 DOI: 10.4194/trjfas.2009.0206

Distributions of Dissolved Forms of Manganese and Iron in the Water Column of the Southeastern Black Sea

Nigar Alkan[1,]*, Mehmet Tüfekçi[2]
[1] Karadeniz Technical University, Surmene Marine Science Faculty, Surmene, Trabzon, Turkey.
[2] Karadeniz Technical University, Department of Chemistry, 61080, Trabzon, Turkey.

* Corresponding Author: Tel.: +90.462 7522805; Fax: +90.462 7522158;
E-mail: nalemdag@ktu.edu.tr

Received 03 February 2008
Accepted 12 May 2009

Abstract

Dissolved forms of manganese and iron elements and some physical parameters in the water column of the Southeastern Black Sea were investigated. Samples were collected from 14 different depths of the water column in the station. Sea Bird SBE 25 Sealogger CTD was utilized for measurement of temperature, salinity, sigma-t and conductivity. However, Winkler method was used for dissolved oxygen measurements. Also, hydrogen sulphide was determined by using the titration method. Dissolved iron and manganese were analyzed with GBC 905 FAAS after pre-concentration of MIBK.

The Black Sea water surface temperature, salinity and oxygen were recorded as 16.23±6.87°C, 17.80±0.23 S‰ and 289.68±47.66 µm, respectively. The concentration of oxygen decrease to 10 µm and H_2S was recorded as 5 µm when the water column depth was 150 m depth. It was seen that the H_2S concentration increased depending on depth and it reached to 155.22±11.81 µm in 600 m depth. It was observed that the iron and manganese metals concentration clearly increased in depths at which oxygen consumed and hydrogen sulphide appeared. It was confirmed that the evaluation of many parameters in the Black Sea water column depending on sigma-t was more suitable than that depth profile. The behavior of trace metals were considerably influenced by conditions with hydrogen sulfide and without oxygen.

Keywords: Black sea, water column, dissolved metals,sigma-t, dissolved oxygen, hydrogen sulfide.

Introduction

The Black Sea is an important place among world seas because of oxic and anoxic characteristics of water column. It has multilayer structure because of being a close basin and having some dynamics characteristics.

Because of the strong density, stratification limits the oxygen supply to the deep waters. The Black Sea has become the biggest anoxic water mass in the world because the oxygen transfer is restricted by vertical mixtures, influencing upper borders of halocline. Surface water with oxygen in the Black Sea water column is separated with a passage layer from the deeper water with anoxic and sulfuric. Although the beginning of anoxic layer changes depending on the regions, it starts where sigma-t (σt) is almost 16.15-16.20 kg/m^3. In the ecosystem of Black Sea, the water with H_2S begins at 90-100 m in open waters where cyclonic circles are effective and after 160-180 m near the shore. The regional changes of hydro-chemical properties in oxic-anoxic passage areas are much more obvious than seasonal changes (Baştürk *et al*., 1994; Yılmaz, 2001; Yemenicioglu *et al*., 2006).

The concentration of trace elements in the Black Sea is in micromolar level (Spencer and Brewer, 1971). Dissolved manganese and iron are redox sensitive elements and the distribution of Mn and Fe in the water column depends on the biogeochemical dynamic of oxygen, sulfur, metals and organic particles. The maximum concentrations of dissolved manganese and iron in the Black sea are much higher than the other seas and oceans (Lewis and Landing, 1991).

Iron and manganese easily form in soluble oxyhydroxides and oxides in weak basic seawater. In seawater, dissolved oxides and hydroxides are formed by inorganic reactions which are occurred by dissolved iron and manganese compounds oxidized by oxygen in air. Some plankton and similar organisms living in the sea obtain these metal compounds from the water. These elements can rejoin the water from the contaminants gathered at the bottom by their deaths or interfuse to the bottom dregs by giving their hard dissolving compounds (Spencer *et al*., 1971; Nakayama *et al*., 1995).

In this study, seasonal distributions of dissolved iron and manganese have been studied at the oxic, suboxic and anoxic zones of the South Eastern Black Sea water column for two years. Also, some physical and chemical parameters were investigated at same period. This is the first time that a long-term research such as this has been done in the South Eastern Black Sea.

