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Effects of fine grain size on distribution of Mn in shallow and deep water Black Sea sediments: A comparison between oxic and anoxic depositional environments

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Abstract The uppermost 5–6 cm of the sediments (between 8 and 2248 m water depths) were studied to understand the effects of varying redox conditions on the Mn distribution in the recent sediments of the Black Sea. It was found that most Mn concentrations are consistent with the average abundance in crustal and/or sedimentary rocks. There exist no important differences between Mn concentrations in oxic (shallower water; <70 m) and anoxic (deeper water; 120 m) sediments. Previously reported Mn-enrichment above the Black Sea oxic/anoxic interface, due to the peculiar redox cycling, shows no significant contribution of Mn to the bottom sediments. A marked relationship between total Mn concentrations and clay/mud contents at shelf depth along the southern Black Sea margin indicates increased accumulation of Mn in association with the fine-grained particles and eastward water circulation.

Introduction

Because of its strong vertical salinity stratification, and thus a density gradient and permanent halocline, which prevents vertical mixing, the Black Sea (Fig. 1) has long been known as the world's largest, stable, anoxic marine basin (e.g., Degens and Ross 1974; Izdar and Murray 1991; Murray 1991; and many references cited therein).

A distinctive feature of the hydrography of the Black Sea is the presence of an oxic/anoxic (oxygen/hydrogen sulfide) interface in the water column (Fig. 2) that separates the low-salinity (≈ 18) surface water of river origin from the high-salinity (≈ 22) deep water of Mediterranean origin (e.g., Caspers 1957; Sorokin 1983). This boundary forms a transition zone (10–50 m thick) (Jorgensen et al., 1991) between the surface oxic waters and deep anoxic waters (Figs. 2 and 3) and is generally dome-shaped, being found at greater depths near the margins (100–150 m) (Codispoti et al. 1991) than in the centers of the western and eastern basins (80–120 m) (Murray et al. 1991). This boundary zone has been a site of considerable scientific interest, since it is here that the sharpest physical (e.g., Murray et al. 1991), chemical (e.g., Kempe et al. 1991; Lewis and Landing 1991), and biological (e.g., Jannasch 1991) gradients exist.

For example, this suboxic, boundary region (chemocline), is characterized by a distinct maximum in the concentrations of particulate manganese, which decreased rapidly in the deeper anoxic waters (Brewer and Spencer 1974; Lewis and Landing 1991) (Fig. 3). In or close to this zone, Mn is found in dominant quantities in the form of finely dispersed microspherules (ca. 0.5 μm diameter), probably consisting of Mn oxide particles. (Kempe et al. 1991) (Fig. 3). A manganese pump mechanism was suggested (Kempe et al. 1991) to explain such elevated Mn particles in the upper part of the oxic/anoxic interface, a process which results in mobilization of Mn(II) from the reduced, coastal surface sediments, upward transportation of Mn(II) through internal waves warping the pynocline near the coast, and finally, the precipitation and adsorption of Mn(IV) oxides onto fine-grained particles, forming macroflocks. The Mn precipitates above the fine particle layer (FPL) can then be reduced and dissolved while they sink below the FPL, into the deeper anoxic waters (Kempe et al. 1991). This regeneration–precipitation–scavenging cycle with Mn oxyhydroxides across the oxic/anoxic interface may be greatly enhanced by bacterial activity (Lewis and Landing 1991; Tebo et al. 1991).

The aforementioned previous studies in the Black Sea have largely reported on the enrichment of Mn at or just above the oxic/anoxic boundary in the water column but have generally lacked information about the distribution

