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Heavy-metal geochemistry of surface sediments from the southern Black Sea shelf and upper slope

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ABSTRACT

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A wide variety of sediment types (mud to sandy gravel) was obtained at fourty-seven stations on the southern Black Sea shelf and upper slope and analyzed for their heavy-metal geochemistry. Distribution of grain size, carbonates, organic carbon and heavy metals show marked changes in the topography, biological activity and land geology of the region studied.

Sediments constitued up to 39% $CaCO_3$, mainly of biogenic origin from the shell remains of benthic organisms. Organic carbon contents of the sediments (0.13–3.09%) usually reflect the prevailing primary productivities in the Black Sea although significant terrigenous influences are also inferred.

The heavy--metal concentrations largely indicate the influences from the geochemical weathering of terrigenous sources on land. In comparison with the average sedimentary rocks and other modern sediments from the adjacent regions, the concentrations of Cr, Ni, Cu, Zn and Pb are somehow higher in the surface sediments from the southern Black Sea. In particular, Cr, Ni and Cu are found in high abundances in the eastern parts of the study area. This is thought to reflect not only the well-mixed fine-grained nature of the sediments but also the possible contribution from metal-rich rocks (mafic and ultramafic sources) and associated economic mineral deposits in the catchment areas of rivers which drain this part of the coast. The presence of significant positive correlations between the concentrations of Cr and Ni, and Zn and Pb strongly suggest common sources and/or similar enrichment mechanisms for these metals. The relationships among the geochemical variables revealed that Fe and Mn (oxides, hydrates and sulfides), and organic phases together with the clay- and silt-sized grain fractions are the important associations of the studied heavy metals.

1. Introduction

The Black Sea with its world's largest anoxic basin is situated between the folded Alpine belts of the Caucasus and Crimea Mountains to the north and northeast and the North Anatolian Mountains ("Pontids") to the south, with an area of 432,000 km^2 and a volume of 534,000 km^3 (Ross et al., 1974; Fig. 1). To the south and southwest, the Strait of Bosphorus ("Istanbul Boğazı") connects the Black Sea to the Sea of Marmara, which in turn, is connected to the Aegean Sea and Mediterranean Sea (Fig. 1) through the Strait of Dardanelles ("Çanakkale Boğazı").

In contrast to the northern Black Sea shelves, which are up to 200 km wide and break at ~120-m depth, the southern shelf areas along the Turkish coasts rarely exceeds 20 km in width and break generally at 100-m depth. Similarly, the slopes of the Black Sea are generally smooth in the north, compared to the steep and highly-dissected slopes in the south (Ross et al., 1974; Fig. 2). The annual supply

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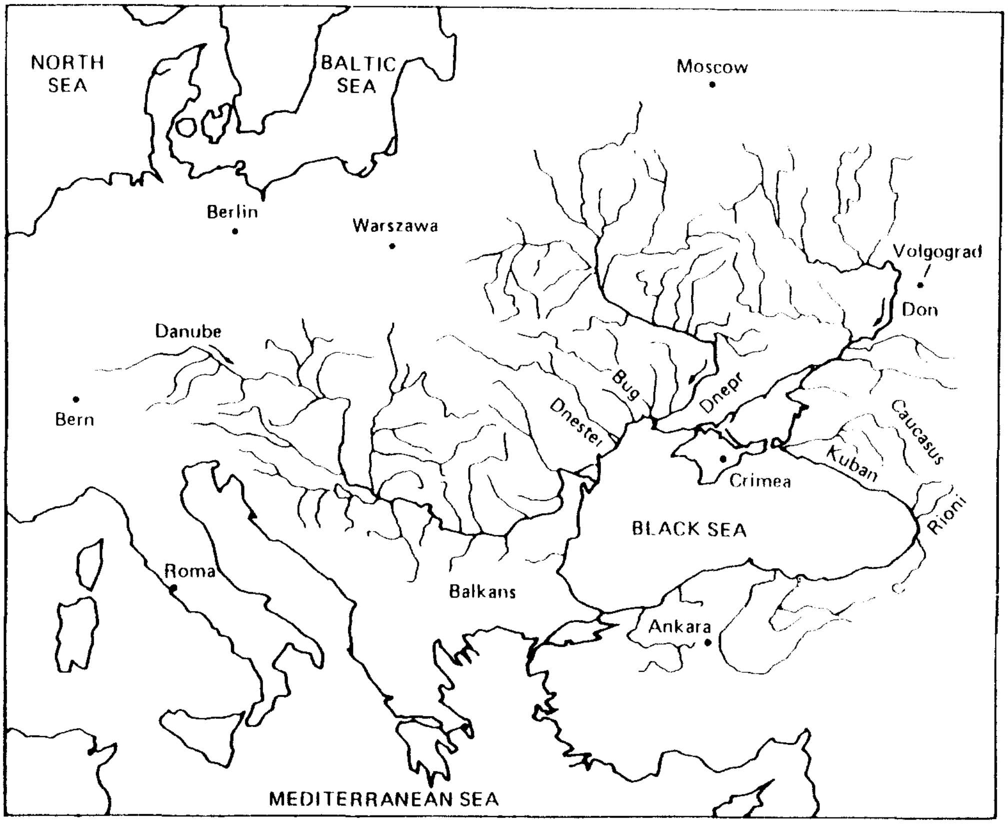


Fig. 1. Drainage area of the Black Sea (slightly modified after Müller and Stoffers, 1974).

of sedimentary material to the Black Sea by all debouching rivers amounts to $\sim 150 \cdot 10^6$ t* (Degens et al., 1980). About 15% drainage comes from the south, where relatively smaller but extremely erosive rivers (Kızılırmak, Yeşilırmak, Sakarya and Filyos) discharge into the Black Sea (Table 1). The average, annual rainfall in the southern Black Sea area is 90 mm and it is highest in winter, being ~ 130 mm (*Meteoroloji Bülteni*, 1984).

In general, two major cyclonic, and numerous mesoscale anticyclonic eddies largely control the circulation in the Black Sea (Shimkus and Trimonis, 1974; Oğuz et al., 1992a; Fig. 3). Particularly, along the topographic slope near the continental shelf, the speed of the cyclonic boundary currents increases up to 40 cm s^{-1} (Shimkus and Trimonis, 1974). Based on the salinity and temperature distribution, the Black Sea water column can be divided into three distinct water masses: (1) an upper layer (0–150 m, 17–18.5-ppt salinity); (2) a cold intermediate layer (100–200 m, 6.5–8.0°C), part of a larger intermediate layer (200–1000 m, >21-ppt salinity, >8.5°C); and (3) a bottom/deep convective layer (>1000 m; 22.2–22.3-ppt salinity; 9–9.2°C) (Ovchinnikov and Popov, 1986; Oğuz et al., 1990, 1992a). Due to the presence of a strong halocline which separates the less saline (18 ppt) and oxygen-rich surface waters (0–100 m in offshore, and 0–200 m in near-coastal waters) from the saltier (22 ppt) and poorly-oxygenated subsurface waters, there exists a permanent lack of vertical mixing, and thus, anoxic conditions are prevailing in the Black Sea (Emery and Hunt, 1974; Oğuz et al., 1990). At the lower bound-

*1 t = 1 metric tonne = 10^3 kg.

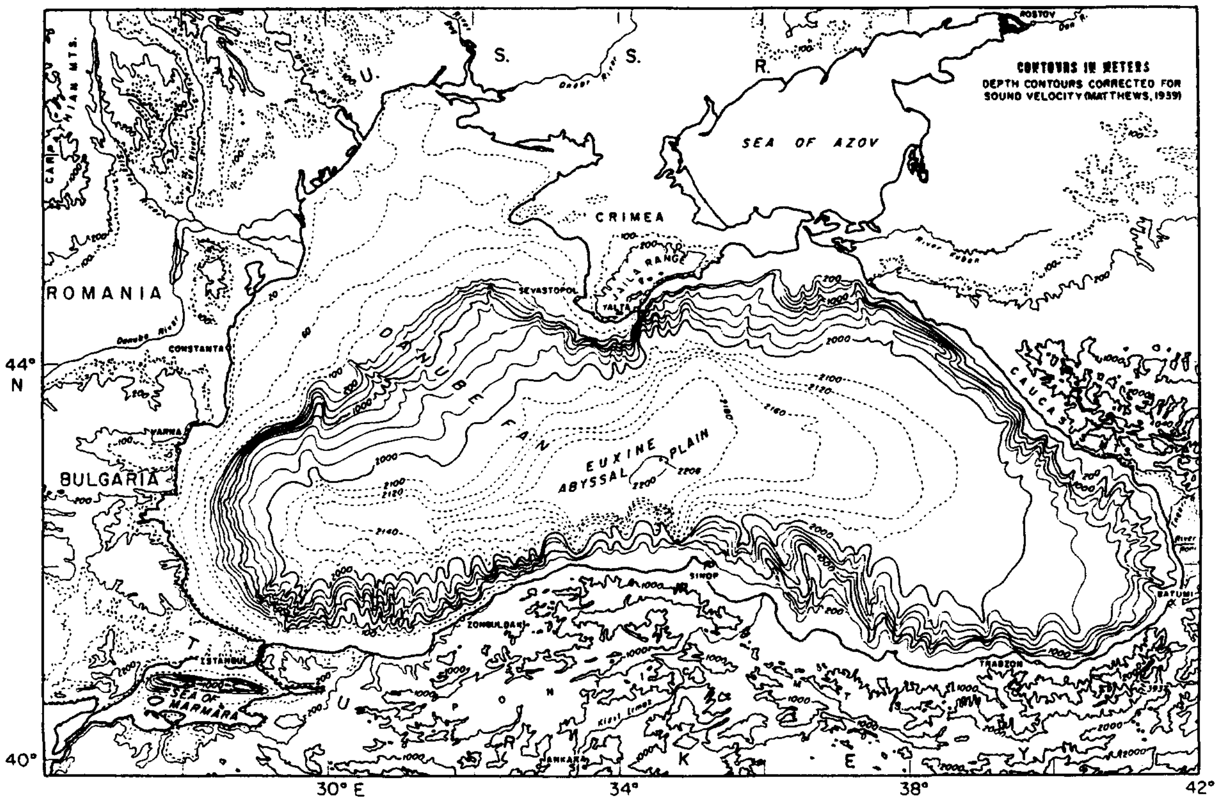


Fig. 2. Bathymetry of the Black Sea (from Ross et al., 1974).

