

Distribution of dissolved forms of iron and manganese in the Black Sea

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Abstract

Dissolved forms of the redox-sensitive elements manganese (Mn_{DISS}) and iron (Fe(II) and Fe(III)) were measured in the oxic/anoxic transition zone, or suboxic zone, of the Black Sea. An offset was found between dissolved manganese and iron gradients at all stations. In the western cyclonic gyre of the Black Sea, the onset of dissolved Mn ($>0.1 \mu M$) was located at a density of about $\sigma_t = 15.85$, where the concentration of dissolved oxygen (DO) was less than $5 \mu M$. The onset of dissolved Fe(II) ($>0.025 \mu M$) was at $\sigma_t = 15.90$, just above the increases in hydrogen sulfide. These characteristic features were modified in the southern coastal waters by such physical processes as the rim current, formation of anticyclonic eddies, and injection of saline, oxygenated Marmara Sea waters from the Bosphorus in the Bosphorus Plume.

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1. Introduction

The Black Sea is a meromictic sea with a strong vertical stratification (permanent halocline) determined by salinity. The strong density stratification limits the supply of oxygen to the deep waters, making the Black Sea the world's largest anoxic basin. The onset of anoxia starts at about 100 m ($\sigma_t = 16.15$ – 16.2) where sulfide first appears ($>10 \mu M$) and extends to the bottom at depths 2200 m (Tugrul et al., 1992; Buesseler et al., 1994; Sorokin, 1983). One distinct feature of the basin that makes it different from other basins is the formation of a transitional layer between the oxic and anoxic layers (the “suboxic layer”) (Murray

et al., 1989, 1995; Tugrul et al., 1992; Vinogradov and Flint, 1989). The suboxic layer is defined as the region at which sulfide and oxygen concentrations are extremely low and there is no perceptible vertical gradient.

A multi-centered, time-dependent cyclonic cell occupies the interior of the Black Sea (Fig. 1), and a series of anticyclonic eddies are confined inshore of the Rim Current (Oguz et al., 1993; Sur et al., 1994, 1996; Ozsoy and Mikaelyan, 1997). A detailed description of the general characteristics (morphometry, current systems, etc.) of the basin has been published by several authors (Sur et al., 1994, 1996; Ovchinnikov et al., 1993; Besiktepe et al., 1994; Oguz and Besiktepe, 1999; Sorokin 2002).

The water column of the Black Sea can be subdivided into four main layers. A shallow euphotic zone covers the uppermost part from the

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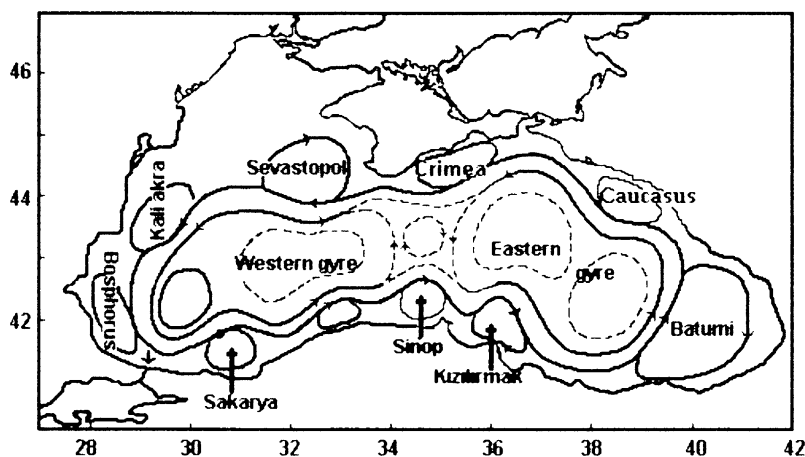


Fig. 1. General circulation of surface waters in the Black sea (Oguz et al., 1993).

surface to the depth of 1% light level (≤ 50 m), and is characterized by high oxygen concentrations ($\sim 300 \mu\text{M}$). Below the euphotic zone, a region of active particulate organic material degradation coincides with intense oxygen consumption and efficient nitrogen cycling, as suggested by rapid changes with depth of oxygen and nitrate. At the base of this “oxycline/upper nitracline”, oxygen decreases to about $10 \mu\text{M}$, and nitrate increases to $6\text{--}8 \mu\text{M}$. At a slightly deeper and more oxygen-deficient part of the water column, organic matter decomposition proceeds via denitrification. The “lower nitracline” zone is characterized by sharp decrease in nitrate concentrations to trace levels about 30–40 m below the nitrate maximum. This layer is called the “suboxic layer” (Murray et al., 1989). Below the suboxic zone is the deep anoxic layer, with high concentrations of hydrogen sulfide and ammonium. The boundary between the suboxic and anoxic layers involves a series of complicated redox processes, with characteristic features in the vertical distributions falling on the same density surfaces (Murray et al., 1995; Rozanov, 1995). As a result, it is customary to identify the positions of all these characteristic features of the biogeochemical structure using density as the vertical coordinate rather than water depth. This allows for direct comparison of vertical profiles from different stations throughout the basin.

The distribution and biogeochemical properties of sulfur compounds are key factors controlling redox conditions and processes, including speciation of iron and manganese. The wide valance range between reduced (S (-II)) and oxidized (S (VI)) forms of sulfur creates an energy bridge across the

interface between oxic and anoxic zones. The depth of the boundary between suboxic and anoxic zones, marked by the onset of sulfide changes, varies from 80 to 200 m. These depths correspond to a fixed density ($\sigma_t = 16.2$) at the center and peripheries of the cyclonic gyres (Murray et al., 1995; Sorokin, 2002). In the Black Sea trace elements are present in micromolar concentrations (Spencer and Brewer, 1972; Rozanov, 1995). The cycling of Mn and Fe in the water column is related to the biogeochemical dynamics of oxygen, sulfur, metals, and organic particles. Maximum concentrations of dissolved manganese and iron (8.26 and $0.35 \mu\text{M}$, respectively) are much higher in the Black Sea than in other seas and oceans (Lewis and Landing, 1992). The scavenging behavior of manganese and the recycling and scavenging behavior of iron work together with the redox conditions to determine the concentrations and distributions of these metals in the water column.

The goal of the present study was to examine the distribution of the redox-dependent manganese and iron dissolved phases across the oxic/anoxic interface in the Black Sea with particular attention to Fe redox state. This is important as it presents, in comparison to Lewis and Landing’s 1992 work, a temporal context as well as new material. This study have added more sites to the existing knowledge base of Mn and Fe distributions and taken care to analyze both dissolved Fe(II) and Fe(III). The latter point is important for understanding the biological influences on dissolved Fe distributions in suboxic environments. This study also compare the results of Lewis and landing, with the present study to find out changes (if any) in their concentrations and

distributions since the 1988 expedition of R/V *Knorr*. Samples from different regions of the Black Sea were visited to examine spatial and temporal variations of Mn and Fe species in the water column, especially in the suboxic/anoxic transition zone of the Black Sea ecosystem.