Materials and Methods

Seawater Sampling

The research was performed in the Southeastern Black Sea at 40°07'50" N 40° 40'41" E, Rize-Çayeli shores. Samplings were done eight times from

October 1995 to September 1997 on a seasonal basis. Samples were collected on 14 different depths of the Black Sea water column depending on different layer characteristics (Table 1).

The Nansen water bottles, capacity of which is 5 L for each, were used to take water samples from the required depths of water column (TUBITAK, 1989).

Seawater Analyses

Sea Bird SBE 25 Sealogger CTD was used for the temperature, salinity, sigma-t and conductivity measurements in water column. Dissolved oxygen was measured by Winkler titration method (Crompton, 1989).

For hydrogen sulphide analysis, the seawater sample was transferred to BOD glasses from Nansen bottles without air inlet and some water was overflowed. Approximately 20 ml sample was transferred back in a sensitive way from seawater sample, volume of which was fixed by shutting the cover of bottle, and 10-20 ml standard iodine solution was added to remaining sample according to the expected H_2S concentration. Then, the sample was back titrated with standard sodium thiosulphate solution and starch indicator by adding 2 ml 6N HCl solution. The concentrations of H_2S in the sample were estimated by thiosulphate solution which was consumed (TUBITAK, 1989).

The samples, which were gathered from seawaterto determine the dissolved iron and manganese, were transferred by filtering with GF/F filters to the 1 L polyethylene containers cleaned with acid and deionise water. pH was reduced under 2 by adding 2 ml nitric acid per L and the cover of container was tightly closed. The seawatersamples were pre-concentrated by using solvent extraction method in the laboratory. For this purpose, seawatersamples, pH of which was about 7-8, were complicated by ligand APDC and the complexes were taken to organic phase by MIBK. The metal complexes were transferred to water and acid phases by treating with nitric acid. The analyses of the dissolved iron and manganese in the pre-concentrated samples were done by using GBC 905 FAAS (Huang *et al*., 1995; Li *et al*., 1996).

Results and Discussion

The average variations of temperature, sigma-t, salinity and conductivity profile in the water column of Black Sea were presented in Figures 1-4.

The existence of the termocline and halocline layers in the Black Sea which has a stratified structure is obvious. It was determined that the variation of temperature depending on the depth was important ($P<0.001$). The time-dependent temperature variations occur in the water mass existing over cold intermediate layer (Table 1). Also, it was observed that termocline layer can exist under 50 m depth. Cold intermediate layer bottom border go down 150-175 meter depth.

The average salinity values obtained from depths by sampling during the research period and standard deviation were given in Table 1. It was seen that the standard deviations related to the variation of salinity in the halocline layer is higher due to mixes.

Average conductivity was determined at 2.47±0.37 S/m at the surface waters and minimum value was found about 2.00±0.03 S/m in the cold intermediate layer. Also, sigma-t was measured as 12.32±1.43 on the surface waters while it was measured as 14.43±0.08 at 75 meter in the cold intermediate layer.

Water column average dissolved oxygen and hydrogen sulfide data are presented in Figure 5 and 6. Dissolved oxygen concentration in the surface water was measured approximately as 250 µm as the minimum in summer and as 350 µm as the maximum levels in the winter. It was concluded that the seasonal variation of dissolved oxygen in the Black Sea water column is important. It was seen that the dissolved oxygen concentration in the water column decreased highly sharply under 75 m depths and it was reduced

Table 1. Sampling depth and the variation of temperature and salinity in Black Sea station

Depth (m)	Temperature (ºC)	Salinity (S‰)	Sigma-t (kg/m^3)
2	16.23±6.87	17.80±0.23	12.32±1.43
25	14.09±5.88	18.06±0.09	12.96±1.10
50	10.15±4.08	18.34±0.15	13.88±0.67
75	7.31±0.54	18.51±0.21	14.43±0.08
100	7.28±0.35	19.35±0.67	14.96±0.33
125	7.67±0.38	20.02±0.62	15.49±0.34
150	8.06±0.27	20.53±0.52	15.91±0.25
175	8.36±0.13	21.00±0.29	16.22±0.14
200	8.52±0.07	21.25±0.21	16.44±0.10
250	8.68±0.04	21.53±0.13	16.63±0.05
300	8.76±0.01	21.68±0.06	16.76±0.04
350	8.80±0.01	21.82±0.12	16.82±0.01