TABLE 1

Discharges of the main rivers into the southern Black Sea [compiled from EIE (1981, 1989) and DSI (1987)]

River/stream	Drainage area (km^2)	Annual flow rate ($m^3 s^{-1}$)	Annual solid discharge ($mg l^{-1}$)	Annual organic matter discharge (ppm)
Sakarya	56,869	19– 977 (226)	10– 5,790 (528)	0.5 -3.2
Filyos	13,300	3–2,780 (123)	6– 7,210	0.00–5.00
Yeşilırmak	37,421	14–1,914 (155)	0– 7,350 (317)	0.00–3.00
Kızılırmak	76,238	18–1,673 (187)	138–17,641	0.00–7.40
Malet	1,859	1–1,140 (26)	n.d.	0.00–7.40
Değirmen	737	1– 224 (10)	n.d.	n.d.
Iyidere	855	4– 504 (28)	2– 1,760	0.00–8.60
Fırtına	940	4– 560 (28)	n.d.	n.d.

Numbers between parentheses indicate average values. n.d. = not determined.

ary of the halocline, the oxygenated zone passes into a redox-gradient zone (also called "transition" or "intermediate" zone) (Sorokin, 1983). The vertical O_2 distribution measured in the study area is illustrated in Fig. 4. Further hydrographic characteristics of the Black Sea have been described by Murray et al. (1991) and Oğuz et al. (1992b).

Numerous studies dealing with petrology and geochemistry of the Recent Black Sea sediments have been carried out and the results are presented in works of, for example, Ross and

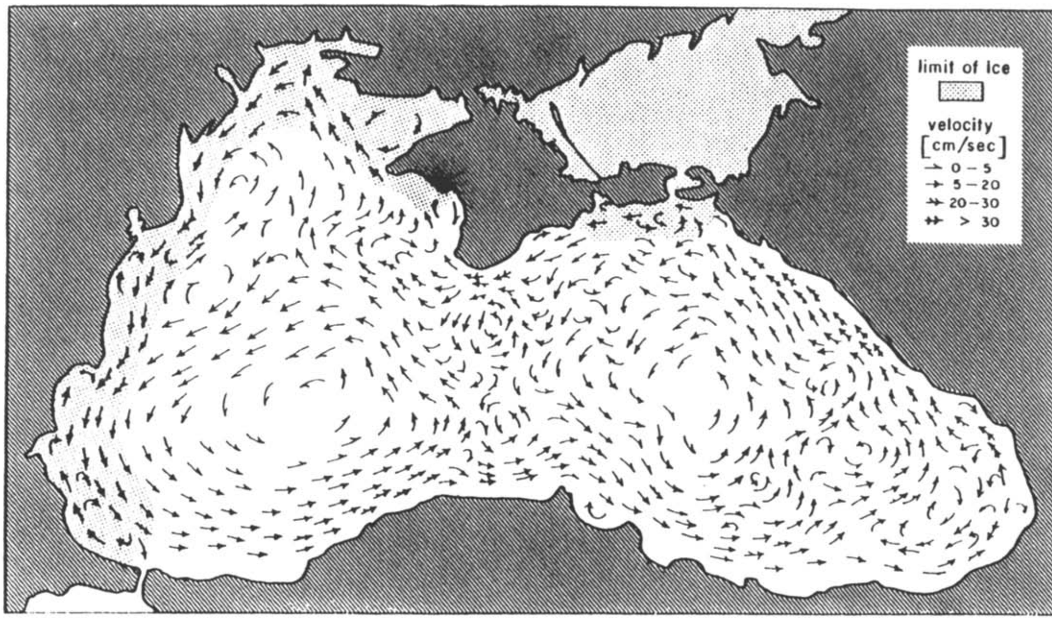


Fig. 3. Current system in the Black Sea (from Shimkus and Trimonis, 1974).

Degens (1974), Baykut et al. (1982), Saltoğlu et al. (1986), Degens et al. (1987), Hay (1988), and Hay et al. (1990). However, relatively little is known about the heavy-metal geochemistry of surficial Black Sea sediments adjacent to the North Anatolian coasts. The main purpose of this study is to understand the mechanisms of incorporation of the heavy metal to sediments and to constrain the primitive source of heavy metals in surface sediments from the southern Black Sea shelf and upper slope. More specifically, it involves the regional variations in lithology, bottom topography, and associated hydrodynamic and biologic conditions.

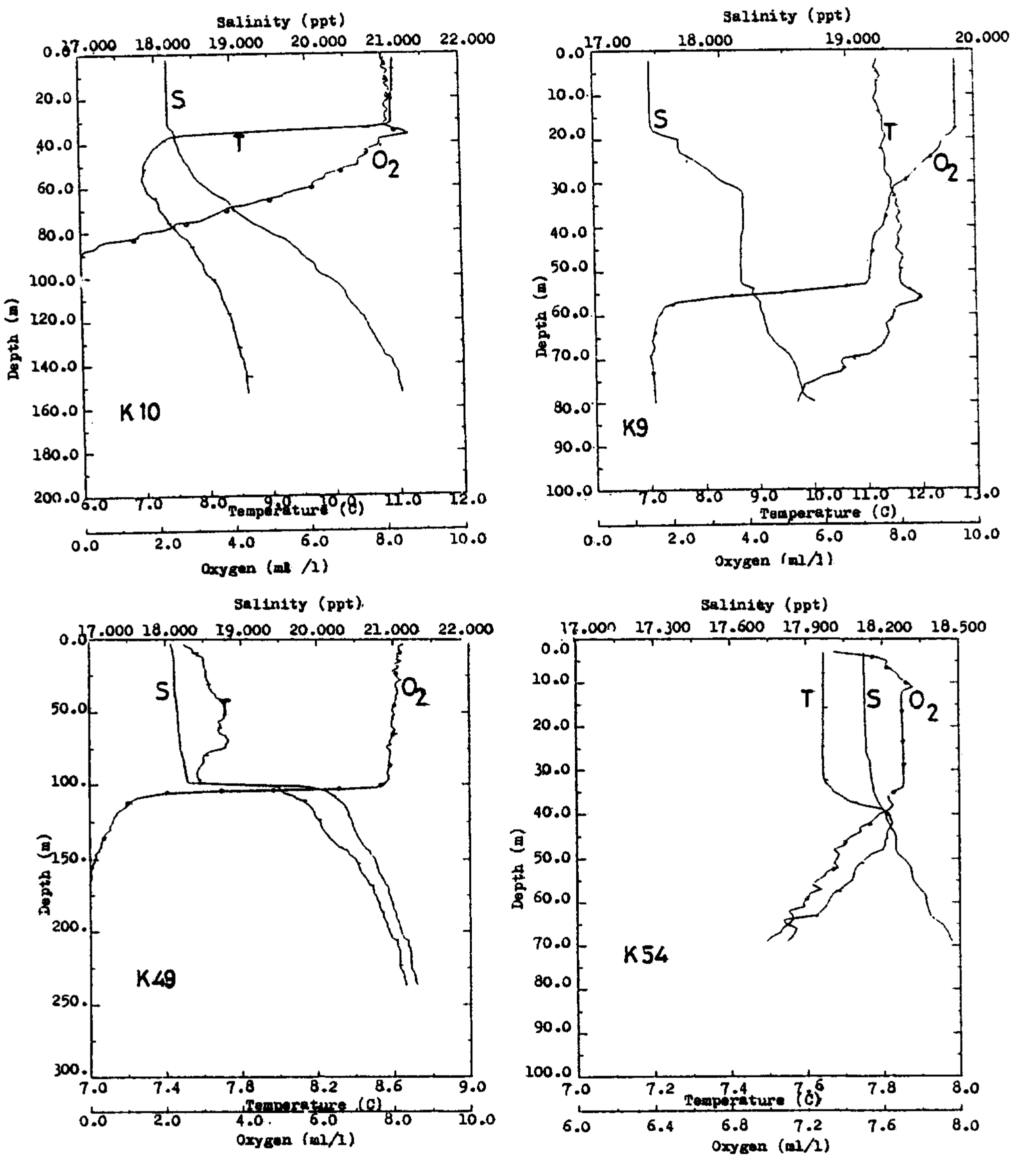
2. Method and materials

The material used in this investigation was collected during the 1988–1989 cruises of IMS–METU on the southern Black Sea shelf and upper slope aboard the R/V "Bilim". Fourty-seven surface sediment samples were obtained using a Dietz Lafonde® grab (~10 cm^3) from 47 stations (Fig. 5; Table 2). Of these, six samples are taken from relatively reducing environments (stations K*10*, F*45*, K*49*, K*68*, K*45* and K*75*) while the remaining samples represent oxygenated environments (stns. K*8*, K*9*, KO, B*15*, KOC, F*43*, F*36*, S*5*, F*44*, K*44*A, F*46*, F*38*, K*54*, F*16*, K*83*, P*86*, K*47*), as inferred from the available oxygen profiles in the study area (i.e. Fig. 4). In general, the sediment samples used here correlate with the Holocene lithologic Unit *1* (Arthur et al., 1988) which must been have deposited during the last 1000 yr B.P. in the Black Sea (Hay, 1988). Immediately after collection, sediment samples were stored in plastic bags in a freezer until the end of the cruise. Granulometric analyses have been made using standard sieve and pipette analysis techniques (Folk, 1974; Lewis, 1984). Total organic carbon levels were determined by titration with dichromate (Gaudette et al., 1974; accuracy is ±0.25%). Total carbonate contents were determined by treating ground dry sample with 10% HCl and measurement of the CO_2 released from the samples (absolute error is ±0.5%). Analar grade $CaCO_3$ and several organic substances are used as standard. To determine the concentrations of the heavy metals Fe, Mn, Cr, Ni, Cu, Co, Pb and Zn, dried and ground bulk sediment samples were prepared using combined HF–HNO_3 digestion. All the samples were then analyzed by an atomic absorption spectrophotometer (Varian® model AA-*6*), some in dublicate or triplicate. International standards, such as CRM *142* from the CBR (Community Bureau of Reference) and blanks were included in each set of samples to check the precision and accuracy of the analysis. The analytical precision was normally better than ±1% for Cr, Ni, Zn, Co and Cu (Table 3). Precision was ±3% for Fe and Mn, and ±4% for Pb.