2. Materials and methods

The data used in this paper were collected in the Black Sea in June 2001 during Leg 2 of an R/V *Knorr* cruise (J.W. Murray, chief scientist; Fig. 2, Table 1). Information about the participants, station locations as well as hydrographic, O₂/H₂S and nutrient data are available on the web at: <http://www.ocean.washington.edu/cruises/Knorr2001>.

Seawater samples were collected from predetermined density depths using Go–Flo bottles attached to a CTD-rosette. Sub-samples were collected directly into acid-washed 50-ml Poly Ethylene tubes. Since the particles causes light scattering during the measurements, the samples were filtered online with acid-washed GF/C filters to remove the particles from the solution. Great care was taken to minimize contamination during sampling and sample handling. Colorimetric reagents were added to the analytical tubes before transferring samples, in order to save time and reduce contact with atmospheric oxygen. Due to the abrupt redox change at the oxic anoxic interface and the surrounding density surfaces, we focused on sampling at

isopycnal depths from $\sigma_t = 15.4$ to 16.5, i.e. the suboxic zone. The upper density layer ($\sigma_t = 15.4$) corresponds to the lower boundary of the oxycline/nutricline, and the lower density layer ($\sigma_t = 16.5$) corresponds to the maxima in dissolved manganese and iron.

Dissolved Fe(II) and Fe(III) were analyzed colorimetrically using the Fe(II)-ferrozine purple color development at pH 3.5–5 (Grasshoff et al, 1999). Measurement of Fe(III) was accomplished by measuring total iron after reduction of Fe(III)–Fe(II) and subtracting the Fe(II) from this value. Fe(III) was reduced by addition of 1 ml of 0.8 M ascorbic acid to each 50-ml sample. After reduction to Fe(II) the procedure used for Fe(II) determination was followed. Dissolved manganese (Mn_{DISS}) concentrations were measured colorimetrically using formation of the brick-red complex of formaldoxime (Brewer and Spencer, 1971; Grasshoff et al., 1999). A 10-cm-long quartz cell was used

Table 1
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Cruise	Station no.	Latitude	Longitude
June 2001	2	42°28.77′N	30°45.62′E
R/V <i>Knorr</i> leg 2	3	44°07.47′N	30°54.99′E
	10	44°26.13′N	31°30.82′E
	12	44°21.33′N	32°04.05′E
	14	41°27.30′N	30°15.86′E
	11	44°21.28′N	32°03.94′E

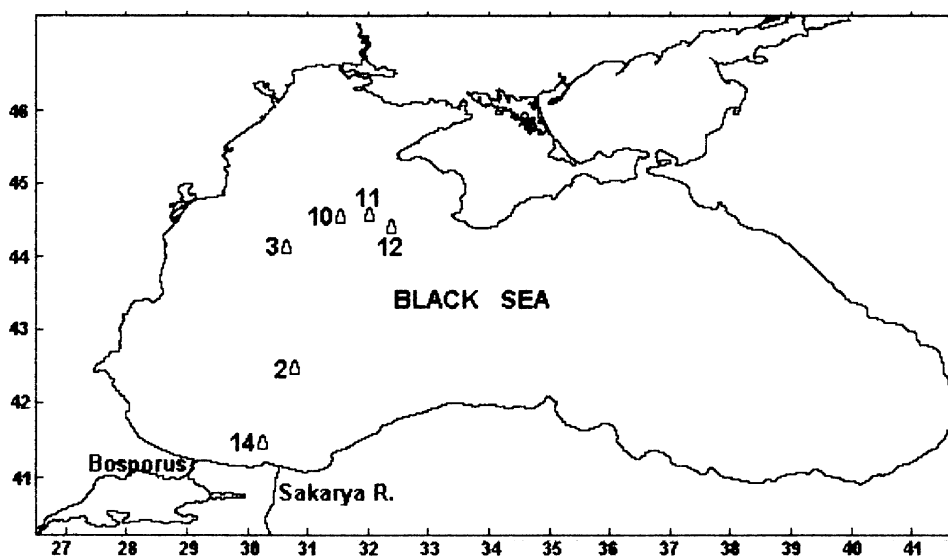


Fig. 2. Locations of the stations at which the samples were collected during the 2001 Black Sea expedition of R/V *Knorr* leg 2.

for all analyses. The analytical results were calibrated by standard additions.

The redox potential was measured using an SBE 27 pH and ORP (Redox) sensor, which combines a pressure-balanced glass-electrode, Ag/AgCl reference probe, and platinum ORP electrode to provide in-situ measurements to a depth of 1200 m. The redox sensor was attached to an SBE911 plus CTD profiler.

3. Results

Results for Mn, Fe, O₂ and H₂S are shown in Figs. 3–6. These profiles are representative of different regions of the Black Sea and will be described in sequence. The maximum dissolved iron

(Fe(II)) concentrations ($\sim 0.3 \mu\text{M}$) were typically an order of magnitude smaller than those of dissolved manganese (Mn_{DISS}) ($\sim 8 \mu\text{M}$). Lewis and Landing (1991) reported similar values of $0.2\text{--}0.3 \mu\text{M}$ for dissolved iron and $8\text{--}9 \mu\text{M}$ for dissolved manganese. Analyses of filtered and unfiltered samples showed that prefiltration is necessary to remove the contribution of iron from suspended matter. Experiments with different type of filters showed that the GF/C filter was sufficient to remove particulate matter ($>1 \mu\text{m}$) from solution before analyses of dissolved iron and manganese.

Since the redox cycling of iron and manganese is influenced by the concentrations of oxygen and sulfide, the concentrations of these parameters are included with dissolved iron (Fe(II)) and manganese