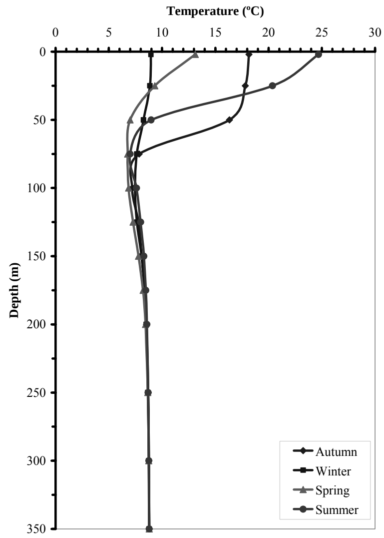

Figure 1. Seasonal changes of average temperature in the Black sea water column.

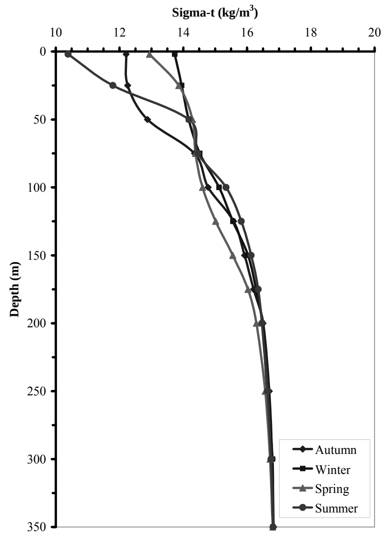

Figure 2. Seasonal changes of average sigma-t in the Black sea water column.

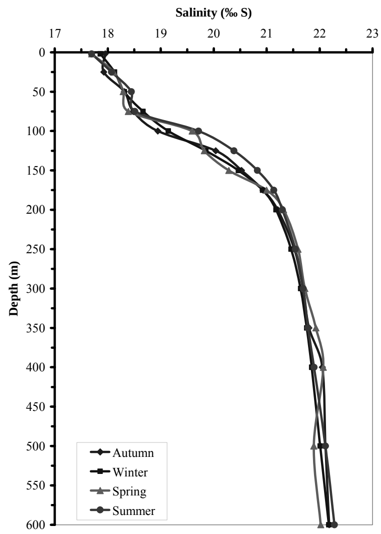

Figure 3. Seasonal changes of average salinity in the Black sea water column.

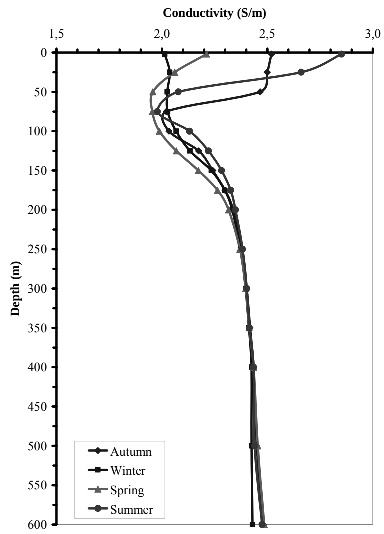

Figure 4. Seasonal changes of average conductivity in the Black sea water column.

to zero when the depth was almost at 200 m depth.

Dissolved oxygen increment was seen because of vertical mixing influence under 150 meter depth water especially in autumn. Also, vertical mixture is restricted in summer and sulphide concentration raised higher than others seasons.

It was determined that sulphide concentration at 150 m, 200 m, 300 m, 400 m, 500 m, and 600 meter depths was 1.83±0.73 µm, 8.54±6.75 µm, 38.77±8.81 µm, 85.79±2.48 µm, 122.84±16.24 µm, 152.22±6.52 µm, respectively.

It was seen that the oxygen transfer was restricted to deep water and the beginning of seawater with H_2S was measured almost 175 m as the vertical mixtures has influenced up to upper borders of halocline layer.