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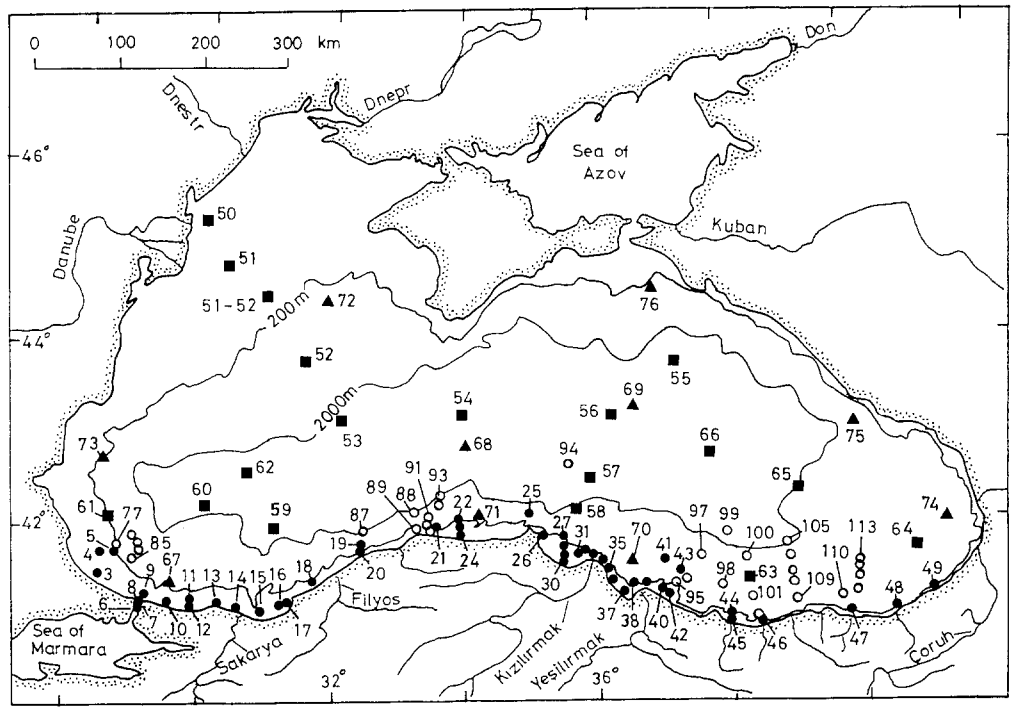


Fig. 1 Map of the Black Sea showing the locations of the studied surface (top 5–6 cm of sea floor) sediments. Based On data from Hirst (1974; filled triangles), Baykut et al. (1982; empty circles), Yücesoy and Ergin (1992; filled circles), and Kıratlı (1992; filled squares)

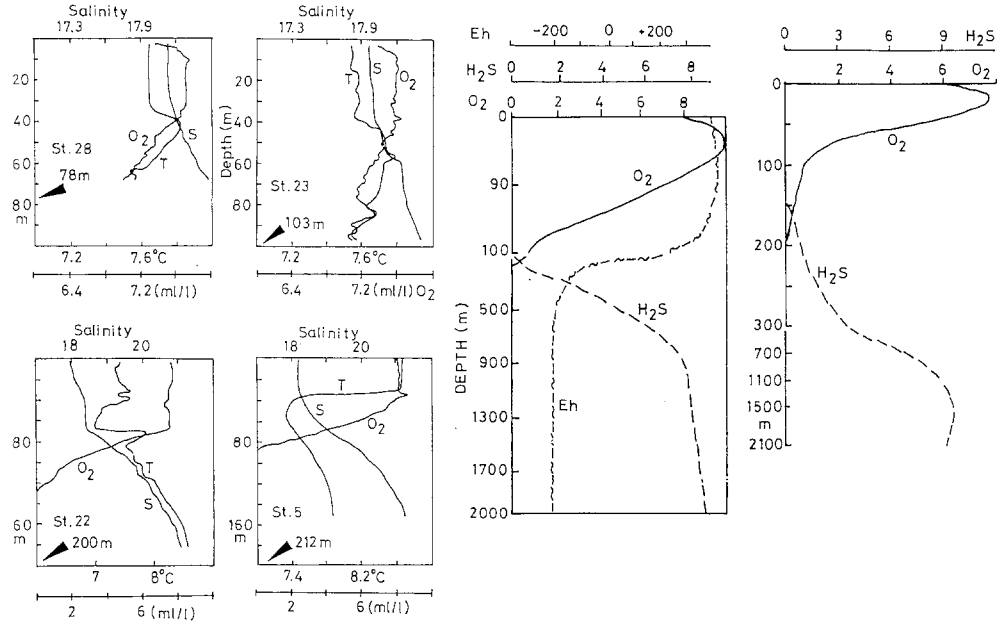


Fig. 2 Vertical profiles of some physical and chemical parameters in the water column from the Black Sea. At left (after Yücesoy and Ergin 1992) arrowheads indicate depths of sediment sampling stations (see also Fig. 1). Note the oxic (stn. 28), suboxic (stn. 23), and anoxic (stns. 5 and 22) sediment samples. Vertical profiles of O_2–H_2S (middle: after Sorokin 1972; and right: after Sorokin 1983)

of Mn in the oxic and anoxic bottom sediments in this sea.