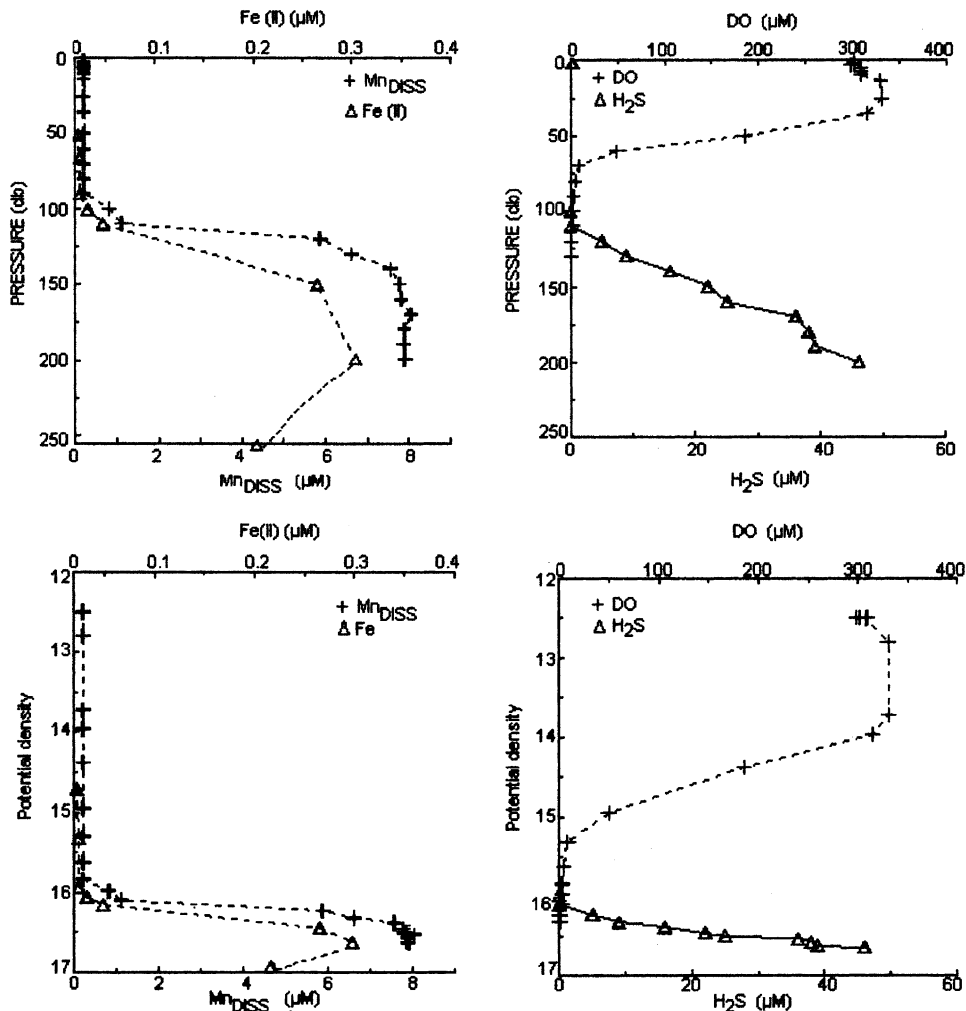


Fig. 3. Vertical profiles with respect to depth and density in the western-cyclone (station 2) of the Black Sea. DO and H₂S data are from Tugrul and Salihoglu (2002).

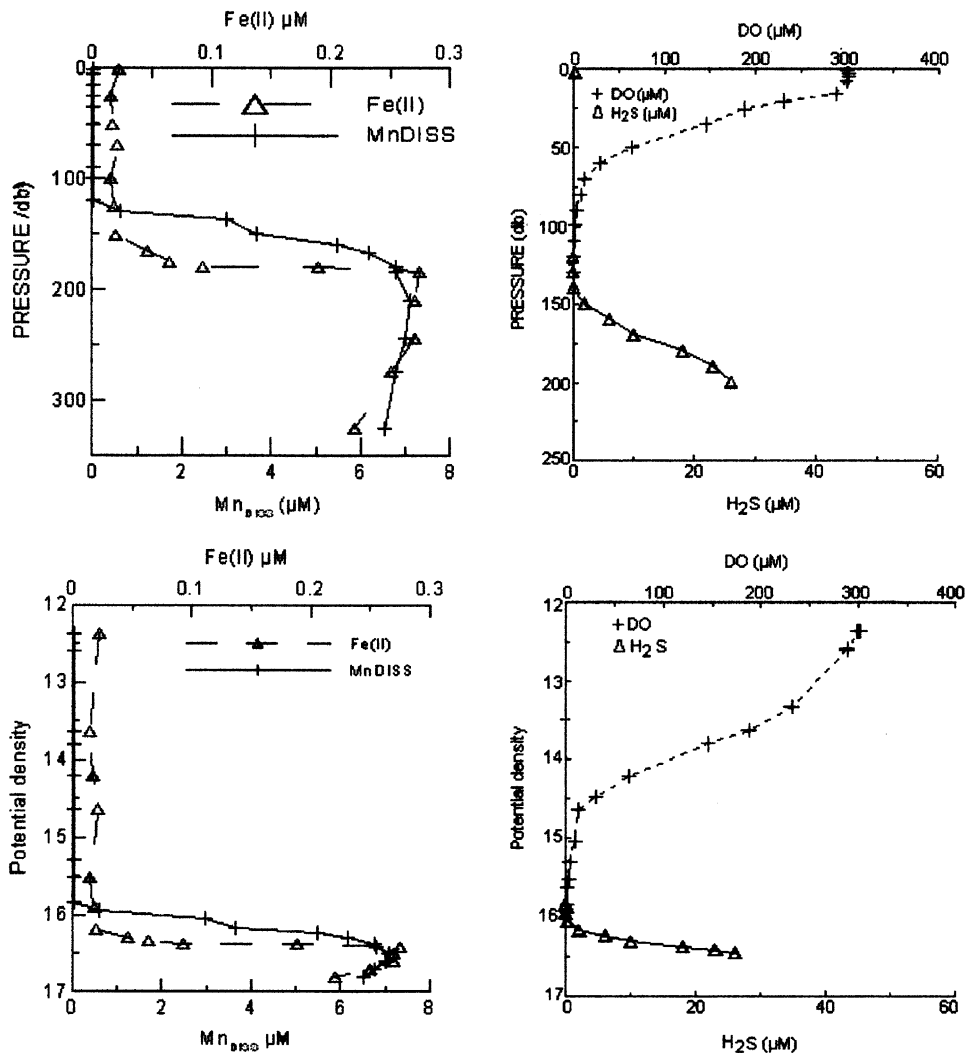


Fig. 4. Vertical profiles with respect to depth and density in the northwestern Black Sea (station 3). DO and H₂S data are from Tugrul and Salihoglu (2002).

(Mn_{DISS}). Vertical distributions of these parameters showed remarkable variations with both depth and region. The western gyre is influenced by injection of oxygenated Bosphorus inflow (Konovalov et al., 2003), and the chemical and physical features of the continental shelf zone are anomalous and extend into the open sea (Sorokin, 2002). Thus, we present the distribution of dissolved iron (Fe(II)) and manganese (Mn_{DISS}) in distinctly different regions of the Black Sea: the northwest shelf (station 3), northwest slope (station 12), western cyclonic region (station 2), and southwestern coastal waters (station 14). When the vertical distributions of Mn_{DISS}, Fe(II), DO and H₂S were evaluated with respect to water depth, features such as the depth at which

these parameters were first observed, or the depth at which the maximum concentrations differed between stations. On the other hand, when plotted versus density the profiles of Fe(II), Mn_{DISS}, DO and H₂S (Figs. 4–8) indicate that similar features from different regions appeared at similar density surfaces, as also emphasized in previous studies (Lewis and Landing, 1991; Tugrul et al., 1992). Nevertheless there are distinct regional differences both in the depth and magnitude of the characteristic chemical features inherent to the Black Sea. Moreover, regional variations in hydro-chemical properties of the oxic/anoxic transition zone are more pronounced than seasonal changes (Erdogan, 2002). Spatial variations of Mn_{DISS} and Fe (II)

