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

Selehattin Erdoğan, Semal Yemenicioğlu, Süleyman Tuğrul

*sels@ims.metu.edu.tr, semal@ims.metu.edu.tr, tugrul@ims.metu.edu.tr*
*METU-Inst. Mar. Sci. P.O.BOX. 28, 33731 Erdemli-Mersin-Turkey*

**Abstract-** This study was done to determine the behaviour and distribution of dissolved and particulate forms of manganese (Mn) and iron (Fe) in the water column of the Black Sea. We focused our work particularly to the suboxic zone (oxic-anoxic interface). In the western cyclonic region dissolved Mn ($Mn_{DISS}$) commences at the density sig-t =15.85 depth. Dissolved Fe (Fe(II)) onset at greater density depth (sig-t=15.90). These features are disturbed in the southern coastal regions as a result of the physical processes such as, intrusion of oxygenated Bosphorus water, formation of anticyclonic eddies and rim currents. These physical processes shift the onset of dissolved Fe (Fe(II))and dissolved Mn ($Mn_{DISS}$)to greater density depths.

**Keywords-** Black Sea, suboxic layer, dissolved Mn, particulate Mn, dissolved Fe, particulate Fe.

## Introduction

The Black Sea is a land-lock basin having limited interaction with the Mediterranean Sea through the Turkish Strait System. Because of strong density stratification vertical mixing and supply of oxygen to the deep waters by lateral influxes is very poor. This make Black Sea worlds largest anoxic basin. A distinct characteristic of the Black Sea basin is the formation of a transitional layer, so called suboxic layer, between the oxic and the anoxic layers. This interaction is manifested by an abrupt change of redox potential (Bezberedov, 1993: Skopintzev *et al.* 1966). The redox zone is established by two opposite fluxes; upward flux of reduced species $H_2S$, $S^0$, $S_2O_3$, $Mn^{2+}$, $Fe^{2+}$, $CH_4$, $NH_4$ against the downward flux of oxidized species, $O_2$, $NO_3$, $Mn^{4+}$, $NO_2$, $Fe^{3+}$. These counter fluxes generate a wide range of redox potential within a narrow segment of the water (Lewis and Landing, 1991). In this study the vertical distributions of dissolved and particulate forms of manganese and iron species (Table1) in the suboxic zone of the open and coastal regions of the Black Sea (Fig. 1) was determined. The present data are also compared with the previous works.

## Material and Method

Hydro chemical data in this study were collected during the cruises of R/V Bilim and R/V Knorr in the Black Sea. Seawater samples were collected by 5 L niskin bottles. Sub–samples were taken from niskin bottles directly into 50 ml PE

tubes by passing through GF filter adapted hose and taking care to avoid diffusion of atmospheric oxygen that cause oxidation of the reduced species. $Mn_{DISS}$ and Fe(II)) were measured by colorimetric method (Grasshoff, 1983). The detection limits of the method under our laboratory conditions are 100 nM for $Mn_{DISS}$ and 25 nM for Fe(II). Particulate forms of Mn and Fe were measured by atomic absorption spectrophotometer.

Table 1. Methods used to measure iron and manganese.

| Metal species | Instrument used for analysis | Method of Measurement |
|---|---|---|
| $Mn_{DISS}$[Mn(II+III)] | Colorimeter | Automated and manual |
| Fe(II) | Colorimeter | Automated and manual |
| Fe(II+III) | Colorimeter | Manual |
| Mn particulate [$Mn(OH)_2$,$Mn_XO$] | Atomic Absorption spectrophotometer | Graphite Furnace |
| Fe particulate [$Fe_2S_3$ $FeS_2$ FeS] | Atomic Absorption spectrophotometer | Graphite Furnace |