3. Results and discussion

3.1. Sediment texture

The results of grain-size analysis are summarized in Fig. 6 and Table 4. The surface sed-



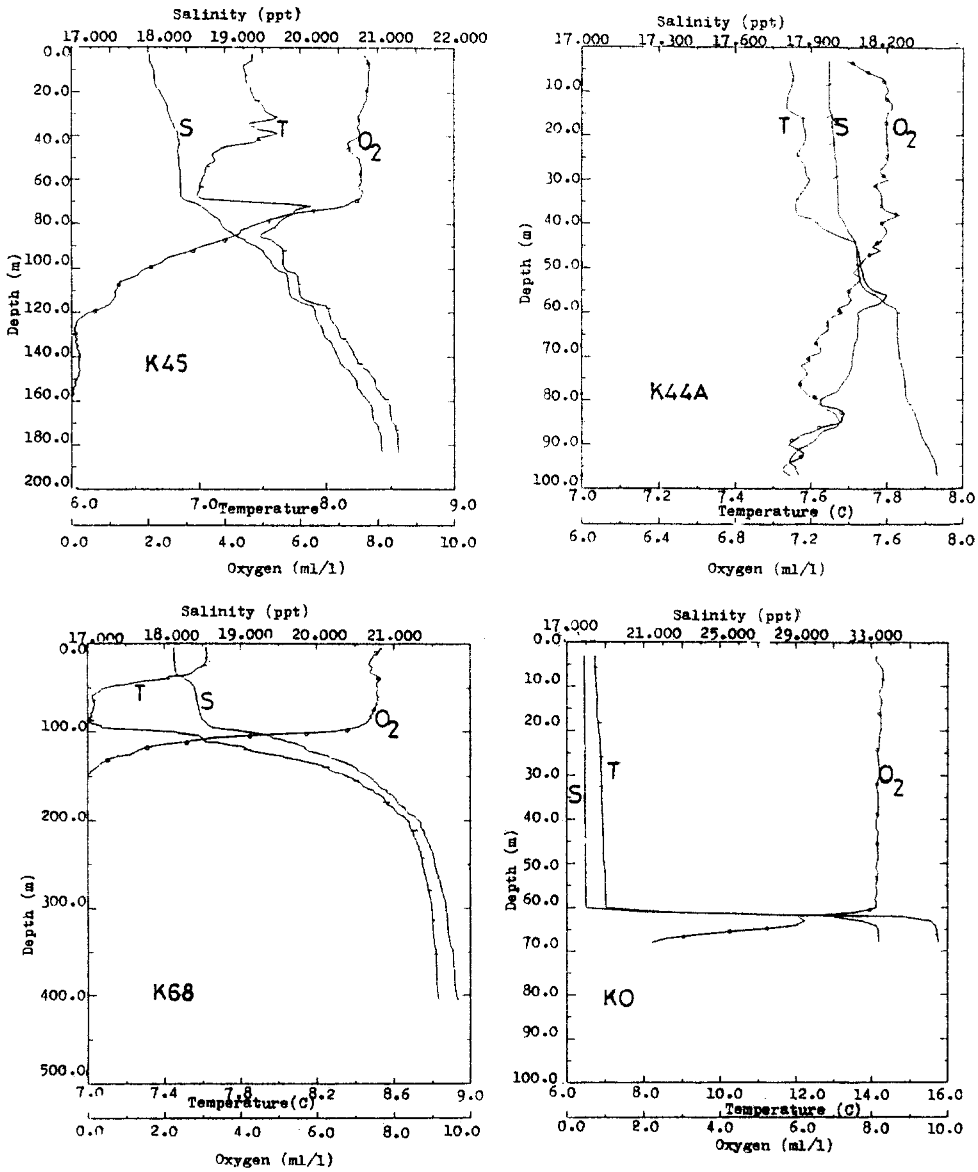


Fig. 4. Typical profiles of salinity, temperature and dissolved oxygen at some stations of this study in the southern Black Sea obtained during winter 1989 (IMS-METU, unpublished data). T=temperature; S=salinity; O_2=dissolved oxygen.

iments of the investigated area were found to consist of a wide variety of textural classes, from mud to sandy gravel (Table 4). Detailed microscopic investigations of the sand and gravel fractions of the sediment samples revealed that both terrigenous and biogenic materials are present in varying abundances (Table 5).

Pelecypods, gastropods, bryozoa and foraminifera are the main biogenic constituents. Quartz, feldspars, micas, and fragments of igneous, metamorphic and carbonate rocks, on the other hand, appear in substantial amounts to represent the terrigenous constituents (Yücesoy, 1991).

In general, sediments from the eastern parts

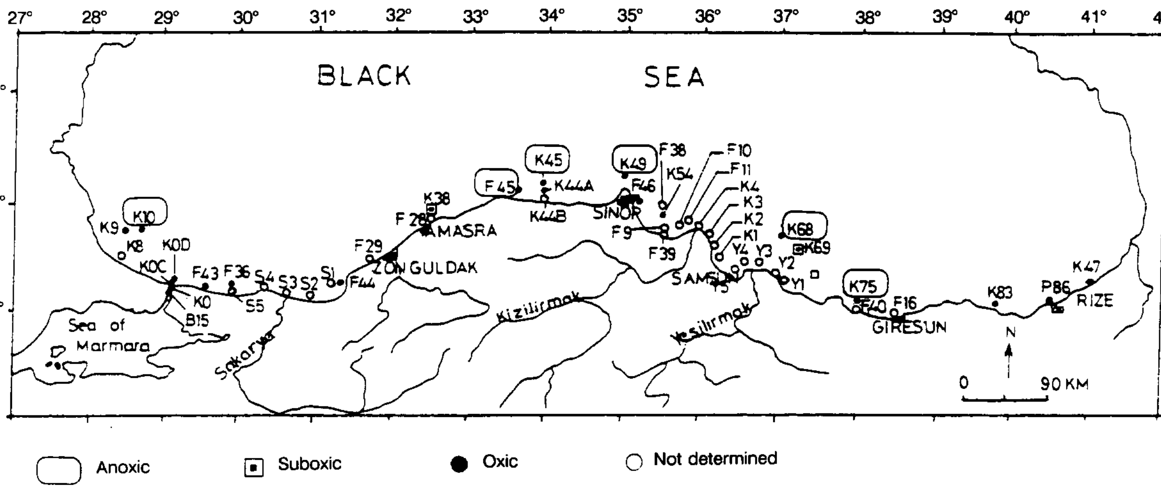


Fig. 5. Locations of the surface sediment samples used in this study.

of the southern Black Sea, particularly off the mouths of major rivers, the Kızılırmak (stns. K*4*–K*1*) and Yeşilırmak (stns. Y*5*–Y*1*), are characterized by relatively high mud (clay plus silt) portions (94–99% of the bulk sample; Fig. 6), which can be attributed to the contributions of high sediment loads from these two rivers. Similarly, sediment samples from the Sakarya River mouth (stns. S*1*–S*4*) displayed relatively high mud contents (Fig. 6). High mud percentages are also prominent in sediments from relatively deeper waters (stns. K*10*, F*45*, K*45*, K*44*A, K*49*, F*38*, K*68*, K*75*; Fig. 6; Table 4) and in areas (e.g., stns. K*9*, K*38*) of quite depositional conditions. On the other hand, coarse sediments (sand and gravel dominant) from the Bosphorus (stns. B*15*, KOC, KOD) and eastern Rize (stn. F*47*) regions are mainly of terrigenions origin, indicating the prevailing topography-related high-energy conditions in these waters. Exceptions are stns. K*69* (off the Yeşilırmak River mouth) and P*86* (off Rize), where benthic activities and the associated coarse sediments are prominent. Other stations (F*43*, S*5*, F*46*) with coarse-grained bottom deposits seem to be controlled by both terrigenous and biogenic factors (Table 5).

3.2. Carbonate distribution

Total carbonate contents (% $CaCO_3$) of the bulk sediment samples range from < 1% to 39% (Table 4), whereby the majority of the values fall between 5% and 15% (Fig. 7). Highest carbonate percentages (>20% $CaCO_3$) are obtained in the samples from stns. F*46*, K*69*, F*43*, KOD, KOC and B*15* where biogenic calcareous components and carbonate rock fragments are found to be sufficient in the coarse sediment fractions to form such $CaCO_3$ percentages.