In the present study, an attempt was made to compare the available Mn data from water and sediments of the whole Black Sea in order to better understand whether or not the well-known Mn enrichment at the oxic/anoxic boundary zone in the Black Sea water column influences the distribution of Mn in the bottom sediments significantly. The results of this report have revealed that the Mn distribution in surficial Black Sea sediments was greatly controlled by the relative abundance of fine-grained material rather than the redox conditions in the overlying water column.

Materials

Sedimentary Mn data used in this work and related analytical methods are presented elsewhere (Hirst 1974; Baykut et al. 1982, Yücesoy and Ergin 1992; Kıratlı 1992). Sediment samples recovered from a total of 113 stations

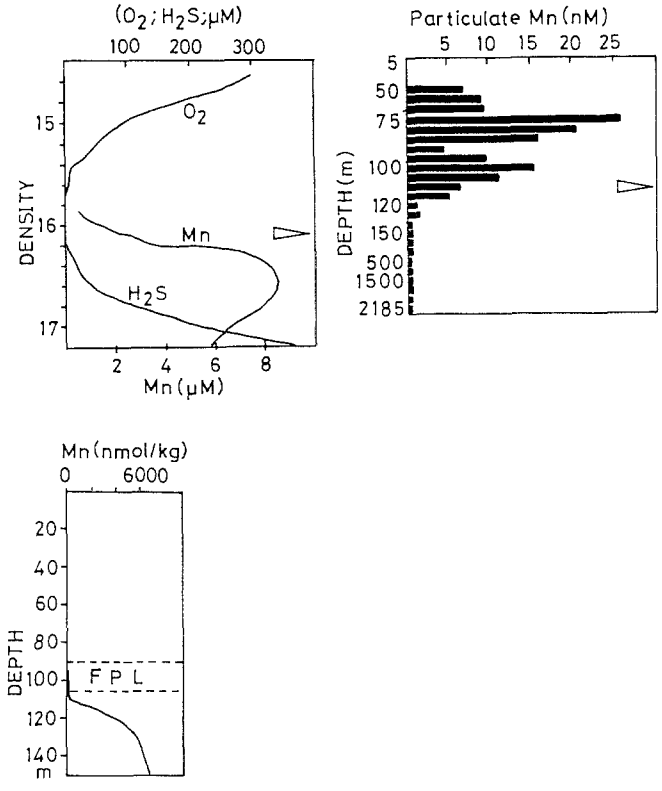


Fig. 3 Vertical profiles of some hydrochemical parameters in the water column of the Black Sea. Left (dissolved oxygen, total manganese, and sulfide obtained from a southwesterly station BS3-3 close to the middle of stns. 18 and 19 of this study) (after Friederich et al. 1990, in Lewis and Landing 1992); middle (particulate Mn concentration in a central station BS3-6 close to the middle of stns. 54 and 68 of this study) (after Lewis and Landing 1991); right (total Mn concentration in the eastern Black Sea, stn. HC-9 close to the middle of stns. 64 and 65 of this study) (from Kempe et al. 1991) (note the Mn-rich fine particle layer, FPL). Arrowheads in the left and middle figures indicate the sulfide interface. See Fig. 1 for locations of the stations of this study

between 8 and 2248 m water depths are illustrated in Fig. 1. The shallow- and deep-water sediments used in the present investigation should therefore provide an excellent opportunity to compare the concentrations of sedimentary manganese between the oxic and anoxic depositional environments of the Black Sea. To make the results comparable, only surface sediments (top 6 cm material) are considered, and the metal levels obtained are normalized on a carbonate-free basis in this work.

Results and discussion

Data on total concentrations of Fe and Mn together with other available physical and chemical parameters of the studied surface sediments are presented in Table 1 and Fig. 1. Since the increases in carbonate contents reflect dilution in bulk sediment Mn concentration (Fig. 4), the discussion below relies upon concentrations of Mn on a carbonate-free basis.