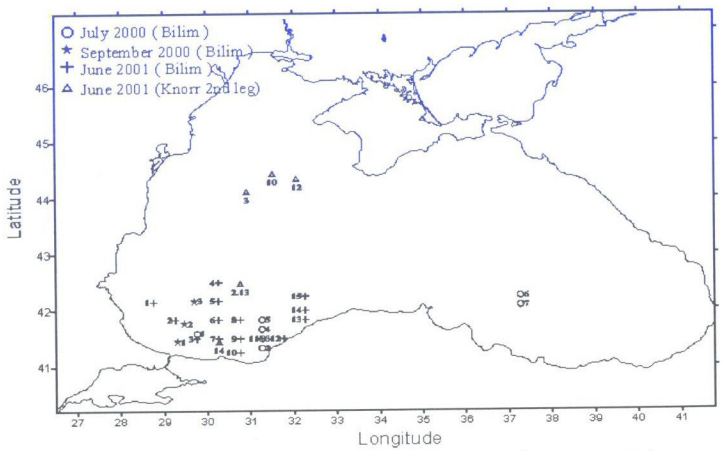


Fig. 1. Stations visited during the course of the present study.

**Results and Discussion**

The results obtained in this study are summarized Fig. 2. Since the redox changes control the distribution of the species of Fe and Mn, dissolved oxygen (DO) and hydrogen sulfide ($H_2S$) also included in the Fig. Depending on the hydro chemical characteristics of the studied area general profiles of DO and $H_2S$ show some typical distinguishing features. Since Mn and Fe are redox sensitive elements the changes in redox potential which is the result of variation in DO and $H_2S$ concentrations, produce some characteristic profiles of Fe(II) and $Mn_{DISS}$ commences at sig-t = 15.85 (95 m) density surface where dissolved oxygen (DO) concentration was about 5.0 µM. Fe(II) first appeared at sig-t = 16.10 (105 m) density surface. This finding is very consistent with the findings of Lewis and Landing, (1991).



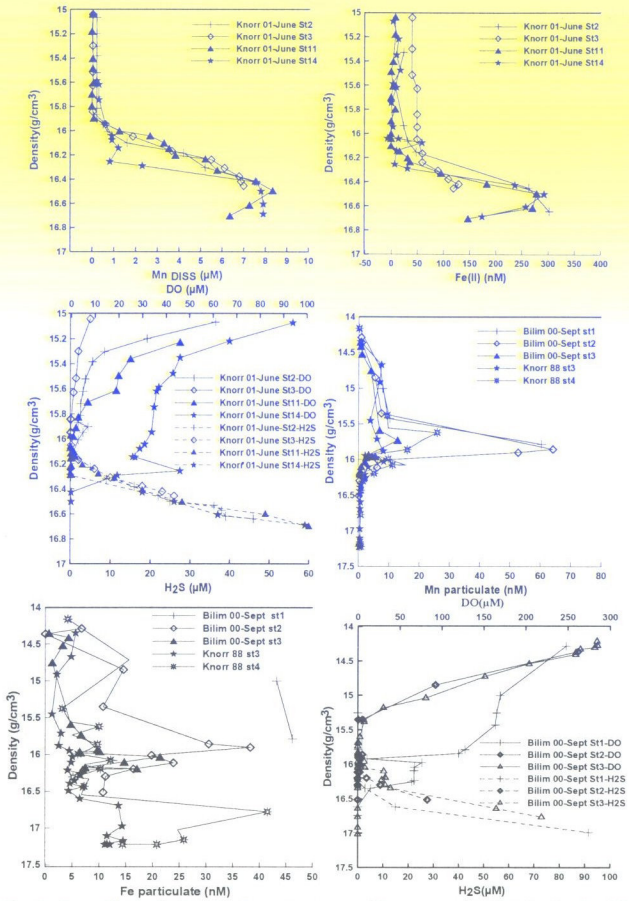


Fig. 2. Vertical profiles of chemical parameters with respect to density in the Black Sea