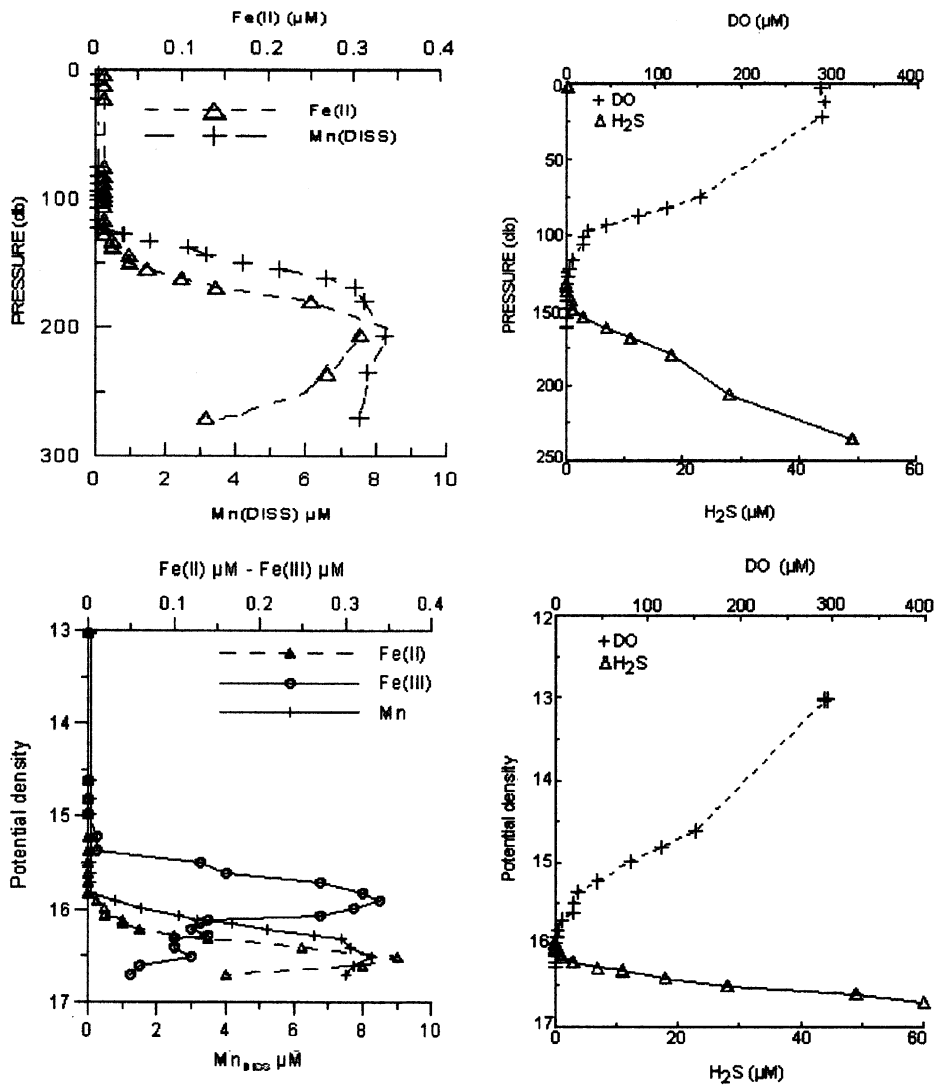


Fig. 5. Vertical profiles with respect to depth and density in the northwestern slope of Black Sea (station 12). DO and H₂S data are from Tugrul and Salihoglu (2002).

profiles are principally determined by changes in the thickness of the suboxic zone.

3.1. Western cyclonic region (station 2)

Data from station 2 in the western cyclonic gyre are shown in Fig. 3. The onset of dissolved manganese ($\text{Mn}_{\text{DISS}} > 0.1 \mu\text{M}$) was located at 95 m ($\sigma_t = 15.85$) where the dissolved oxygen (DO) concentration was $\leq 5 \mu\text{M}$. Fe(II) increased above the detection limit ($0.025 \mu\text{M}$) at 105 m ($\sigma_t = 16.10$). Comparison of the vertical profiles of Fe(II) and Mn_{DISS} clearly show that the onset of Fe(II) in the cyclonic region occurred about 10 m deeper (0.25

greater density units) than the onset of Mn_{DISS} . Thus, there exists an offset between the onsets of Mn_{DISS} and Fe(II) in the open sea.

The Mn_{DISS} gradient at the suboxic/anoxic interface was very steep, increasing from 0.1 to 8.1 μM over a 20–25-m ($\sigma_t = 16.0$ – 16.5) interval. This is consistent with the findings of Landing and Landing (1991), who reported a dramatic increase of dissolved Mn through the suboxic zone at central basin stations. The increase in Fe(II) was not as steep as dissolved Mn; it increased over a depth interval of about 50 m ($\sigma_t = 16.10$ – 16.5). Mn_{DISS} reached its highest values of 8.1 μM in the anoxic layer below 150 m ($\sigma_t = 16.50$). Fe(II) reached its