It is known from previous work (i.e., Fig. 3) that the oxygenated surface/near-surface waters of the Black Sea contain unusually high concentrations of the suspended Mn particles, as compared to the deeper, anoxic waters. To test this hypothesis, the carbonate-normalized Mn concentrations of sediments from the entire Black Sea basin are plotted in Fig. 5 versus water depths. This figure displayed no major trend of sedimentary Mn with water depths, and thus no relation could be observed to the well-known effects of oxic (Mn-enriched) and anoxic (Mn-depleted) depositional conditions at the sampling sites. For example, at stations 22 (200 m, anoxic), 23 (103 m, suboxic), and 24 (50 m, oxic) along a transect located on the central part of the southern Black Sea shelf/upper slope (Fig. 1), Mn concentrations in sediments (433–558 ppm on CFB; Table 1) were not significantly different from each other, and these sediments can be considered to be texturally equivalent (76–91% mud; 9–10% $CaCO_3$) for comparative purposes. Similarly, along transect stations 44 (330 m, anoxic) and 45 (63 m, oxic) located on eastern part of the southern Black Sea shelf/upper slope, Mn concentrations (489–589 ppm on CFB) remained within nearly the same range. These results further suggest that there are no significant differences between the total concentrations of Mn in the oxic and anoxic sediments of the southern Black Sea shelf/upper slope. This is in contrast to the widely accepted view that Mn enrichments in the surface marine sediments normally reflect, if there is no evidence for unusually high input from hydrothermal, biogenic, hydrogenetic, and detrital sources (i.e., Elderfield 1977), the effects of changing oxidizing and reducing conditions, such as chemical diagenesis (e.g., Calvert and Pedersen 1993).

In the deep sea, in general, the low sedimentation rates lead to high concentrations of Mn at the sediment surface (i.e., Horn et al. 1972). Although recent sedimentation rates in the deep Black Sea waters vary significantly, being low (0–10 cm 1000 yr^{-1}) in the western basin but high (>30 cm 1000 yr^{-1}) in the eastern basin, the majority of the bulk sediment Mn concentrations did not follow the same trend (i.e., 586–916 ppm Mn CFB in the west and 624–822 ppm Mn CFB in the east). It therefore seems that the flux rates of sediment particles to the sea floor have very little influence on the distribution of Mn in the Black Sea sediments. This is further indicated by the behavior of Th; its concentration in many parts of the world seas is controlled by the flux rate of sediment particles (i.e., Bacon and Anderson 1983). In the Black Sea, however, the distribution of Th is largely determined by the Mn redox cycle (Wei and Murray 1991).

The pattern of Mn distribution appears to be more prominent in shallower water (<120 m) sediments, lying at or just above the well-known oxic/anoxic interface (Figs. 2 and 3), where metal values were marked by large fluctuations, between 180 and 1100 ppm (on CFB), when compared to the deeper water sediments having Mn values

Table 1 Analytical data of uppermost 5–6 cm of Black Sea sediments[a]