Comparison of density dependent vertical profiles of Fe(II) and $Mn_{DISS}$ shows that there is a shift of about 0.2-density unit (about 20) m between the depths of the onset of dissolved iron (Fe(II)) and $Mn_{DISS}$. The onset of Fe(II) corresponds to greater density surfaces of about 0.2-0.25 density unit than the onset of $Mn_{DISS}$ profile in the cyclone region. The concentration gradient of the $Mn_{DISS}$ in the suboxic zone became very large within a short depth interval and in the anoxic layer at 160 m (sig-t = 16.50) its concentration reaches its peak values of 8500-9000 nM. At the same depth Fe(II) also reaches its maximum with a concentration of 350 nM. These findings are consistent with the findings of Lewis and Landing, (1991), Haraldsson and Westerlund, (1988). While the densities of onset for Fe(II) and $Mn_{DISS}$ in southern Black Sea are similar to that of western cyclone, increase of $Mn_{DISS}$ and Fe(II) shifted to sig-t =16.25 and 16.35 respectively. At the stations located at north western shelf of the Black Sea onset of $Mn_{DISS}$ was located at sig-

t=15.85 which is similar to the one obtained at cyclonic region. The depth at which this density surface established is 120 m. In cyclonic region the depth of sig-t = 15.85 was met at much shallower depth (95 m) where dissolved oxygen (DO) concentration reduced to about 5 μM. Fe(II) was first appeared at the depth of sig-t=16 density surface which corresponds to 130 m water depth. Dissolved Fe profile displays two characteristic peaks in the suboxic zone at the stations in North Slope where suboxic zone was relatively thick. The first one is located at sig-t=15.85 and coincides with the onset of reduced Mn, and the second one at sig-t =16.0. There is another regional difference that affects the distribution of Fe and Mn. Fine particle layer (FPL) is relatively thick and intense in southern coastal water where DO intrusion brings it up to about sig-t = 16.30 and rapid increase zone of $Mn_{DISS}$ and Fe (II) concentrations shifted to higher density surfaces than the usual. Data obtained from station 14 at the western slope of the Black Sea indicate that the onset of $Mn_{DISS}$ was located at the depth of sig-t = 15.85 as usual but the water depth at which this density met was 115 m. At this density surface DO concentration was about 35.0 μM. At the depth of sig-t = 16.15 (130 m), where DO is about 25.0 μM, Fe(II) exceeded the detection limit of 25 nM. Unexpectedly, the onset of dissolved Fe(II) was at smaller density surfaces than the upper border of suboxic layer (sig-t = 16.3 165 m). The onset of reduced iron was at shallower depths of about 0.25 density unit, as compared to the boundary of hydrogen sulphide bearing water layer of sig-t = 16.40.

In South west coastal coastal regions, we observed some anomalies in the main characteristics of the oxic/anoxic transition layer which are likely to be a result of a powerful and rapid propagation of oxygen rich waters in the upper boundary of the hydrogen sulphide bearing water bodies (sig-t = 16.4). Tugrul and Salihoglu in 1992 reported that like reduced Mn, dissolved ammonium that is oxidized by DO gives anomalous distributions in the suboxic-anoxic interface layer near the Sakarya canyon. In the Bosphorus plume, particulate Mn ($MnO_2$, $Mn_2O_3$, $Mn_3O_4$) profiles indicate that there is a coherent maximum at about sig-t = 15.85 density surfaces. Below this density depth the oxidized $Mn^{4+}$ is reduced to $Mn^{2+}$ where mildly reducing environment exists (DO ≤ 5μM). On the other hand, reduced Mn diffusing from the anoxic interface is oxidized to particulate Mn by bio-mediated processes in the suboxic zone (Tebo *et al.* 1984; Cowen and Bruland, 1985).

Particulate manganese profiles obtained during this work are in good agreementwith those reported by Lewis and Landing, (1992). Particulate iron makes a maximum dominated by FeS (mackinawite) and $Fe_3S_4$ (greigite) in anoxic zone. Scavenging of Fe(II) in redox boundary presumably mediated by bacterial action as in the case of Mn, (Jacobs *et al.* 1985, Landing and Westerlund, 1988). Increase in the concentration gradient of Fe(II) and Mn(II), from sig-t≅16.0 to sig-t≅16.5 slows down and after giving a primary peak at sig-t ≅ 16.5 density surface, their concentrations decrease gradually.