3.3. Organic carbon distribution

Total organic carbon contents of the bulk sediment samples vary between 0.13% and 3.09% (avg. 1%; Table 4; Fig. 8). These values are similar to those from the southern Black Sea previously reported elsewhere (1–2%; Rozanov et al., 1974; Shimkus and Trimonis, 1974) but higher than those found in the Aegean and Eastern Mediterranean Seas (0.28–0.80%; Emelyanov, 1972; Voutsinou-Taliadouri and Satsmadjis, 1982; Ergin et al., 1988, 1990). In general, this can be explained by the primary productivity rates, which are rela-

TABLE 2

Locations of the studied surface sediment samples

Station	Depth (m)	Location	
		lat. (°′″N)	long. (°′″E)
K8	76	41 30 00	28 30 00
K9	80	41 45 00	28 32 30
K10	212	41 45 20	28 45 33
B15	75	41 12 55	29 07 20
KO	70	41 13 36	29 07 58
KOC	56	41 15 10	29 09 50
KOD	70	41 15 37	29 10 10
F43	30	41 12 51	29 27 08
F36	58	41 14 00	30 00 00
S5	46	41 11 00	30 00 00
S4	63	41 13 00	30 22 50
S3	32	41 08 48	30 39 30
S2	95	41 10 06	31 00 00
S1	82	41 14 00	31 16 00
F44	18	41 16 25	31 23 25
F29	79	41 28 00	31 44 00
K38	80	41 50 00	32 30 00
F28	77	41 49 30	32 30 00
F45	220	42 05 00	33 37 00
K45	200	42 11 00	34 00 00
*K44*A	103	42 05 00	34 00 00
*K44*B	50	42 01 30	34 00 00
K49	310	42 12 30	35 00 00
F46	17	42 01 00	35 09 10
F38	101	41 55 00	35 30 00
K54	78	41 45 00	35 30 00
F9	45	41 40 00	35 30 00
F39	28	41 39 30	35 30 00
F10	45	41 44 00	35 43 30
F11	40	41 46 18	35 48 42
K4	8	41 45 48	35 57 30
K3	60	41 39 30	36 07 36
K2	116	41 35 00	36 13 36
K1	55	41 26 30	36 16 00
Y5	49	41 20 00	36 30 00
Y4	100	41 24 30	36 39 00
Y3	53	41 23 42	36 52 00
Y2	64	41 20 00	37 00 00
K68	445	41 39 00	37 05 00
Y1	82	41 16 12	37 08 00
K69	150	41 30 00	37 15 00
K75	330	41 05 00	38 00 00
F40	63	41 00 00	38 00 00
F16	49	40 55 30	38 22 42
K83	36	41 01 00	39 46 00
P86	20	41 03 18	40 31 00
F47	8	41 12 30	41 00 00

TABLE 3

Accuracy of the method using BCR standard CRM *142*

	Standard value	This study
Co	(7.9)	7.6±2.0
Cr	(74.9)	75.7±1.0
Cu	27.5±0.6	27.4±0.3
Mn	(569)	583.5±3.1
Ni	29.2±2.5	30.7±1.0
Pb	37.8±1.9	39.4±1.6
Zn	92.4±4.4	92.0±1.4
Fe_2O_3	(28.0)	27.2±0.1

Data are given in ppm except for Fe_2O_3. See text for reproducibilities. ( ) = not certified value.

tively high in the Black Sea (52–250 g m^{-2} yr^{-1} C; Sorokin, 1964, 1983; Göçmen, 1988) but low in the Aegean and Mediterranean waters (24–25 g m^{-2} yr^{-1} C; Murdoch and Onuf, 1974). Water exchanges between the organic-rich Black Sea and organic-poor Eastern Mediterranean Sea are already recognized in the Recent bottom sediments of the transitional Marmara Sea (0.20–1.72% C_{org}; Ergin et al., 1991a).

The highest C_{org} concentration (3.09%) was obtained in sample from stn. *F40* (63-m water depth) where abundant wood and plant remains are found to be derived from the land-based sources. This appears to be in good agreement with the organic matter data obtained in rivers draining into the southeastern Black Sea (Table 1), where the terrigenous input of organic matter can be more important than that of the marine production. Other high C_{org} values (2.23% at stn. K*10* at 212-m depth and 2.60% at stn. K*68* at 445-m depth) are associated with the high mud contents (up to 99%) of sediments which are typically for the the anoxic, deeper waters of Black Sea (Shimkus and Trimonis, 1974). Of course, this should have also resulted from the differences in availability of organic matter to microbial degradation, whereby terrestrial organic matter from nearshore waters is somewhat more

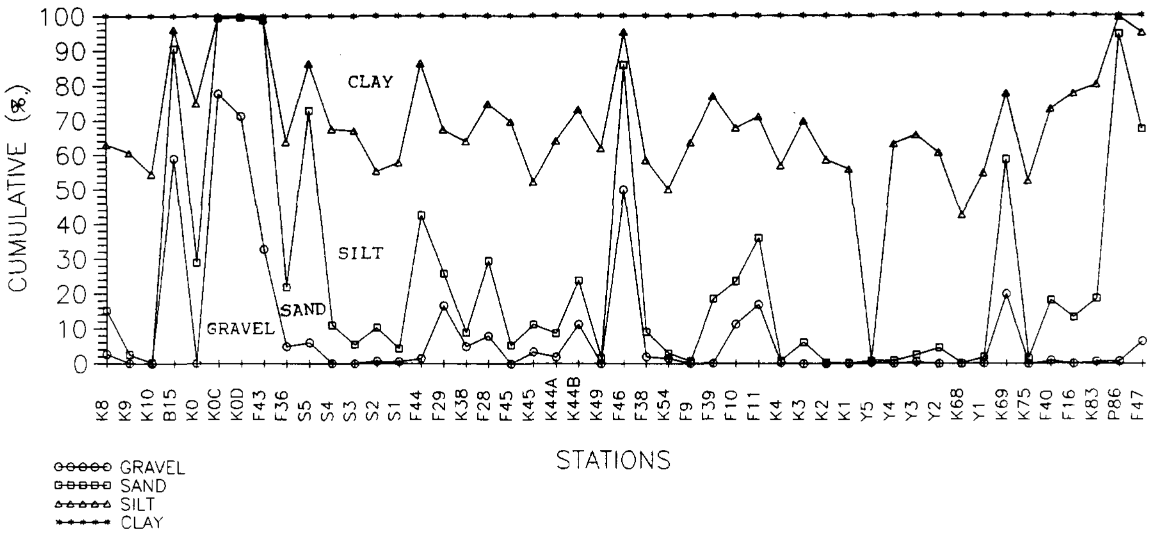


Fig. 6. Cumulative grain-size distribution in the surface sediments along the southern Black Sea.

resistant relative to marine organic matter from offshore waters (Glenn and Arthur, 1985).

Compared to relatively oxidizing sediments from stns. K*8* (1.51% C_{org}), K*9* (1.30%), F*38* (1.20%), the reducing sediment samples from stns. F*45* (1.13%), K*49* (1.54%), K*75* (1.35%), etc., do not clearly indicate organic carbon enrichment within the sediment, although the reducing sediments in the deeper Black Sea waters are known to contain significantly high organic matter (Volkov and Fomina, 1974). However, in relatively shallower waters, the additional quantity of reduced forms of reactive iron may lead to the loss of organic matter so that the contents of organic matter in both oxidizing and reducing sediments may remain nearly similar (Rozanov et al., 1974). Apparently, and apart from this, the recent results indicate to be a prerequisite for the preservation of organic matter in bottom sediments (Calvert et al., 1991). The proximity of sampling stations to the nearshore and, thus, the abundant organic influxes from the land-based sources may contribute increased amounts of organic matter to the sediments in order to mask the effects of oxidizing/reducing conditions, particularly in the studied shelf regions.

3.4. Heavy-metal distribution

Results of analyses for the studied heavy metals are shown in Table 6 and Fig. 9.

. In comparison with the average composition for sedimentary rocks, the southern Black Sea sediments, in general, are similar in their Fe, Co and Mn concentrations (Table 7) and thus, the deviations from them suggest differences in the types and amounts of the lithogenic and biogenic admixtures. However, the concentrations of Cr, Ni, Cu, Zn and Pb in the southern Black Sea sediments are markedly higher than those found in average sedimentary rocks (Table 7). In particular, Cr, Ni and Cu, and to a lesser degree, Fe and Mn appear to be more abundant in sediments from the eastern part of study area (Fig. 9). This is thought to reflect not only the well-mixed fine-grained nature of the sediments (Fig. 6) but also the presence of economic mineral deposits as associated with the mafic and ultramafic rocks in the catchment areas of the rivers (Fig. 10) which drain this part of the coast, and these provide a ready source of clastic material most probably rich in Cr, Ni, Cu, Mn and Fe.

Although there are no data available on the

TABLE 4

Grain-size distribution in sediment samples (textural sediment classification after Folk, 1974)

Station	Depth (m)	Gravel (%)	Sand (%)	Mud (%)	Silt (%)	Clay (%)	$CaCO_3$ (%)	C_{org} (%)	Textural classification
K*8*	76	3	12	85	48	37	10	1.51	slightly gravelly sandy mud
K*9*	80	< 1	2	97	58	39	4	1.30	slightly gravelly mud
K*10*	212	< 1	< 1	99	54	45	5	2.23	mud
B*15*	75	59	32	9	5	4	28	0.25	muddy sandy gravel
KO	70	< 1	28	71	46	25	2	1.03	slightly gravelly sandy mud
KOC	56	78	21	< 1	< 1	< 1	33	0.13	sandy gravel
KOD	70	71	28	< 1	< 1	< 1	29	0.18	sandy gravel
F*43*	30	33	66	1	< 1	< 1	30	0.16	sandy gravel
F*36*	58	5	17	78	42	36	8	1.41	slightly gravelly sandy mud
S*5*	46	6	67	27	13	14	15	0.53	gravelly muddy sand
S*4*	63	< 1	10	89	57	32	6	1.61	slightly gravelly sandy mud
S*3*	32	< 1	5	94	61	33	8	0.73	slightly gravelly mud
S*2*	95	1	10	89	45	44	8	1.02	slightly gravelly mud
S*1*	82	1	4	95	53	42	8	0.89	slightly gravelly mud
F*44*	18	2	41	57	44	13	4	0.80	slightly gravelly sandy mud
F*29*	79	17	9	74	41	33	9	1.25	gravelly mud
K*38*	80	5	4	91	55	36	14	0.95	slightly gravelly mud
F*28*	77	8	22	70	45	25	12	1.00	gravelly mud
F*45*	220	< 1	5	95	65	30	5	1.13	mud
K*45*	200	3	8	89	41	48	15	1.28	slightly gravelly mud
K*44*A	103	2	7	91	55	36	9	0.97	slightly gravelly mud
K*44*B	50	11	13	76	49	27	10	0.99	gravelly mud
K*49*	310	< 1	2	98	60	38	7	1.54	mud
F*46*	17	50	36	14	9	5	39	0.52	muddy sandy gravel
F*38*	101	2	7	91	49	42	9	1.20	slightly gravelly mud
K*54*	78	2	1	97	47	50	10	1.06	slightly gravelly mud
F*9*	45	< 1	< 1	99	63	36	10	1.17	mud
F*39*	28	< 1	18	81	58	23	6	1.33	sandy mud
F*10*	45	11	13	76	44	32	20	0.96	gravelly mud
F*11*	40	17	19	64	35	29	16	0.81	gravelly mud
K*4*	8	< 1	< 1	99	56	43	5	0.69	slightly gravelly mud
K*3*	60	< 1	6	94	64	30	6	0.65	mud
K*2*	116	< 1	< 1	99	58	41	5	0.83	mud
K*1*	55	< 1	< 1	99	55	44	6	0.88	mud
Y*5*	49	< 1	< 1	99	48	51	6	0.89	slightly gravelly mud
Y*4*	100	< 1	1	99	62	37	6	0.81	mud
Y*3*	53	1	2	97	63	34	6	0.72	slightly gravelly mud
Y*2*	64	< 1	4	96	56	40	5	0.99	mud
K*68*	445	< 1	< 1	99	42	57	11	2.60	mud
Y*1*	82	< 1	2	98	53	45	6	0.89	slightly gravelly mud
K*69*	150	20	39	41	19	22	33	0.76	gravelly mud
K*75*	330	< 1	2	98	51	47	4	1.35	mud
F*40*	63	1	17	82	55	27	1	3.09	slightly gravelly sandy mud
F*16*	49	< 1	13	87	664	23	2	1.40	sandy mud
K*83*	36	1	18	81	61	20	3	1.19	slightly gravelly sandy mud
P*86*	20	1	94	5	5	< 1	1	0.16	slightly gravelly sand
F*46*	8	6	61	33	28	5	3	0.61	gravelly muddy sand