The variations of dissolved manganese and iron in water columns were highly affected by the concentrations of dissolved oxygen and hydrogen sulphide (Tebo, 1991). The distributions of iron and manganese in water column were given in Figures 7 and 8.

The variations of dissolved iron and manganese depending on the depth were similar. The maximum concentration of the dissolved Fe^{+2} was relatively lower than the dissolved manganese concentration.

The existing manganese and iron were nearly reduced in the middle layer of oxic- anoxic. It was observed that the dissolved iron and manganese concentrations were maximum at interface. It was

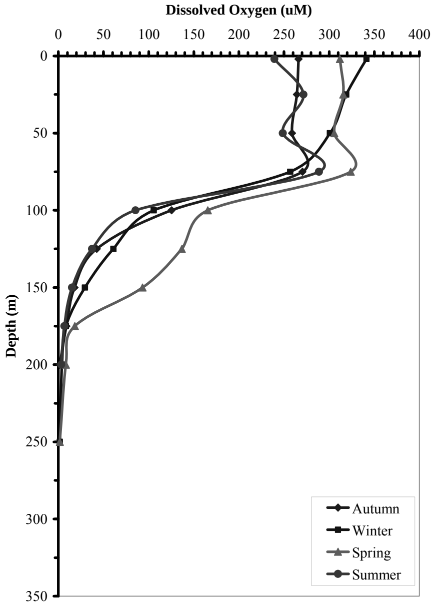

Figure 5. Seasonal changes of dissolved oxygen in the Black sea water column.

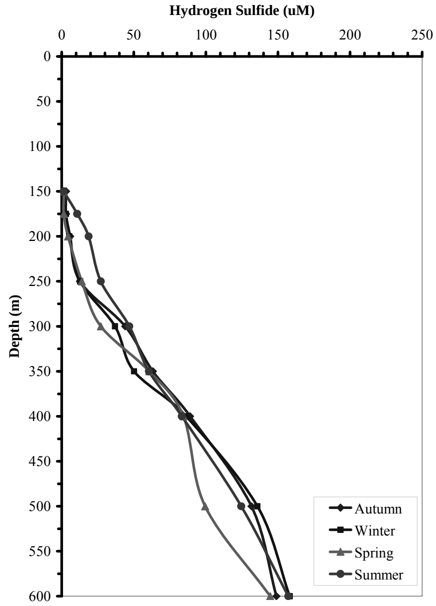

Figure 6. Seasonal changes of H_2S in the Black sea water column.

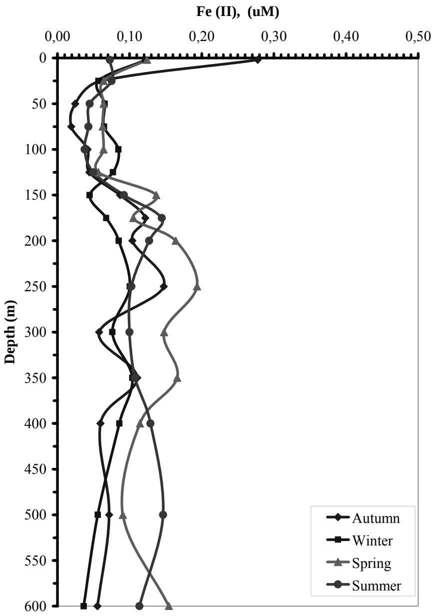

Figure 7. Seasonal changes of dissolved iron in the Black sea water column.

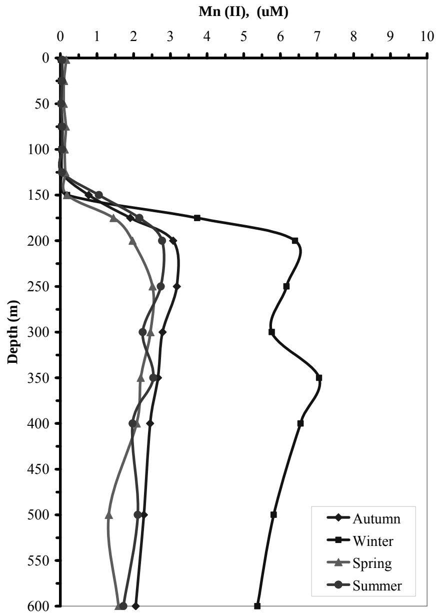

Figure 8. Seasonal changes of dissolved manganese in the Black sea water column.

determined that the maximum dissolved iron concentration existed under the region where the oxygen was zero and the concentration decreased because of reduction and precipitation in further depths (Murray *et al*., 1977; Murray *et al*., 1991).