## Conclusions

Depending on hydro chemical characteristics of the region general profiles of iron and manganese show the following typical distinguishing features:

– $Mn_{DISS}$ commences at sig-t = 15.85 in the open sea; but it shifts to sig-t = 16.25 density depth in southwest coastal water where fine particular layer was observed. Dissolved manganese concentration increases steeply in suboxic anoxic interface.

– There is a constant shift of 0.2 density unit between the depth of the onset of dissolved iron and $Mn_{DISS}$. Fe(II) onset at the density surface of 0.2 density unit greater than the density surface of $Mn_{DISS}$ commencement.

– Dissolved Fe (III) profile displays two characteristic peaks in suboxic zone of North Slope. The first one is located at sig-t = 15.85 and coincides with the onset of reduced manganese, and second one at sig-t =16.0. There is another regional difference that affects the distribution of iron and manganese. FPL is relatively thick and intense in southern coastal water where DO intrusion brings it up to about sig-t = 16.30 and $Mn_{DISS}$ and Fe(II) onsets shifted down to higher density surfaces than the usual.

Thus scavenging character of iron and manganese determines the distribution of these metals throughout the Black Sea.

## References


Bezberedov. A.A., Eremeev. V.N., 1993. Black Sea: the oxic/anoxic interface. Marine Hydrography Institute, Sevastopol. 299p (in Russian) In: Sorokin. Y.I. The Black Sea Ecology and Oceanography. pp. 238

Cowen, J. P., Bruland, K. W., 1985. Metal deposites associated with bacteria: implications for Fe and Mn marine geochemistry. *Deep-Sea Research*, **32,** 253-272.

Grasshoff, K., Erhardt, M., Kremling, K., 1983, Determination of trace metals. Methods of Seawater Analyses. Second edition, Verlag Chemie GmbH Weinheim, 236-242.

Haraldsson, C. and Westerlund, S., 1988. Trace metals in the water columns of the Black Sea and Framvaren Fjord. *Marine Chemistry*, **23**, 417-424.

Jacobs, L., Emerson, S. and Skei, J. 11985. Partitioning and transport of metals across the O2/H2S interface in a permanently anoxic basin: Framvaren Fjord, Norway. *Geochimica Cosmochimica Acta*, **49**, 1433-1444.

Landing, W.M., Westerlund, S., 1988. The solution chemistry of iron (II) in Framvaren Fjord. *Marine Chemistry*, **23**, 329-343.

Lewis B.L. and W .M. Landing (l991). The biogeochemistry of manganese and iron in the Black Sea. *Deep-Sea Research,* **38**, Supp1.2, 773-S803.

Lewis B.L. and W.M. Landing l992. The investigation of dissolved and suspended–particulate trace metal fractionation in the Black Sea. *Marine Chemistry*, **40**, 105-141.

Murray, J.W., Codispoti, L.A., Friederich, G.E., 1995. Oxidation-reduction environment : the suboxic zone in the Black Sea. In: Huang, C.P., O'Melia, C.R., Morgan, J.J. (Eds.), Aquatic Chemistry: Interfacial and Interspecies Processes .ACS Advances in Chemistry Series No. 224. 157-176.

Skopintzev, B.A., Timofeeva, S.N., Danilenko, A.F.,1967. Organic carbon, nitrogen, and phosphorus and their inorganic derivatives in the Black Sea water. Oceanology (Moscow), 7:475-465, In: Sorokin. Y.I. The Black Sea Ecology and Oceanography. pp.245

Tebo, B. M., Nealson, K. H., Emerson, S., Jacobs, L. 1984. Microbial mediation of Mn(II) and Co(II) precipitation at the $O_2/H_2S$ interfaces in two anoxicfjords. *Limnology and Oceanography,* **29**, 1247-1258.