metal fluxes from the rivers, it is not hard to imagine that the contents of Cr, Ni, Cu, Mn and Fe in the sediments show anomalies related to particular geological sources and their weathering products. For instance, the relatively high Fe contents determined in sedi-

TABLE 5

Relative proportion of the biogenic and terrigenous components in the sand and gravel fractions of sediment samples

Station	Sand fraction		Gravel fraction	
	biogenic	terrigenous	biogenic	terrigenous
K*8*	91	9	100	–
K*9*	25	75	100	–
K*10*	9	91	–	–
B*15*	5	95	64	36
KO	9	91	71	29
KOC	8	92	41	59
KOD	5	95	62	38
F*43*	8	92	85	15
F*36*	57	43	100	–
S*5*	11	89	90	10
S*4*	15	85	100	–
S*3*	1	99	100	–
S*2*	49	51	100	–
S*1*	51	49	100	–
F*44*	1	99	100	–
F*29*	75	25	100	–
K*38*	76	24	100	–
F*28*	61	39	99	1
F*45*	13	87	–	–
K*45*	66	34	100	–
K*44*A	86	14	100	–
K*44*B	58	42	100	–
K*49*	62	38	–	–
F*46*	45	55	74	36
F*38*	54	46	98	2
K*54*	76	24	96	4
F*9*	39	61	–	100
F*39*	3	97	14	86
F*10*	94	6	100	–
F*11*	94	6	100	–
K*4*	19	81	100	–
K*3*	8	92	–	–
K*2*	18	82	–	–
K*1*	29	71	–	–
Y*5*	75	25	100	–
Y*4*	7	93	–	–
Y*3*	30	70	100	–
Y*2*	5	95	–	–
K*68*	48	52	–	–
Y*1*	25	75	100	–
K*69*	92	8	99	1
K*75*	14	96	–	100
F*40*	3	97	–	100
F*16*	7	93	–	–
K*83*	1	99	50	50
P*86*	17	83	100	–
F*47*	2	98	–	–

ments from the eastern part of study area (mostly $>4\%$; Table 6), where important occurrences of heavy-mineral deposits such as magnetite- and ilmenite-rich placers are reported, derived from Cretaceous to Tertiary mafic rocks (Gümüş, 1979). Mn concentrations are relatively high not only in the east but also in the west (Fig. 9). The latter is possibly related to the post-orogenic, volcanogenic–sedimentary deposits of Paleozoic–Tertiary age which crop out along the coastal hinterland of the southwestern Black Sea (Fig. 10; Gümüş, 1979).

The maximum Mn content (1064 ppm) was found at stn. F*44* (Fig. 9) which is located off the Ereğli–Zonguldak coast where Mn- and coal-mining activities are very important (Gümüş, 1979; Ketin, 1983). Similarly, but to a greater degree, Cr and Ni contents of sediments are generally high in the eastern part of study area (Fig. 9). As compared with other coastal parts of Turkey where ophiolitic series from the hinterland are the major sources of Cr and Ni in the marine sediments (Shaw and Bush, 1978; Bodur and Ergin, 1988; Ergin et al., 1992), the ophiolitic rocks show limited distribution on the Black Sea coasts. Here, the occurrences of mafic/ultramafic rocks/minerals of Cretaceous to Tertiary ages and the ilmenite–magnetite placers with chromite and other heavy-mineral associations along the southeastern Black Sea coasts/coastal hinterland (Göksu et al., 1974; Gümüş, 1979) are most likely the important supplier of Cr and Ni to the sediments. It has been well known that ultramafic rocks and their associations are characterized by an unusually high content of Cr and Ni (Rose et al., 1979). In addition, Ni, in part, may also be derived from the pyrite–chalcopyrite veins which are of economic value and thus, commonly mined along the coastal hinterland southeast of the Black Sea (Gümüş, 1979). Most ultramafic rocks in Turkey are irregularly distributed and normally belong to the Alpine tectogenic events during the Paleo-

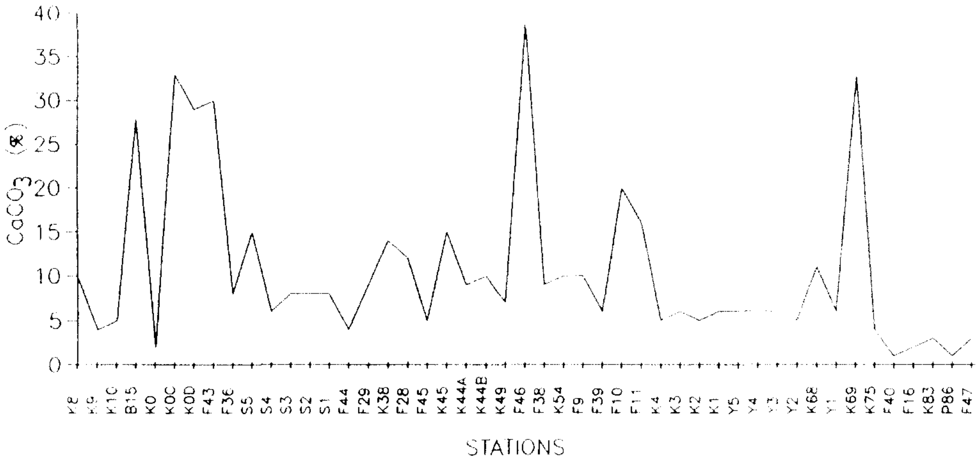


Fig. 7. $CaCO_3$ distribution in the surface sediments along the southern Black Sea.

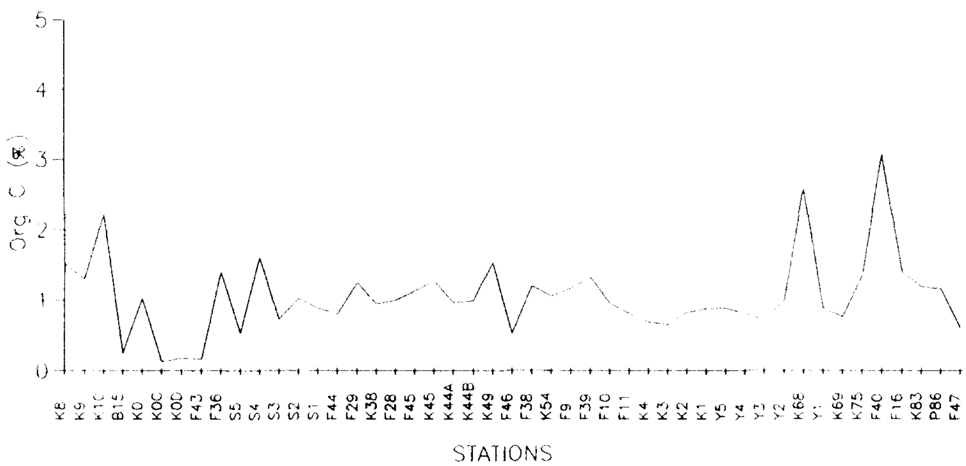


Fig. 8. Organic carbon distribution in the surface sediments along the southern Black Sea.

zoic, Mesozoic and Tertiary periods (Brinkman, 1976; Ketin, 1983).

The highest Cu contents are found in sediments from the eastern part of the study area (Fig. 9). In contrast to the western parts, the eastern parts of study area, namely its coastal hinterland, is marked by economically important cupriferous sulfide (pyrite, chalcopyrite, bornite) mines related to Cretaceous to Tertiary volcanic/post-volcanic activities (Göksu et al., 1974; Gümüş, 1979). For example, the maximum Cu content was found at stn. K*69* (82 ppm) where the Yeşilırmak River enters the southern Black Sea and its drainage basin contains important occurrences of Cu from ophiolitic volcanism and related hydrothermal deposits (Gümüş, 1979). In general, the coastal hinterland of the southeastern Black Sea is referred as the Eastern Black Sea metallogenic province of Cu which is associated with Cretaceous–Tertiary volcanic rocks (Brinkman, 1976; Ketin, 1983).