The iron and manganese in redox loop are affected by hydrogen sulphide and dissolved oxygen concentrations. The hydrogen sulphide and dissolved oxygen, manganese and Fe^{+2} show similar characteristics depending on both depth and sigma-t in different periods (Konovalov *et al*., 2004; Schıppers *et al*., 2004).

The variations of hydrogen sulphide and dissolved oxygen, manganese and Fe^{+2} in water column were presented depending on sigma-t (density) in Figures 9-12. The upper border of anoxic layer remained in same density (σ_t=16.2) during this period.

The concentration of iron increased remarkably in autumn surface layer, because of rainfall. Under surface layers concentrations of iron were not different seasonally and concentration level was 0.1 µm. The dissolved Mn concentration began to increase, where oxygen had decreased below dedection limits.

Geochemical form of iron are a key parameter to

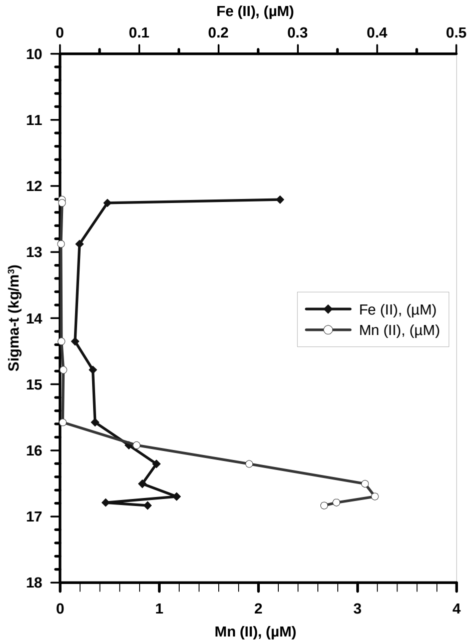

Figure 9. Distribution of dissolved iron and manganese in autumn in the Black sea water column.

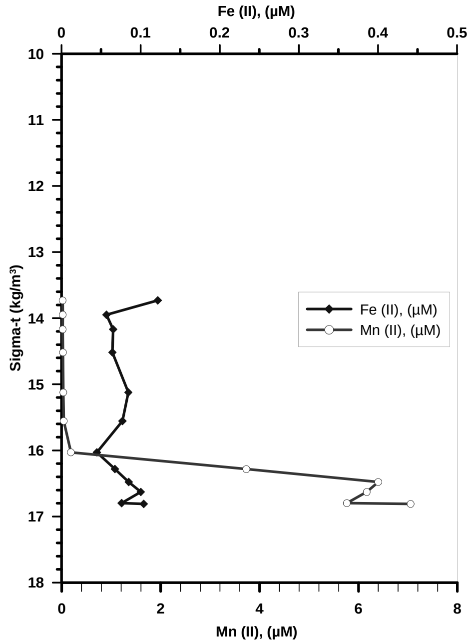

Figure 10. Distribution of dissolved iron and manganese in winter in the Black sea water column.

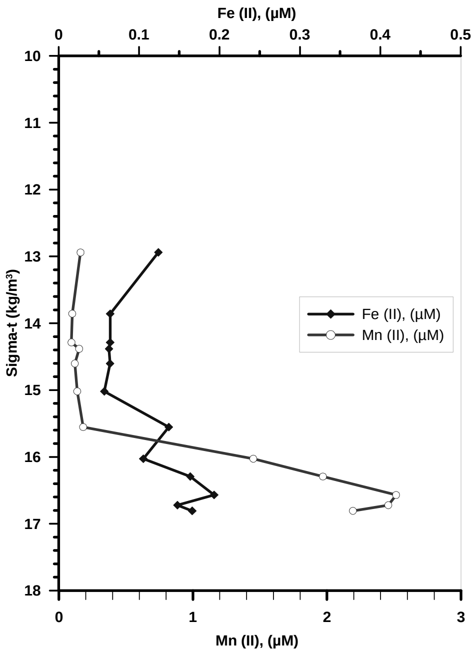

Figure 11. Distribution of dissolved iron and manganese in spring in the Black sea water column.