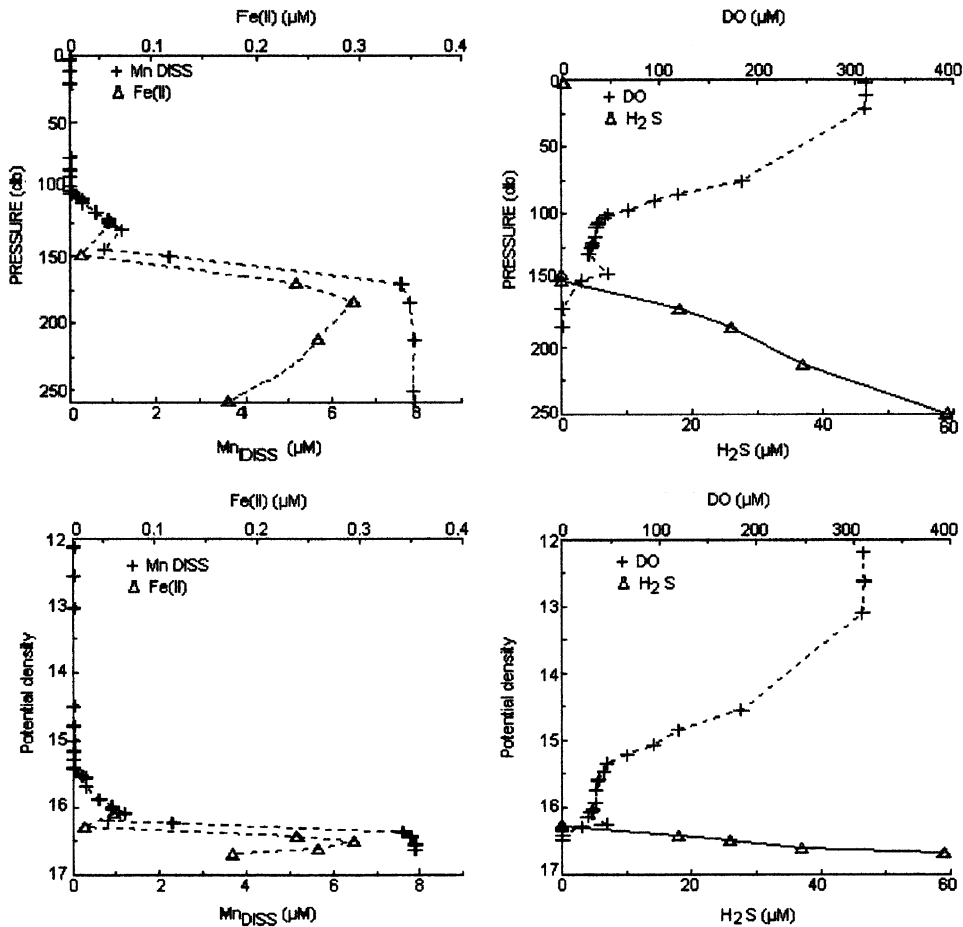


Fig. 6. Vertical profiles with respect to depth and density in the southwestern of Black Sea (station 14). DO and H₂S data are from Tugrul and Salihoglu (2002).

maximum concentration of 0.32 μM at about 200 m. These features are consistent with the observations of Lewis and Landing (1991) and Haraldsson and Westerlund (1988).

3.2. Northwestern shelf (station 3)

At station 3 on the NW shelf the onset of Mn_{DISS} (>0.1 μM) was located at 120 m ($\sigma_t = 15.85$) (Fig. 4). At this depth, Fe(II) was below the detection limit (0.025 μM). The onset of Fe(II) was located at a greater depth (130 m) $\sigma_t = 16.0$, but still above the sulphidic layer. Comparisons of density-dependent vertical profiles of Fe(II) and Mn_{DISS} on the NW shelf indicate that the Fe(II) onset was located approximately 0.15 density units (10 m) below that of Mn_{DISS} in the northwestern shelf (Fig. 4). Mn_{DISS} increased steeply in the suboxic–anoxic interface. The Mn_{DISS} concentration reached

its maximum value of 7 μM at 200 m ($\sigma_t = 16.50$), in the anoxic layer. The Fe(II) profile also displayed a maximum of 0.28 μM at about the same depth.

3.3. Northwestern slope (station 12)

The results at station 12 on the NW slope indicate that the onset of dissolved manganese (Mn_{DISS} >0.1 μM) was located at 125 m ($\sigma_t = 15.85$), where DO concentration was about 5 μM (Fig. 5). At the depth of suboxic/anoxic interface, where DO and H₂S became undetectable, Fe(II) was still below the analytical detection limit of 0.025 μM and became detectable at 140 m ($\sigma_t = 16.10$), where the hydrogen sulfide was still undetectable (<1.0 μM). The Fe(II) onset was located nearly 0.15 density units (15 m) below the onset of Mn_{DISS} in the anoxic layer; Mn_{DISS} reached its maximum concentration of 8.3 μM at 210 m ($\sigma_t = 16.50$). The Fe(II) profile

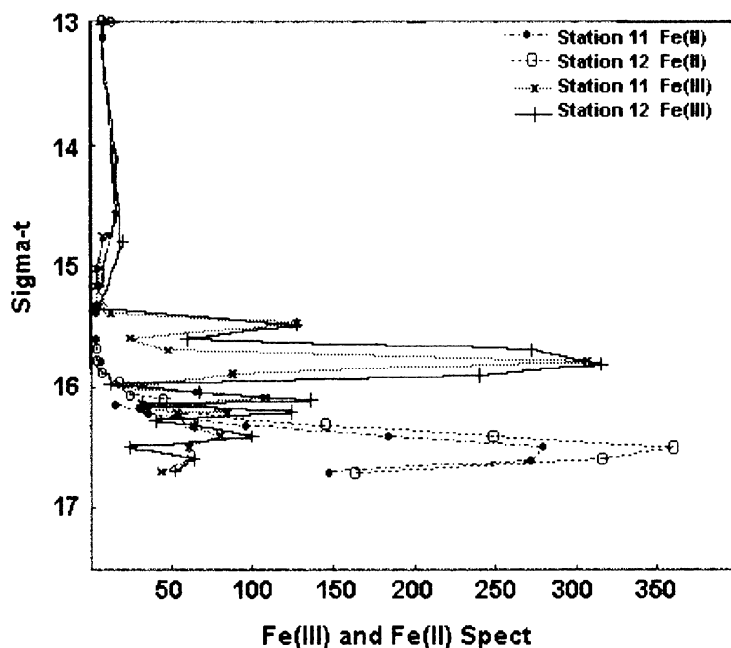


Fig. 7. Dissolved Fe(III) and Fe(II) profiles at stations 11 and 12.

also displayed a maximum at the same depth, reaching $0.315 \mu\text{M}$. Unlike stations 2 and 3, dissolved Fe(III) was also detected at nanomolar levels in the oxic/anoxic transition zone waters (Fig. 7).

The dissolved Fe(III) profile exhibited a primary maximum of greater than 300 nM at $\sigma_t = 15.85$. It decreased sharply to undetectable levels in the anoxic interface, where Fe(II) concentrations became detectable ($>0.025 \mu\text{M}$). The oxidation of the upward flux of Fe(II) by bacteria in the suboxic zone using the downward flux of oxygen (Sobolev and Roden, 2001; Straub et al., 1996) result in accumulation of reactive dissolved Fe(III) species in this zone.

3.4. Southwestern area (station 14)

At station 14 in the SW Black Sea the onset of Mn_{DISS} was located at 115 m ($\sigma_t = 15.85$; Fig. 7). At this depth DO was $35 \mu\text{M}$. Fe(II) was first detected at $\sigma_t = 16.15$ (130 m), where DO is about $25 \mu\text{M}$. Unexpectedly, the depth at which dissolved Fe(II) was first detected was shallower than the upper border of suboxic layer ($\sigma_t = 16.3$; $D = 165 \text{ m}$). The onset of reduced iron was shallower by about $\Delta\sigma_t \cong 0.25$, compared to the boundary of hydrogen sulfide bearing water layer at $\sigma_t = 16.40$. Mn_{DISS} reached concentrations of $8.0 \mu\text{M}$ at depths greater

than 185 m ($\sigma_t = 16.50$). Fe(II) increased to a maximum concentration of $0.295 \mu\text{M}$ at the same depth.

In this SW coastal region, we observed anomalies in the characteristics of the oxic/anoxic transition layer. For example, there were minima in the Mn and Fe profiles at 150 m ($\sigma_t = 16.25$). These were likely due to the propagation of oxygen-rich Mediterranean waters into the upper depths of the sulfide-bearing water bodies ($\sigma_t = 16.4$) by the Bosphorus Plume (Konovalov et al., 2003).