Stations/ Samples	Depth (m)	Fe (%)	Mn (ppm)	Mud (%)	Clay (%)	$CaCO_3$ (%)	Fe/Mn	Mn CFB (ppm)
3	76	3.18	510	85	37	10	62	567
4	80	3.31	491	97	39	4	67	511
5	212	2.59	870	99	45	5	30	916
6	75	0.63	182	9	4	28	35	253
7	70	3.31	450	71	25	2	73	459
8	56	0.29	123	1	1	33	24	184
9	70	0.51	180	1	1	29	28	254
10	30	0.23	112	1	1	30	21	160
11	58	2.88	380	78	36	8	76	413
12	46	2.68	310	27	14	15	86	365
13	63	3.41	464	89	32	6	73	494
14	32	4.01	901	94	33	8	45	979
15	95	3.31	451	89	44	8	73	490
16	82	3.31	510	95	42	8	65	554
17	18	4.11	1064	57	13	4	39	1108
18	79	4.16	533	74	33	9	78	586
19	80	2.75	413	91	36	14	67	480
20	77	2.58	381	70	25	12	68	433
21	220	3.31	505	95	30	5	65	532
22	200	2.75	558	89	48	15	49	656
23	103	2.97	433	91	36	9	69	476
24	50	3.11	487	76	27	10	64	541
25	310	4.63	525	98	38	7	88	565
26	17	1.29	165	14	5	39	78	270
27	101	2.85	558	91	42	9	51	613
28	78	3.51	540	97	50	10	65	600
29	45	2.93	603	99	36	10	49	670
30	28	3.46	709	81	23	6	49	754
31	45	2.38	588	76	32	20	40	735
32	40	2.37	547	64	29	16	43	651
33	8	4.41	936	99	43	5	47	985
34	60	4.57	903	94	30	6	51	961
35	116	4.84	767	99	41	5	63	807
36	55	4.97	808	99	44	6	62	860
37	49	4.63	689	99	51	6	67	733
38	100	4.75	992	99	37	6	48	1055
39	53	4.71	872	97	34	6	54	928
40	64	4.93	800	96	40	5	62	842
41	445	4.31	655	99	57	11	66	766
42	82	4.16	569	98	45	6	73	605
43	150	1.16	370	41	22	33	31	552
44	330	4.04	598	98	47	4	68	623
45	63	4.02	489	82	27	1	82	494
46	49	4.16	538	87	23	2	77	549
47	36	3.97	703	81	20	3	56	725
48	20	3.97	740	5	1	1	54	747
49	8	4.01	812	33	5	3	49	837
50	27	3.11	386	n.d.	n.d.	28	80	536
51	55	1.91	355	n.d.	n.d.	51	54	723
52	102	1.61	2495	n.d.	n.d.	43	6	4347
53	1350	2.31	458	n.d.	n.d.	50	50	916
54	2073	1.91	390	n.d.	n.d.	50	49	780
55	2200	3.71	535	n.d.	n.d.	14	69	624
56	2132	2.61	513	n.d.	n.d.	43	51	897
57	2188	1.31	364	n.d.	n.d.	61	36	924
58	2140	3.61	751	n.d.	n.d.	17	48	906
59	1870	3.51	523	n.d.	n.d.	13	67	600
60	2180	3.11	502	n.d.	n.d.	14	62	586
61	2115	3.41	689	n.d.	n.d.	10	49	766
62	350	3.21	535	n.d.	n.d.	28	60	741
63	2128	2.71	500	n.d.	n.d.	29	54	702
64	1700	4.31	684	n.d.	n.d.	17	63	822
65	1640	2.71	587	n.d.	n.d.	24	46	777
66	2000	2.71	553	n.d.	n.d.	31	49	799
67	2136	1.41	371	n.d.	n.d.	56	38	851
68	663	4.51	832	n.d.	36	8	54	904
69	2248	4.83	852	n.d.	56	47	56	1608
70	2158	3.74	569	n.d.	86	60	65	1423
71	973	4.51	735	n.d.	45	19	61	907

Table 1 (continued)