The highest Zn (135–138 ppm) and Pb (65–66 ppm) contents are determined in sediments from both the easternmost (stn. F*16*) and westernmost (stn. K*10*) parts of the study area (Fig. 9). It is more likely that the Zn and Pb concentrations in the southeastern Black

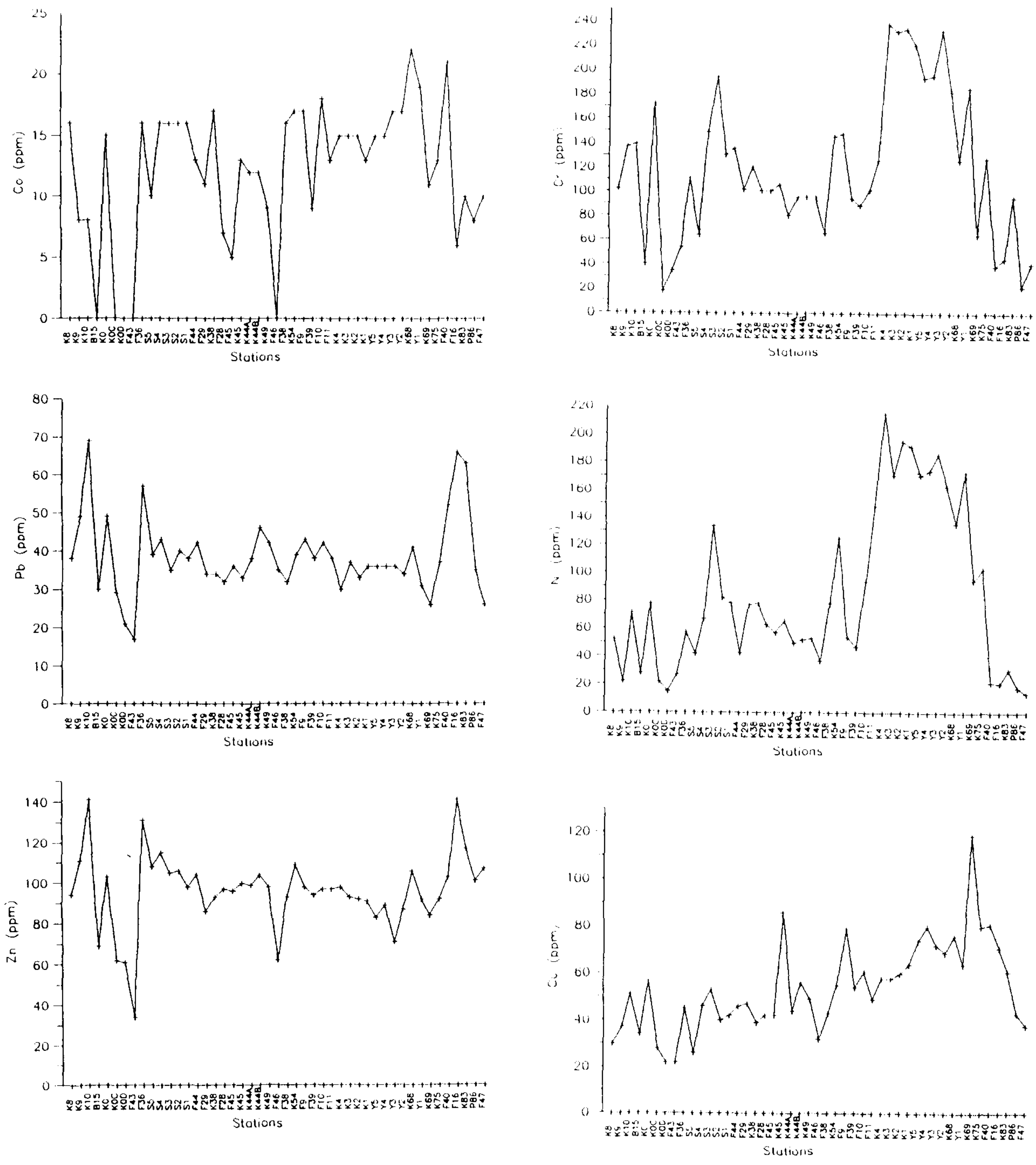
TABLE 6

Heavy-metal concentrations in the sediment samples

Station	Water depth (m)	Cu (ppm)	Cr (ppm)	Zn (ppm)	Pb (ppm)	Co (ppm)	Ni (ppm)	Mn (ppm)	Fe (%)
K*8*	76	27	92	85	34	15	47	510	3.18
K*9*	80	35	131	106	47	8	69	491	3.30
K*10*	212	49	133	135	66	8	69	870	2.59
B*15*	75	24	29	50	22	n.d.	20	182	0.63
KO	70	54	169	101	48	15	75	450	3.30
KOC	56	19	13	42	20	n.d.	15	123	0.29
KOD	70	16	25	44	15	n.d.	11	180	0.50
F*43*	30	15	38	24	12	n.d.	19	112	0.23
F*36*	58	41	102	121	52	15	52	380	2.88
S*5*	46	22	55	93	34	9	36	310	2.68
S*4*	63	44	139	108	41	15	63	464	3.40
S*3*	32	49	179	96	32	15	124	901	4.01
S*2*	95	36	121	98	37	15	71	451	3.30
S*1*	82	39	125	90	35	15	71	510	3.30
F*44*	18	44	98	100	41	13	41	1,064	4.10
F*29*	79	43	111	81	31	10	71	533	4.16
K*38*	80	33	87	80	30	15	52	413	2.75
F*28*	77	37	89	85	28	6	55	381	2.58
F*45*	220	40	102	92	35	5	55	505	3.30
K*45*	200	73	70	86	28	11	56	558	2.75
K*44*A	103	40	84	91	35	11	46	433	2.97
K*44*B	50	50	86	94	42	11	47	487	3.10
K*49*	310	45	88	90	38	9	48	525	4.63
F*46*	17	20	40	44	21	n.d.	22	165	1.29
F*38*	101	40	134	85	30	15	71	558	2.85
K*54*	78	49	133	98	35	15	113	540	3.51
F*9*	45	71	85	88	38	15	48	603	2.93
F*39*	28	51	84	88	35	9	44	709	3.46
F*10*	45	51	85	81	35	15	79	588	2.38
F*11*	40	49	102	78	30	11	119	547	2.37
K*4*	8	55	224	92	28	14	202	936	4.41
K*3*	60	55	218	87	35	14	161	903	4.57
K*2*	116	56	220	86	31	14	183	767	4.84
K*1*	55	60	208	86	34	12	180	808	4.97
Y*5*	49	71	183	78	34	14	161	689	4.63
Y*4*	100	75	185	83	34	14	163	992	4.75
Y*3*	53	67	219	66	34	16	176	872	4.71
Y*2*	64	65	172	81	32	16	153	800	4.92
K*68*	445	66	112	94	36	19	121	655	4.30
Y*1*	82	61	175	86	29	18	162	569	4.16
K*69*	150	82	44	57	18	8	65	370	1.16
K*75*	330	77	123	88	35	13	99	598	4.04
F*40*	63	79	38	101	51	21	22	489	4.02
F*16*	49	70	44	138	65	5	21	538	4.16
K*83*	36	59	92	112	60	10	30	703	3.97
P*86*	20	44	22	101	35	8	15	740	3.97
F*47*	8	37	40	105	26	10	14	812	4.01

n.d. = not detected.

Sea sediments receive significant metal contributions from the onshore mining activities which are genetically related to the volcanogenic massive Zn–Pb–Cu-sulfides formed from the Cretaceous to Tertiary (Gümüş, 1979). This can largely be concluded from the presence of Zn–Pb-rich sediments of stn. F*16* which is located off the Ordu–Giresun coast (Figs. 5 and 9) where the most important Zn–Pb–Cu deposits are mined (Gümüş, 1979). On the



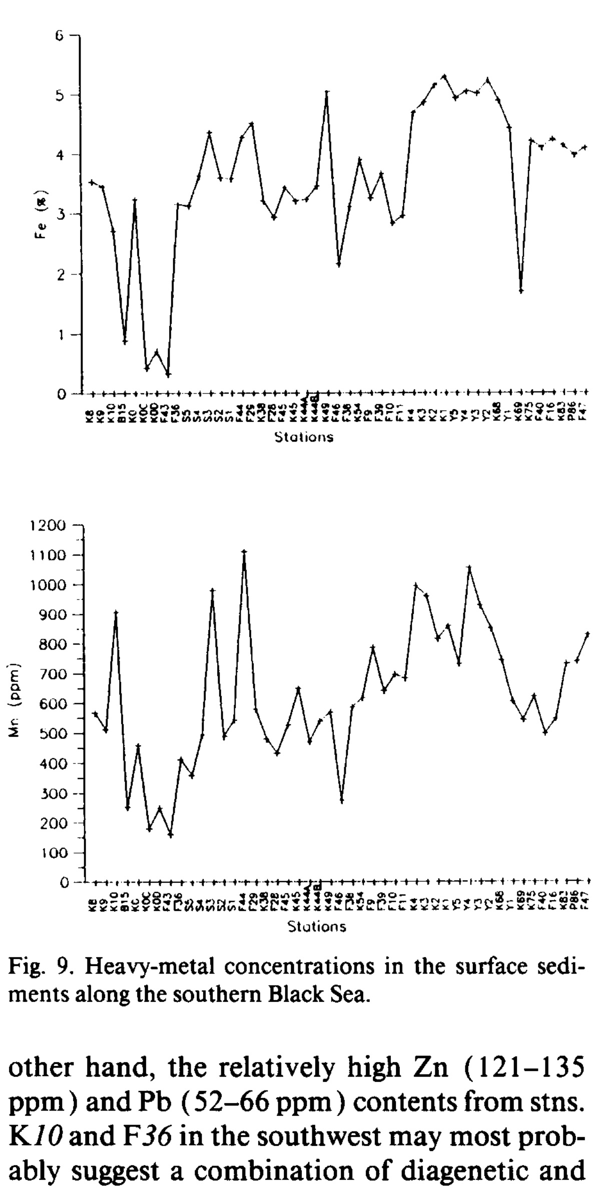


Fig. 9. Heavy-metal concentrations in the surface sediments along the southern Black Sea.

other hand, the relatively high Zn (121–135 ppm) and Pb (52–66 ppm) contents from stns. K*10* and F*36* in the southwest may most probably suggest a combination of diagenetic and anthropogenic effects.

Sediment sample from stn. K*10* with relatively high C_{org} content (2.23%) represent anoxic depositional conditions (Figs. 4 and 5) and thus, a possible Zn enrichment with increased organic matter accumulation is suspected, although the consequence of increased anthropogenic activities in the vicinity of the Bosphorus–Black Sea coastal areas cannot be ruled out because marine sediments from the urbanized and industrialized regions may contain markedly higher metal levels above their natural background (Förstner and Wittmann, 1979; Donazzolo et al., 1981; Ergin, 1990; Ergin et al., 1991b). However, there are no data available which could bring evidence for such elevated anthropogenic input of Zn and Pb in the study area.