4. Discussion

Data from all stations in this study were examined to assess regional variations in features of the Mn_{DISS} and Fe(II) profiles (Figs. 8 and 9). At all stations, the onset of Mn_{DISS} was at $\sigma_t = 15.85$, whereas the onset of Fe(II) occurred at $\sigma_t = 16.10$ – 16.15 . A density difference of $\Delta\sigma_t = 0.25$ – 0.30 existed between the onsets of Fe(II) and Mn_{DISS} . The commencement of Fe(II) at greater densities than the Mn_{DISS} onset is related to the redox potential of the water column. Although the onsets of Mn and Fe reduction occurred at similar density surfaces over the deep basin, the corresponding depths varied by as much as 30 – 35 m between stations. At station 14 the onsets of Mn_{DISS} and Fe(II) were located in the partly oxygenated zone

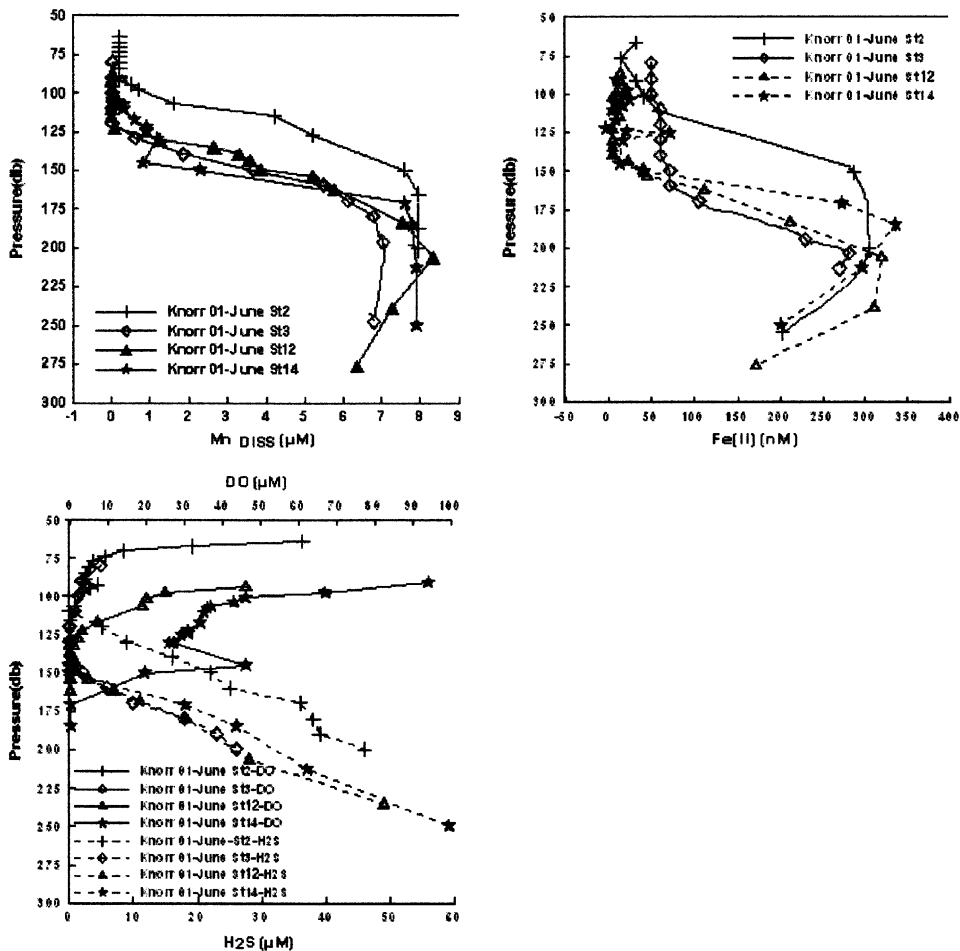


Fig. 8. Composite pressure dependent vertical profiles of Fe(II), Mn_{DISS} , H_2S and DO. DO and H_2S data are taken from Tugrul and Salihoglu (2002).

where DO was in the range of 25–35 μM . The light transmission (Fig. 10) and redox properties (Fig. 11) of the waters of this station differed from the others. These distributions were probably due to the effect of oxygenated Mediterranean waters that flow in via the Bosphorus strait. The chemical characteristics and redox potential of the southwestern region are modified by the lateral injection of oxygenated Bosphorus plume waters into the intermediate depths of the region (Konovalov et al., 2003).

Even though the onsets of Fe(II) and dissolved Mn occurred at different density surfaces, their depth (density) of maximum concentration coincided ($\sigma_t = 16.5$, depth 100–185 m). This could be due to the changing degree of saturation of Fe sulfides as the sulfide concentration increases with depth. The maximum Mn_{DISS} concentrations measured at $\sigma_t = 16.5$ ranged from 7.0 to 8.3 μM ,

with the lower values for northwestern shelf. The maximum Fe(II) concentrations ranged from 0.275 to 0.32 μM , with the lower values for northwestern shelf.

The southwestern region of Black Sea has a distinct hydrochemical signature. For example, at Station 14 the suboxic zone was below 160 m due to lateral injection of oxygen-rich waters of the Bosphorus plume (Konovalov et al., 2003). Accordingly, E_h was altered in the water column and the onsets of Mn_{DISS} and Fe(II) were shifted to slightly greater density values in this region. The light transmission profiles from the stations sampled are displayed in Fig. 10. At station 14 a turbid layer was observed at the depth of the suboxic–anoxic interface. Yakushev and Deborskaya (1997) reported a fine particulate layer (FPL), which was stable during the year. Sorokin (2002) also reported a deep turbid