Stations/ Samples	Depth (m)	Fe (%)	Mn (ppm)	Mud (%)	Clay (%)	$CaCO_3$ (%)	Fe/Mn	Mn CFB (ppm)
72	207	3.94	635	n.d.	52	15	62	747
73	1057	3.89	507	n.d.	50	40	46	845
74	728	3.42	844	n.d.	52	35	40	1298
75	1068	4.09	712	n.d.	62	26	57	962
76	1588	4.34	735	n.d.	43	18	59	896
77	386	3.51	542	n.d.	52	21	64	686
78	270	2.31	422	n.d.	n.d.	n.d.	55	n.d.
79	560	3.01	444	n.d.	n.d.	n.d.	68	n.d.
80	790	2.81	698	n.d.	n.d.	n.d.	40	n.d.
81	1020	3.61	424	n.d.	n.d.	n.d.	85	n.d.
82	990	2.81	424	n.d.	n.d.	n.d.	66	n.d.
83	1330	4.41	679	n.d.	n.d.	n.d.	65	n.d.
84	1480	3.01	498	n.d.	n.d.	n.d.	60	n.d.
85	1530	2.91	385	n.d.	n.d.	n.d.	75	n.d.
86	1440	2.91	235	n.d.	n.d.	n.d.	123	n.d.
87	1470	2.41	716	n.d.	n.d.	n.d.	34	n.d.
88	2051	2.41	524	n.d.	n.d.	n.d.	46	n.d.
89	2060	3.91	591	n.d.	n.d.	n.d.	66	n.d.
90	200	3.61	591	n.d.	n.d.	n.d.	61	n.d.
91	1100	3.41	644	n.d.	n.d.	n.d.	53	n.d.
92	1410	3.71	584	n.d.	n.d.	n.d.	63	n.d.
93	540	3.61	87	n.d.	n.d.	n.d.	414	n.d.
94	2035	3.91	552	n.d.	n.d.	n.d.	71	n.d.
95	2139	3.41	531	n.d.	n.d.	n.d.	64	n.d.
96	2090	6.01	753	n.d.	n.d.	n.d.	80	n.d.
97	280	6.21	457	n.d.	n.d.	n.d.	136	n.d.
98	480	2.71	679	n.d.	n.d.	n.d.	40	n.d.
99	1800	2.41	705	n.d.	n.d.	n.d.	34	n.d.
100	1500	2.11	474	n.d.	n.d.	n.d.	44	n.d.
101	2086	2.51	431	n.d.	n.d.	n.d.	58	n.d.
102	2030	6.91	654	n.d.	n.d.	n.d.	106	n.d.
103	1380	3.19	740	n.d.	n.d.	n.d.	43	n.d.
104	380	3.97	1002	n.d.	n.d.	n.d.	40	n.d.
105	670	4.41	745	n.d.	n.d.	n.d.	59	n.d.
106	1900	2.44	736	n.d.	n.d.	n.d.	33	n.d.
107	1995	7.11	580	n.d.	n.d.	n.d.	123	n.d.
108	1900	3.51	582	n.d.	n.d.	n.d.	60	n.d.
109	1720	1.97	430	n.d.	n.d.	n.d.	46	n.d.
110	1260	4.08	1102	n.d.	n.d.	n.d.	37	n.d.
111	1450	2.58	1041	n.d.	n.d.	n.d.	25	n.d.
112	1440	2.02	263	n.d.	n.d.	n.d.	77	n.d.
113	1700	2.74	537	n.d.	n.d.	n.d.	51	n.d.
114	1934	2.29	492	n.d.	n.d.	n.d.	47	n.d.
115	1910	1.01	515	n.d.	n.d.	n.d.	19	n.d.
116	1377	3.37	578	n.d.	n.d.	n.d.	70	n.d.

[a] See Fig. 1 for location of sampling stations. Based on data from Yücesoy and Ergin (1992; stations 3–49), Kıratlı (1992; stations 50–66), Hirst (1974; stations 67–76), and Baykut et al. (1982; stations 77–116)

(550–900 ppm on CFB) in a much narrower range, except for two stations (Fig. 5). In contrast to Mn, Fe contents exhibit a much broader range both in shallower and deeper sediments (Fig. 6), whereby the Fe/Mn ratios showed no considerable relation to the water depths in general. This overall wide range of the Fe/Mn ratios (Fig. 6) could be attributed to the well-known differences in behavior of these two elements to varying redox and scavenging conditions before and after burial within sediment. The redox cycling of Fe occurs somewhat deeper in the water column (Lewis and Landing 1991).

Furthermore, regional comparisons indicate that there are significant differences in the Mn contents of sediments between the western and eastern sampling stations (Fig. 7). For instance, the Mn concentrations in sediments (on CFB) generally increased from the western to eastern parts of the southern Black Sea shelf (Fig. 7). This may possibly suggest increased Mn supply from the chemocline zone and accumulation in sediment under the influence of lateral transportation by the easterly flowing surface currents that predominate along the southern Black Sea margin. However, as shown in Fig. 8, this trend of increase of the Mn contents in shallower water (< 120 m) sediments seems to be related to the increased clay ($r = 0.40$; $P > 0.95$) and mud contents ($r = 0.56$; $P > 0.95$) of sediments (Fig. 8) in general. Much carbonate in the Black Sea is in the form of clay-sized coccoliths and, thus, they could be effective scavengers of Mn in this sea, but the presence of a negative correlation between carbonate contents and Mn concentrations of bulk sediments (Fig. 4; $r = -0.69$; $n = 45$; $P > 0.95$) do not convincingly support such a relationship. On the other hand, by taking the overall increasing clay con-