The distribution pattern of Co is somehow different. The maximum Co contents are found in the eastern part of the study area (stns. K*68*, Y*1* and F*40*; 18–21 ppm; Table 6; Fig. 9). Since Co also occurs as a minor element incorporated into sulfides (Rose et al., 1979) which are more abundant along the coastal hinterland of the southeastern Black Sea (Gümüş, 1979), it is reasonable to account part of the Co from magmatic–hydrothermal contribution.

It should also be noted here that the concentrations of many heavy metals may be enriched in the shallow-water ferromanganese concretions not only in the Black Sea (Sevast'yanov and Volkov, 19679) but also in other parts of the world (Calvert and Price, 1970). However, the results presented here show that there does not appear to be any preferential enrichment of Cu, Cr, Ni, Pb and Zn in the sediments associated with such ferromanganese concretions. Also, Mn concentrations in the mud sediment samples (>90% mud) from oxic (stns. K*9*, 491 ppm; Y*3*, 872 ppm) and anoxic (stns. K*10*, 870 ppm; K*68*, 655 ppm) environments seem to be not relevant enough to indicate the presence of Mn mineralization at the O_2–H_2S interface as reported from the Black Sea (Arthur et al., 1988; Murray et al., 1989).

3.5. Relationships among the geochemical data

The effect of grain size on concentrations of the studied heavy metals is summarized in Table 8. It has been found that the metal contents of sediments, except for Fe and Co, are uniformly high in the fine-grained (clay and silt) fractions (R=0.30–0.66; Table 8; Figs. 11 and

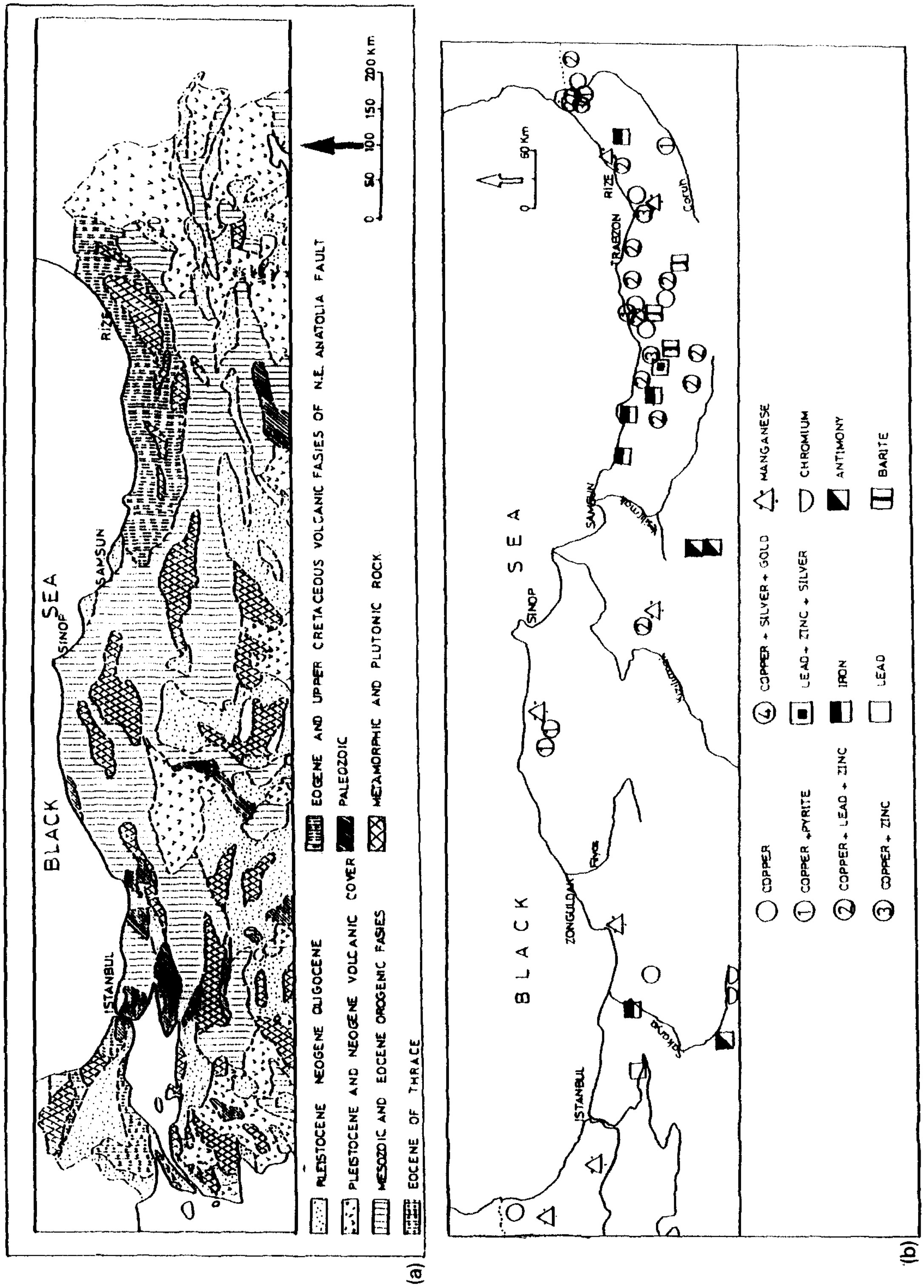


Fig. 10. Simplified maps showing the geology of the North Anatolia (a; from Ilhan, 1976) and economic mineral deposits (b; compiled from MSB (1977) and MTA (1981,1989).

TABLE 7

Comparison of the chemical results obtained in this study with those from others

	Fe (%)	Mn (ppm)	Co (ppm)	Cr (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Pb (ppm)	$CaCO_3$ (%)
1	0.23–4.90	112–1,064	0– 20	13–224	11–202	15– 82	24– 138	12– 66	1–39
2	0.32–5.29	160–1,109	0– 22	18–238	14–215	22– 119	61– 141	17– 69	
3	2.27–4.84	310– 852	21– 32	12–236	10–228	24– 61	59– 145	7– 33	
4	1.97–7.11	235–1,102	n.d.	69–485	47–463	28– 101	51– 693	10– 85	
5	n.d.	200–1,000	5–200	20–300	10–150	7– 40	n.d.	5– 70	
6	2.60–3.80	333– 565	17– 31	242–485	98–167	333–3,900	450–8,750	124–702	15
7	1.09–4.79	197–5,538	9– 30	52–166	28–161	13– 92	42– 149	17– 94	
8	0.80–4.6	167–2.920	8– 25	19–166	14–306	4– 30	24– 98	10–120	1–77
9	5.31–6.31	1,103–2.091	n.d.	340–551	157–326	39– 103	107– 133	n.d.	26–45
10	4.70	850	20	100	80	50	90	20	
11	0.98	50	0.3	35	2	5	16	7	
12	0.38	1,100	0.1	11	20	4	20	9	

1=southern Black Sea, bulk material (this study); *2*=southern Black Sea, on carbonate-free basis (this study); *3*=southern Black Sea (Hirst, 1974); *4*=southern Black Sea (Baykut et al., 1982); *5*=southern Black Sea (Çağatay et al., 1987); *6*=Golden Horn estuary/Bosphorus (Ergin et al., 1991b); *7*=Sea of Marmara (M.N. Bodur, pers. commun., 1991); *8*=Aegean Sea (compiled from Smith and Cronan, 1975, and Vousinou-Taliadori, 1983); *9*=northeast Mediterranean Sea (Shaw and Bush, 1978); *10*=average shale (Krauskopf, 1985); *11*=average sandstone (Turekian and Wedepohl, 1961); *12*=average limestone (Turekian and Wedepohl, 1961). n.d.=no data.

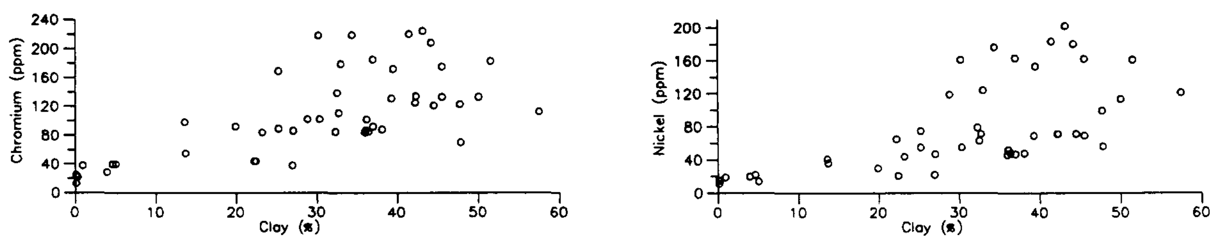


Fig. 11. Relationships between the clay and metal contents in sediment samples.

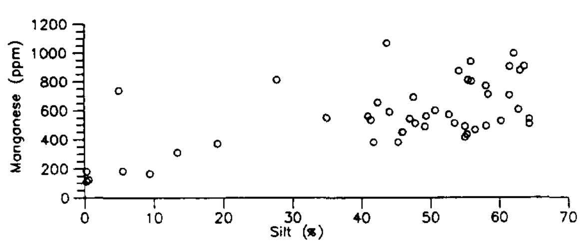


Fig. 12. Relationships between the silt and metal contents in sediment samples.

12). By contrast, low metal values are associated with relatively high amounts of sand-gravel-sized materials ($R=-0.72$ to -0.22; Table 8; Fig. 13). However, a satisfactory relationship was not obtainable for all the metals studied (Table 8). For example, Fe, Mn, Zn, Pb and Cu were found to be dominant in the silt-sized fractions ($R=0.40$–0.61; Fig. 12), while Cr and Ni contents were prominent in the clay-sized fractions ($R=0.64$–0.66; Table 8; Fig. 11). There are some indications that clay minerals (mainly chlorite and montmorillonite) control a considerable proportion of the Cr, Ni and Cu input from mafic and ultramafic sources in the southern Black Sea provenance (Hirst, 1974).