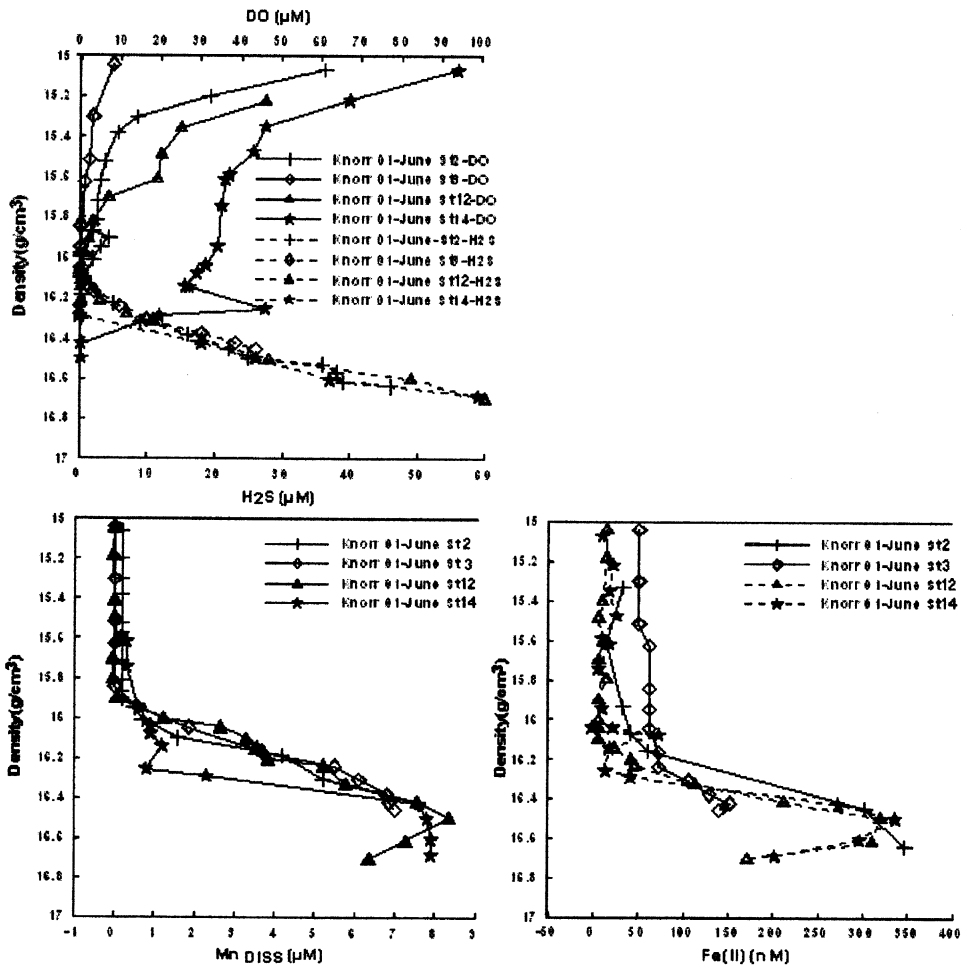


Fig. 9. Composite density dependent vertical profiles of Fe(II), Mn_{DISS}, DO, and H₂S. DO and H₂S data are taken from Tugrul and Salihoglu (2002).

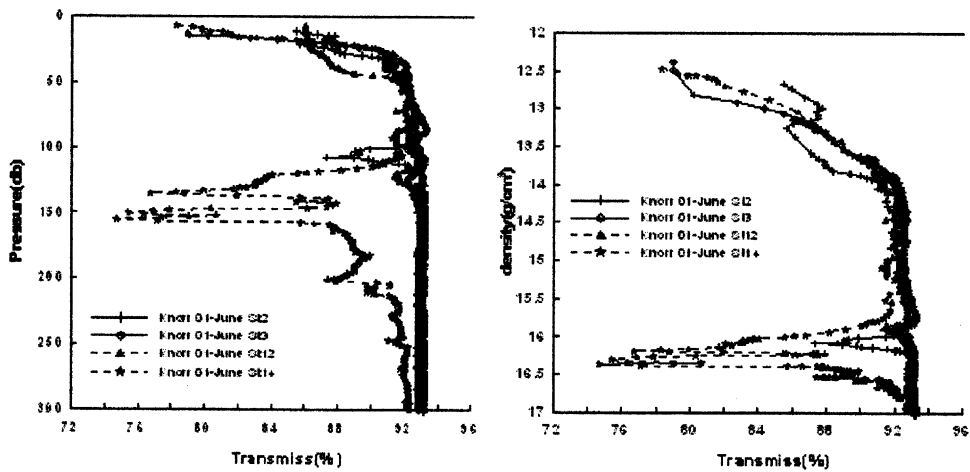


Fig. 10. Vertical profiles of light transmission at the stations visited.

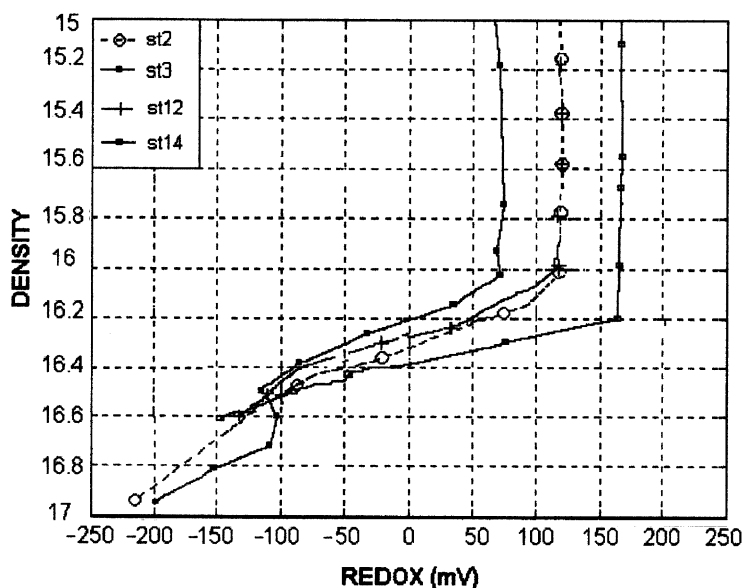


Fig. 11. Redox potentials of the studied stations.

layer that was denser and deeper in the summer than during winter-spring. The turbid layer had a thickness of approximately 50 m, between 125 and 175 m depth ($\sigma_t = 16.0\text{--}16.4$) (Fig. 11). In the FPL, the DO concentrations were in the range of 20–30 μM . It appears that the FPL in coastal regions was partly oxygenated by the stronger advective-diffusive mixing of oxygenated water masses. At Station 14, the first appearance of sulfide was observed at $\sigma_t = 16.35\text{--}16.40$, which was much deeper than in the cyclonic region ($\sigma_t = 16.18\text{--}16.20$). Thus, the onsets of Mn_{DISS} and Fe(II) were established at greater density surfaces ($\sigma_t = 16.10$ and 16.30, respectively).

Whilst the oxic/suboxic interface was located at $\sigma_t = 15.0$ in the northern shelf area, it occurred deeper in the water column in the western cyclonic gyre, where a well-developed oxycline extended down to $\sigma_t = 15.50\text{--}15.60$. In the western cyclone, the thickness of the suboxic zone ($\text{DO} < 5 \mu\text{M}$, $\text{H}_2\text{S} < 1 \mu\text{M}$) was about 30 m, between 80 and 110 m depth, which was thinner than on the northern shelf.

Throughout the Black Sea basin, the $\text{Mn}_{\text{DISS}}/\text{Fe(II)}$ ratio at the depth of maximum concentrations was about 27 (8.0/0.30 μM).

Mn_{DISS} and Fe(II) maxima were located at the same density surface $\sigma_t = 16.5$, which appear at greater depths in south western coastal regions than in the gyre regions (Table 2).

Table 2

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General characteristics	Potential density (σ_t)
Oxycline onset ^a	14.50–14.60
Nitrate maximum ^a	15.30–15.50
DO (< 5 μM) ^a	15.50–15.90
PO_4 minimum ^a	15.85–15.95
Dissolved Mn onset (> 0.1 μM) ^b	15.85–15.95
Particulate Mn max (65 nm) ^c	15.85–15.95
Fe(III) max (300 nM) ^c	15.85–15.95
NH_4 (> 0.2 μM) ^a	16.0–16.10
Fe(II) (> 25 nM) onset ^b	16.10–16.15
Deeper PO_4 maximum ^a	16.15–16.20
H_2S (> 1 μM) ^a	16.15–16.20

^aTugrul et al. (1992).