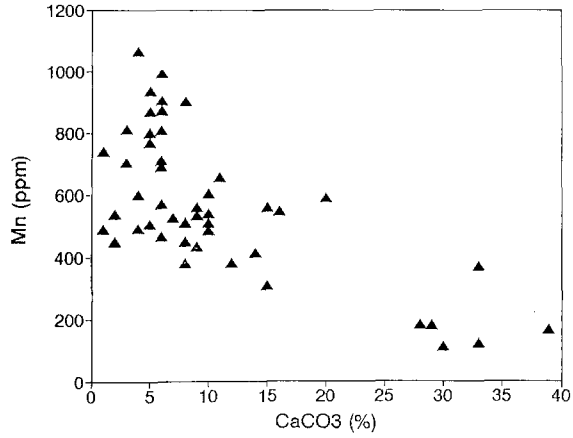


Fig. 4 Total $CaCO_3$ versus bulk Mn concentrations in surface sediments from the southern Black Sea (stns. 3–49, see also Fig. 1 for locations). Based on data from Yücesoy and Ergin (1992)

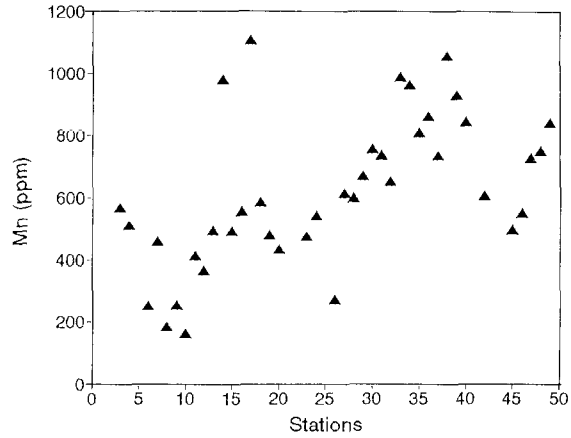


Fig. 7 Total Mn concentrations (on CFB) in shallow-water (< 120 m) surface sediments versus sampling stations, from western (stn. 3) to eastern (stn. 49) parts of the southern Black Sea (see also Fig. 1 for locations). Based on data from Yücesoy and Ergin (1992)

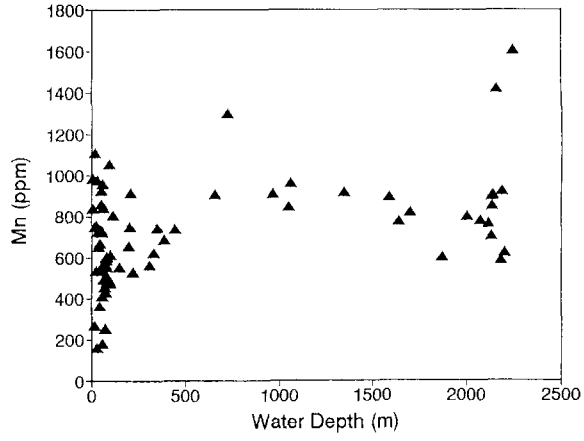
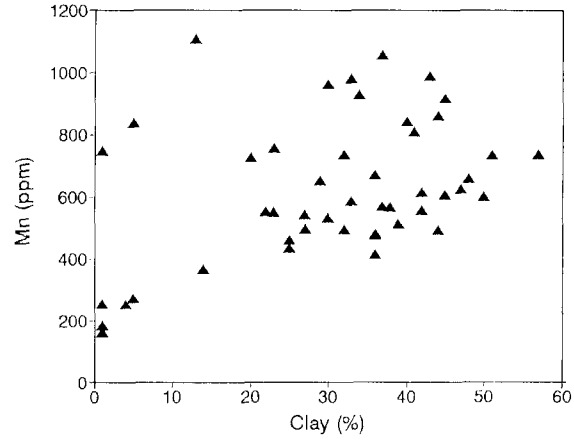


Fig. 5 Total Mn concentrations (on CFB) in surface sediments versus water depths at sampling stations in the Black Sea. Based on data from Hirst (1974), Yücesoy and Ergin (1992), and Kıratlı (1992)