Carbonate contents present in the samples have a dilution effect on the metal levels of

TABLE 8

Correlation coefficient matrix for the studied physical and chemical parameters in surface sediment samples

	Gravel	Sand	Mud	Silt	Clay	$CaCO_3$	C_{org}	Cu	Cr	Zn	Pb	Ni	Mn	Co	Fe
Gravel	1.000														
Sand	0.314	1.000													
Mud	−0.788	−0.832	1.00												
Silt	−0.785	−0.748	0.943	1.000											
Clay	−0.662	−0.802	0.907	0.717	1.000										
$CaCO_3$	0.844	0.294	−0.684	−0.747	−0.493	1.000									
C_{org}	−0.522	−0.310	0.507	0.459	0.485	−0.502	1.000								
Cu	−0.561	−0.413	0.595	0.561	0.540	−0.459	0.447	1.000							
Cr	−0.541	−0.609	0.711	0.655	0.666	−0.516	0.176	0.405	1.000						
Zn	−0.724	−0.216	0.563	0.612	0.409	−0.798	0.606	0.347	0.223	1.000					
Pb	−0.554	−0.263	0.493	0.578	0.305	−0.659	0.637	0.350	0.152	0.869	1.000				
Ni	−0.407	−0.556	0.599	0.487	0.641	−0.334	−0.048	0.494	0.915	0.037	−0.055	1.000			
Mn	−0.655	−0.276	0.562	0.611	0.406	−0.692	0.205	0.554	0.648	0.483	0.339	0.600	1.000		
Co	−0.245	−0.339	0.368	0.198	0.442	−0.084	0.264	0.240	0.394	−0.218	−0.123	0.406	0.138	1.000	
Fe	−0.578	−0.220	0.335	0.401	0.159	−0.698	−0.022	0.592	0.674	0.583	0.441	0.605	0.795	0.271	1.000

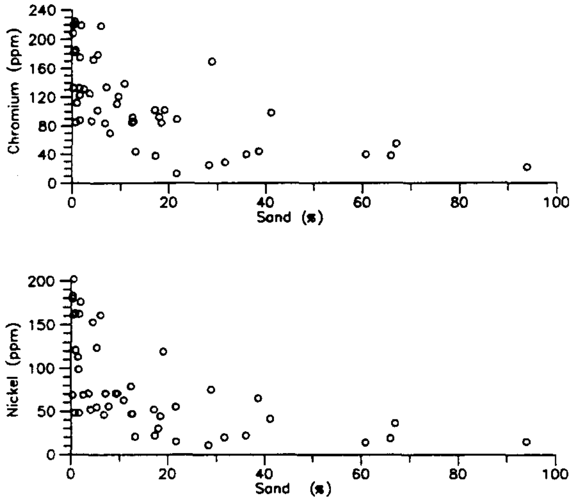


Fig. 13. Relationships between the sand and metal contents in sediment samples.

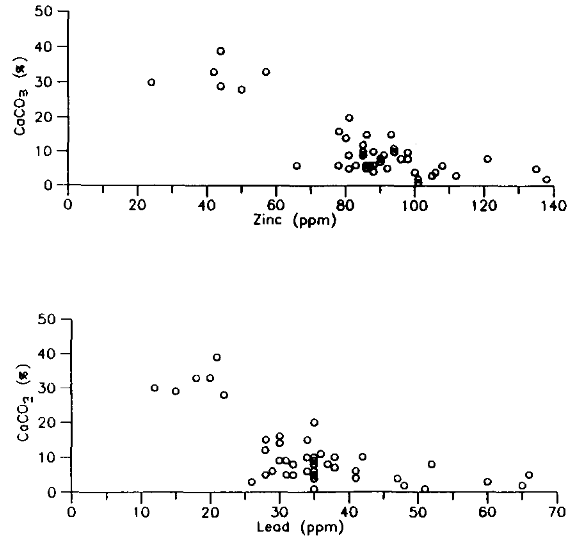


Fig. 14. Relationships between the $CaCO_3$ and metal contents in sediment samples.

sediments (Fig. 14), which must have resulted in the negative correlation between $CaCO_3$ and the metal concentrations measured (Table 8).

There is a general trend of increasing concentrations of Zn, Pb, Fe and Cu with organic carbon contents of the sediment samples (Table 8; Fig. 15) which is in good agreement with the work of Hirst (1974) who suggested the importance of organic matter in the accumulation of heavy metals in the Black Sea sediments, probably by means of the formation of bitumens and humic substances (Volkov and Fomina, 1974) or/and chelated compounds (Manskaya and Drozdova, 1968). According to Rozanov et al. (1974), organic matter is the principal source of the diagenetic reduction of reactive iron in the surficial Black Sea sediments.

The interelement relationships among the studied heavy metals are illustrated in Table 8. The data show that the concentrations of Zn, Pb, Cu, Cr and, to lesser extent, of Ni are seemingly associated with the Fe and Mn phases (R=0.34–0.79), most probably with the oxides, oxyhydroxides and sulfides of Fe and Mn, depending on the prevailing oxidizing or reducing conditions. On the other hand, Fe is substantially associated with Mn (R=0.79; Fig. 16). The role of Fe and Mn to

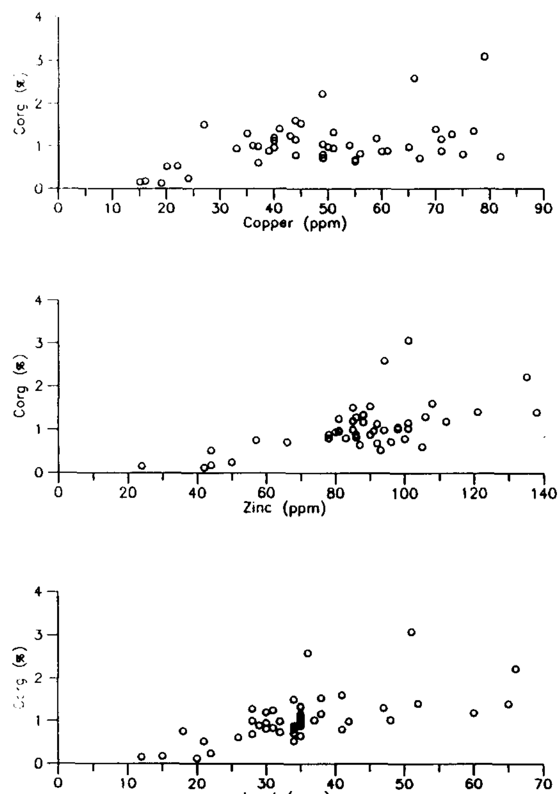


Fig. 15. Relationships between the organic carbon and metal contents in sediment samples.

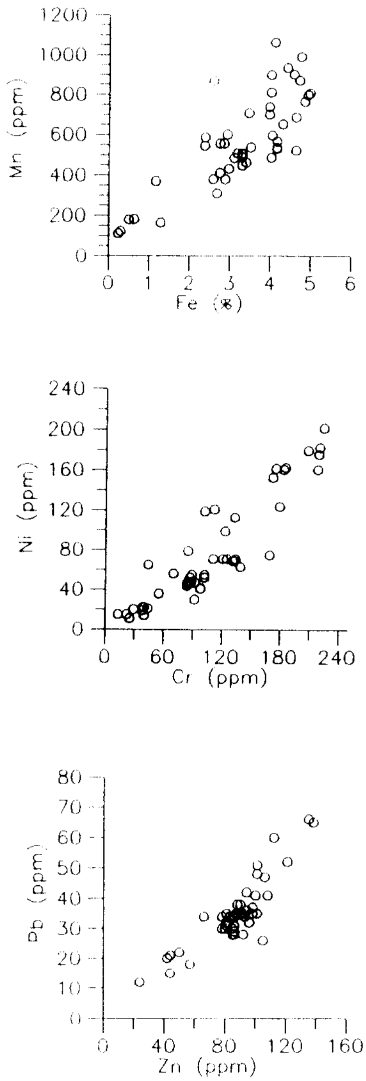


Fig. 16. Inter-element relationships in sediment samples.

accumulate metals in reasonable abundances has been known from numerous studies not only in the Black Sea (e.g., Sevast'yanov and Volkov, 1967; Manheim and Chan, 1974) but also in many other regions (Förstner and Wittmann, 1979 and therein cited literature). For example, sulfides in the presence of organic matter represent an obvious choice, as they can be important associations of Cu, Cr, Ni, Co, Pb and Zn in the Black Sea sediments (Butuzova, 1969; Volkov and Fomina, 1974).

Strong correlations are apparent between the concentrations of Cr and Ni ($R=0.91$; Table 8; Fig. 16), and Zn and Pb ($R=0.87$; Table 8; Fig. 16). This is, to a greater degree, interpreted to be the result of common similar sources and/or similar enrichment mechanisms for these metals. The former is related to the presence of particular geological sources, such as ultramafics and volcanogenic–sedimentary sequences and related deposits which commonly crop out on the coastal hinterland (Fig. 10), whereas the latter includes — in addition to Zn–Pb-sulfides — post-depositional redistribution within the sediment. Cr, which is strongly associated with Ni in ultramafic and volcanogenic sequences (Rose et al., 1979), is one of the economically important ores occurring along the anatolian coasts/coastal hinterland (Brinkman, 1976; Ketin, 1983). Similarly, but to a lesser extent, Cu is associated with Cr, Ni, Zn and Pb (Table 8).

4. Conclusions

The majority of the geochemical variations in the surface sediments of the southern Black Sea shelf and upper slope can be satisfactorily explained in terms of variations in depositional environment and provenance. The main sources of somewhat high Cr, Ni, Cu, Zn and Pb of the sediments, particularly in the east, are related to the ultramafic/volcanic rock series and associated ore deposits of the drainage basin. Cu, Cr, Ni, Zn, Pb and Co, to varying degrees, appear to be associated with the Fe, Mn and organic phases probably present as fine-grained (mainly clay- and silt-sized) material in the sediments. While the $CaCO_3$ contents reflect the proportion of the biogenic material in the samples, the somewhat higher organic carbon percentages indicate the high primary productivity rates and contributions from nearshore terrigenous influxes in the southern Black Sea.

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