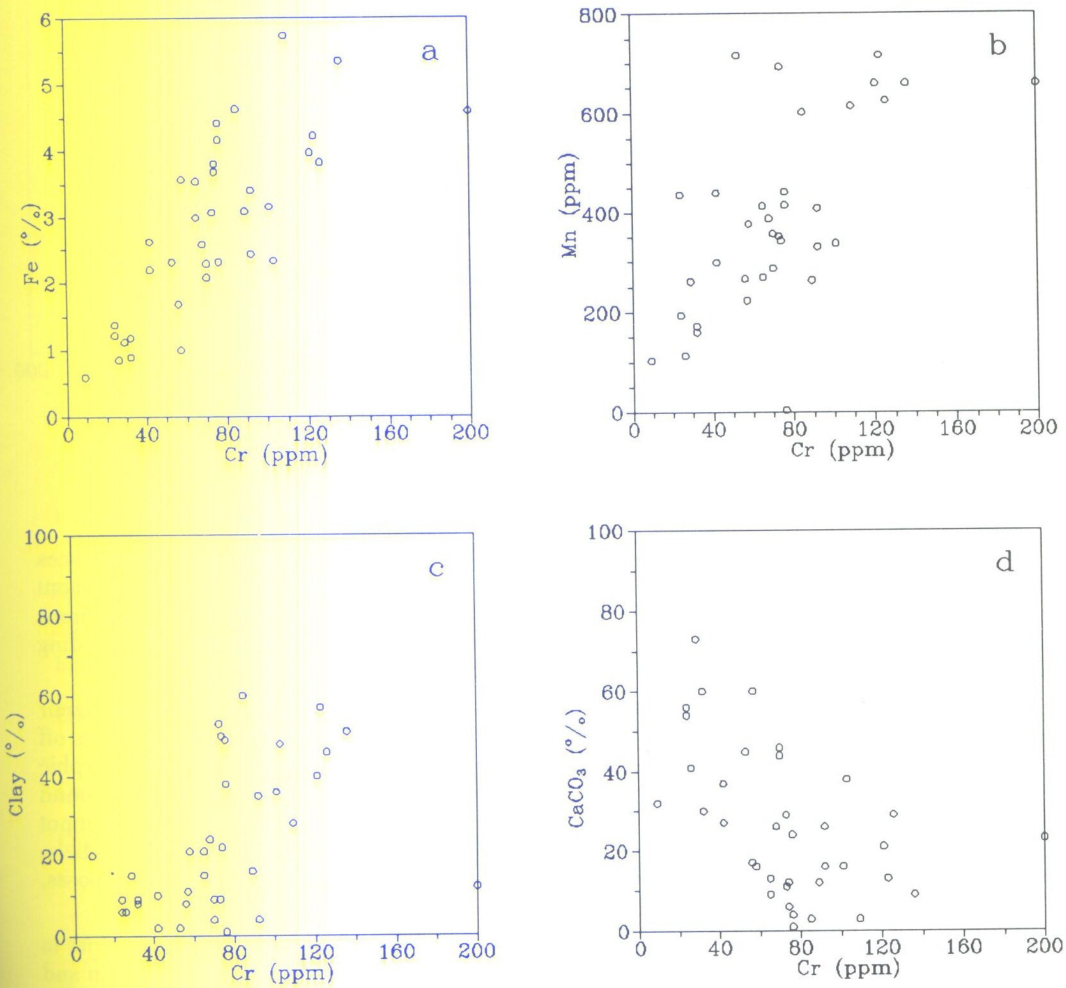
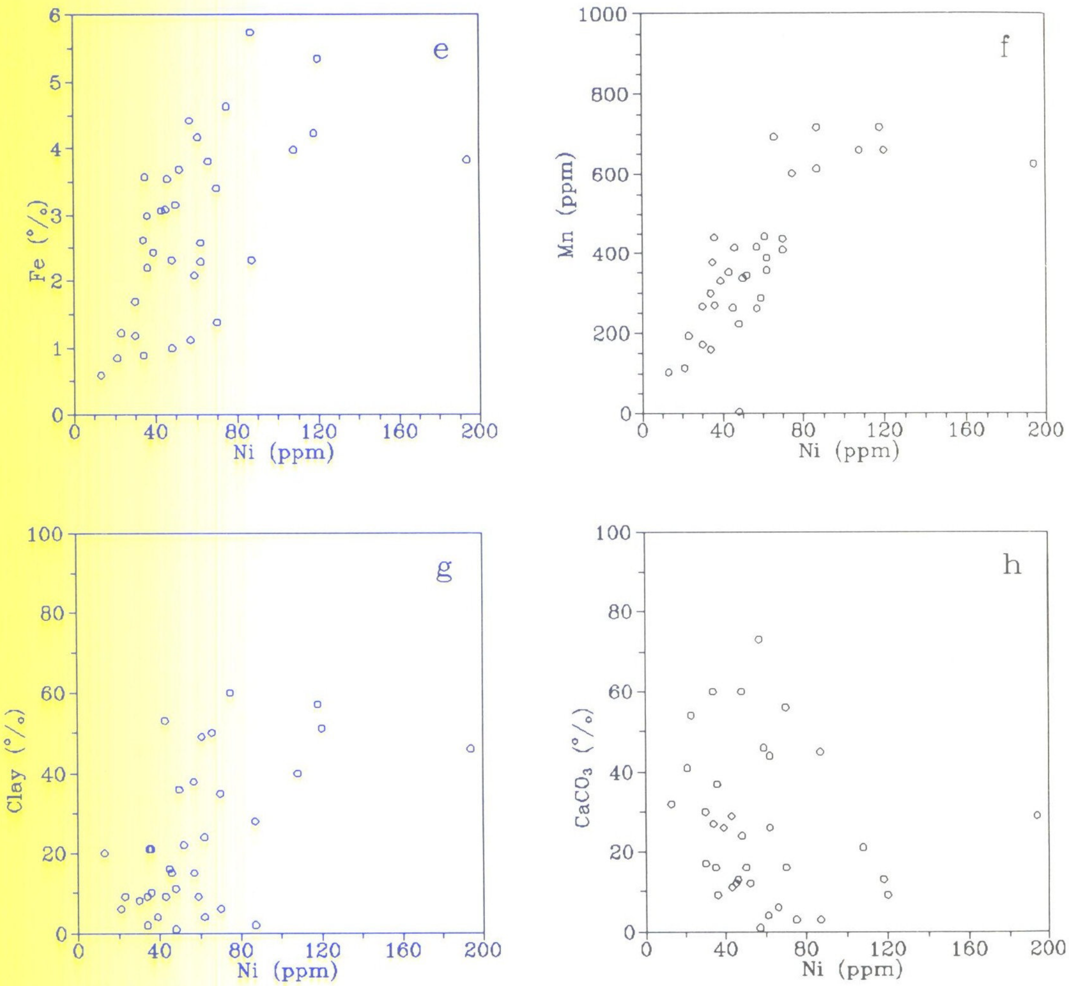