^bThis work.

^cErdogan (2002).

The redox potential varies from 200 to 300 mV in the oxic zone to –180 mV in the anoxic zone in the water column of the Black Sea (Skopintzev et al., 1966). This intense redox gradient is maintained by microbial decomposition processes and the downward and upward fluxes of oxidized and reduced chemical species, respectively (Brewer and Murray, 1973). These counter fluxes result in a rapid decrease in redox potential at the base of the main pycnocline. Along this redox gradient, sinking manganese and iron oxyhydroxides particles undergo reductive dissolution at depths corresponding to

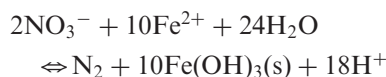
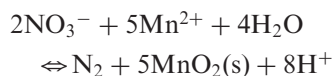
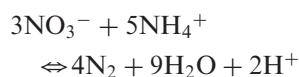
their respective reduction potentials, resulting in the differences observed in the vertical profiles of Mn(II) and Fe(II) reported here and in the previous studies (e.g., Lewis and Landing, 1991; Haraldsson and Westerlund, 1988). Conversely, there is an upward advective-diffusive flux of dissolved Mn(II) and Fe(II). Murray et al. (1995) suggested that the distributions and gradients of Mn(II) and Fe(II) (and NH_4^+) are consistent with “chemo-denitrification” reactions, where NO_3^- reacts with these reduced species to form N_2 and Mn(IV) and Fe(III) oxyhydroxides.

In the shallower parts of the suboxic zone ($\text{DO} > 10 \mu\text{M}$), Mn^{2+} is oxidized by DO, while at the suboxic/anoxic interface zone ($\text{DO} < 5 \mu\text{M}$) it appears to be oxidized by nitrate (NO_3^-) to produce particulate MnO_2 and N_2 . Experiments conducted in the California Borderland (Shaw and Gieskes, 1990) showed that oxidation of Mn^{2+} may occur via NO_3^- rather than DO if the system is poor suboxic. While there is no direct evidence that this reaction occurs in the Black Sea, sediment studies have supported its occurrence in other low-oxygen environments (Shaw and Gieskes, 1990; Schultz et al., 1994; Luther et al., 1997). The reaction between MnO_2 and H_2S also has been shown to take place in natural environments (Burdige and Nealson, 1986). Nevertheless, the kinetics of these reactions and the extent of microbial mediation are still largely unknown.

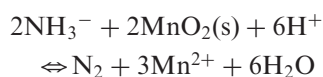
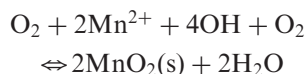
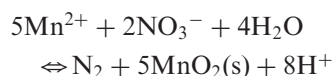
5. Conclusions

The vertical distributions of dissolved manganese and iron, together with those for oxygen and hydrogen sulfide, indicated that the occurrence of complex redox-dependent reactions in DO-depleted waters governs the position and structure of the suboxic/anoxic transition zone in the Black Sea. In general, two known bacterially mediated processes describe the redox cycles of Fe and Mn in any oxic/anoxic water column (Murray et al., 1995). The first one describes oxidation of dissolved Mn (II) and Fe(II) transported by upward diffusion diffusively upward above the anoxic interface to generate particulate oxidized forms of these elements. The second process includes reduction and dissolution of sinking oxides and oxyhydroxides of Fe(III) and Mn(III, IV), which maintains the inventory of dissolved reduced forms of these metals in the anoxic zone. Sinking Fe(III) and Mn(III, IV) oxyhydroxides also can be oxidants of sulfide in

the absence of oxygen. Murray et al. (1989, 1995) discussed possible reactions involving iron and manganese redox cycling in the Black Sea. The following reactions were suggested by Murray et al. (1995) to occur within the suboxic–anoxic boundary.



This model needs constant input of NO_3^- into the redox layer in order to oxidize the reduced species diffusing into suboxic zone. Luther et al. (1997) suggested an alternative model for reactions between manganese and nitrogen species.



Pumping of anoxic waters upward from deep waters by cyclonic circulation in the cyclonic region of the western Black Sea results in an upward shift of the main oxycline. Thus, the DO concentration in the cyclonic region (Station 2) decreased to suboxic levels ($10 \mu\text{M}$) at 75 m ($\sigma_t = 15.35$), much shallower than at the southern coastal stations. Similarly, the onset and maximum concentration depths of iron and dissolved manganese are shifted to shallower depths compared to the southwestern coastal stations.

Based on hydrochemical characteristics of the central gyre and coastal regions, the profiles of iron and manganese showed the following typical distinguishing features:

- (I) Mn_{DISS} was first detected at a density of about $\sigma_t = 15.85$ at most stations, but shifted to $\sigma_t = 16.25$ in southwest coastal stations where a sharp decrease in light transmission was consistently observed. The thickness of the water column with the prominent light

transmission minimum was relatively larger and more intense in the southwestern coastal water, where intrusion of DO enriched water associated with the Bosphorus Plume takes place. Thus, the onsets of Mn_{DISS} and Fe(II) are shifted down to higher density surfaces.

- (II) Fe(II) was first observed at about the $\sigma_t = 16.10$ at most stations, but was shifted to $\sigma_t = 16.15$ in southwest coastal water.
- (III) There was a distinct difference ($\Delta\sigma_t = 0.2$) between the onset densities of Fe(II) and Mn_{DISS} .
- (IV) The dissolved Fe (III) profile displayed two characteristic maxima in the suboxic zone of northernwestern slope, where the suboxic zone was relatively thick. The primary maximum was located at $\sigma_t = 15.85$ and coincided with the onset of dissolved Mn, and secondary one was deeper at $\sigma_t = 16.0$.
- (V) No long-term change has been observed in the major vertical features of Mn_{DISS} and Fe(II) since the 1988 expedition of RV/Knorr.

The dissolved Mn concentration began to increase in the zone of nitrate reduction, where oxygen had decreased to below detection limits. The modeling studies have indicated that vertical mixing of oxygen cannot account for Mn oxidation below 85 m (Lewis and Landing 1991), but nitrate reduction could provide the necessary oxidizing equivalents. The absence of oxygen in the zone where Mn began to increase supports the hypothesis that, in oxygen-depleted waters, dissolved manganese can react with nitrate to produce settling particulate MnO_2 and N_2 (Murray et al., 1995, Luther et al., 1997). The upward flux of sulfide and ammonium is then oxidized by particulate manganese to form elemental sulfur, nitrogen gas and dissolved manganese. Elemental sulfur is reduced back to sulfide by bacteria, whereas dissolved manganese further contributes to nitrate reduction.

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