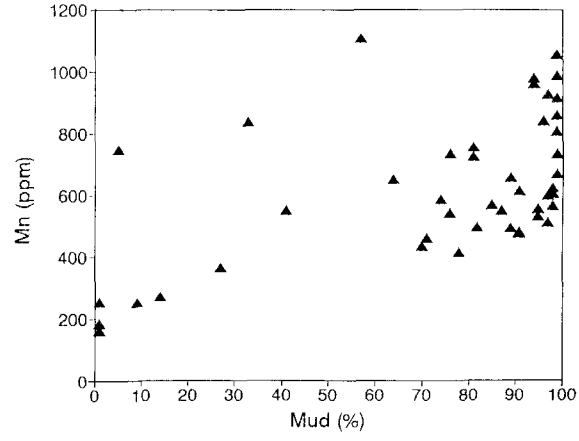


Fig. 8 Total Mn concentrations (on CFB) versus clay- (top) and mud-sized (bottom) fractions in shallow-water (< 120 m) surface sediments from the southern Black Sea (see also Fig. 1 for locations)

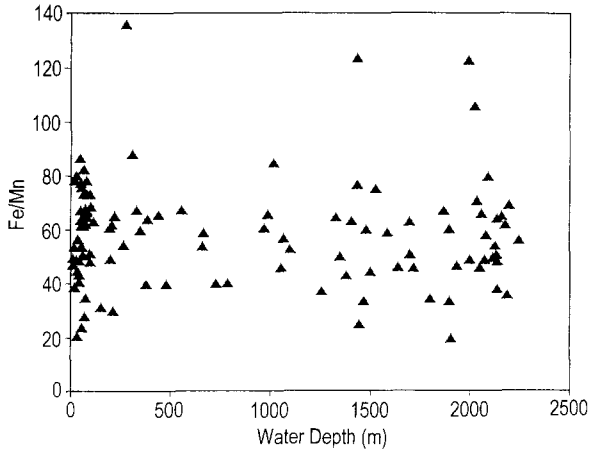


Fig. 6 Fe/Mn ratios in surface sediments versus water depths at sampling stations from the whole Black Sea. Based on data from Hirst (1974), Baykut et al. (1982), Yücesoy and Ergin (1992), and Kıratlı (1992)

tents of sediments from west to east (Fig. 9) into account, it may be suggested that the amounts of fine-grained particles present in the sediments have great influence on the relative abundance of Mn in the sediments.

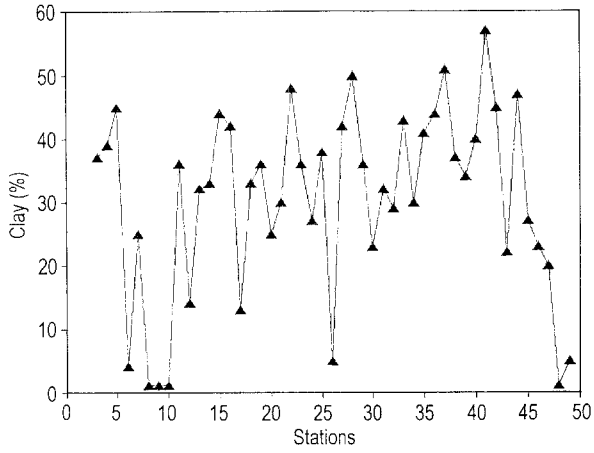


Fig. 9 Distribution of clay-sized fractions in surface sediments versus sampling stations from western (stn. 3) to eastern (stn. 49) parts of the southern Black Sea shelf/upper slope (see also Fig. 1 for locations). Modified from Yücesoy and Ergin (1992)

Conclusions

On the basis of available data used in this work, it can be concluded that the presence of unusually high Mn particulates just above the oxic/anoxic interface of the Black Sea water column does not have much influence on the Mn distribution in the bottom sediments. The wide range of variations in the sedimentary Mn contents, with slight tendencies to increase towards shallower water depths, particularly in the west–east direction along the southern Black Sea margin, reflect the combined effects of water circulation and association of Mn with the fine-grained (i.e., clay- to mud-sized) fractions of sediments. Thus, the expected enrichment of Mn in shallow-water (< 120 m) relative to deeper-water sediments, possibly from a contribution of Mn from the chemocline zone of Black Sea water column remains questionable. Therefore, further geochemical investigations are needed to better understand the effects of Mn from above the oxic/anoxic interface on the bottom sediments, which should be sampled along transects from inshore to offshore waters.

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