Fig. 11 - Plot of relationship between the contents of (a) Cr and Fe (b) Cr and Mn, (c) Cr and clay, (d) Cr and $CaCO_3$, (e) Ni and Fe, (f) Ni and Mn, (g) Ni and clay, (h) Ni and $CaCO_3$ in the surface sediments.



5. Conclusions

The results obtained in this study indicate that the distribution of heavy metal abundances in surficial shelf sediments of the eastern Aegean Sea are controlled by not only the sediment texture (fine-and coarse-grained dominance), and genetic types (terrigenous and biogenous dominance) but also by the proximity to distinct geological provenances in the surrounding hinterlands.

The somewhat high concentrations of Cu and Zn at the Meriç River mouth and inner Izmir Bay in part are thought to have resulted from anthropogenic influences. Fe concentrations off the Menderes and Gediz Rivers showed possible contributions from the Fe-rich metamorphic rocks (i.e., chlorite-bearing) of the Menderes Massif. Mn enrichment in the sediments around Marmaris Peninsula are probably due to the combined effects of increased terrigenous input from Mn-rich source rocks and diagenesis within the sediment. Cr and Ni appear to have been controlled, to a significant degree, by input from ultramafic rocks and associated chromite deposits, which are common on the coastal hinterland.

It should be pointed out, however, that future work is needed using core sediments to distinguish between the terrigenic, anthropogenic, and diagenetic influences prevailing in and around this poorly known, eastern Aegean Sea.

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