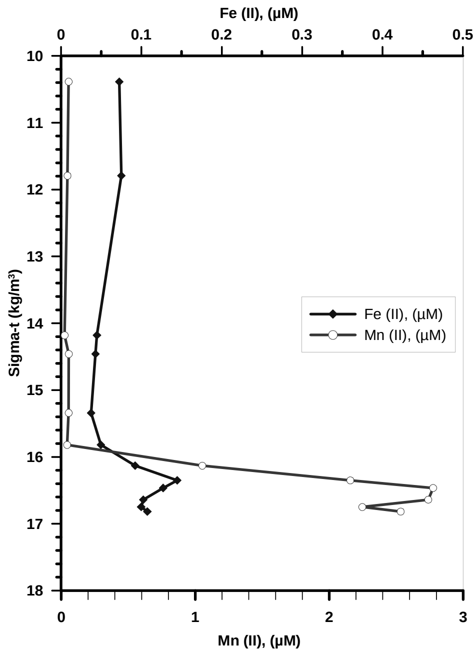

Figure 12. Distribution of dissolved iron and manganese in summer in the Black sea water column.

understand bio-availibility of iron in marine environment. Also, manganese and iron are reduced to divalent form in anoxic water. Despite the increasing dissolved Fe and Mn concentration at different depths, their concentration increase at same density layer of the Black Sea water column.

References

Baştürk, Ö., Saydam, C., Salihoğlu, İ., Eremeva, L.V., Konolov, S.K., Stoyanov, A., Dimitrov, A., Caciasu, A., Doragan, L. and Altabet, M. 1994. Vertical Variations in the Principle Chemical Properties of the Black sea in the Autumn of 1991. Marine Chemistry, 45: 149-165.

Crompton, T.R. 1989. Analysis of Seawater. Butterworth-Heinemann, Co, Oxford, London, 423 pp.

Huang, S.D., Lai, W.R. and Shih, K.Y. 1995. Direct determination of molybdenum, Chromium and Manganese in Seawater by Graphite Furnace Atomik Absorption Spectrometry. Spectrochimica Acta., 50(B): 1237-1246.

Konovalov, S., Samodurov, A., Oguz, T. and Ivanov, L.

2004. Parameterization of iron and manganese cycling in the Black sea suboxic and anoxic environment. Deep Sea Research I., 51: 2027-2045.

Lewis, B.L. and Landing, W.M. 1991. The biogeochemistry of manganese and iron in the Black sea. Deep Sea Research, 38: 773- 804.

Li, X.J., Schramal, Wang, H.Z., Grill, P. and Kettrup, A. 1996. Determination of Trace Metal Ions Co, Cu, Mo, Mn, Fe, Ti, V in Reference River Water and Reference Seawater Samples by Inductively Coupled Plasma Emission Spectrometry Combined with the Third Phase Preconcentration. Fresenius. J. Anal Chem., 356: 52-56.

Millero, F.J. 1991. The Oxidation of H_2S in the Black sea Waters. Deep Sea Research. 38, 2: 1139- 1150.

Murray, J.W. and Brewer, P.G. 1977. Mechanisms of removal of manganese, iron and other trace metals from sea water. Marine Manganese Deposits. Elsevier Oceanographic Series, 15: 291-325.

Murray, J.W., Top, Z. and Ozsoy, E. 1991. Hydrographic Properties and Ventilation of the Black sea. Deep Sea Research.38(2): 663- 690.

Nakayama, E., Obata, H., Okamura, K., Isshiki, K., Karatani, H. and Kimoto, T. 1995. Iron and Manganese in the Atmosphere and Oceanic Waters. Biogeochemical Processes and Ocean Flux in the Western Pasific, 53-68.

Schippers, A., Neretin, N.L., Lavik, G., Leipe, T. and Pollehne, F. 2004. Manganese (II) Oxidation driven by lateral oxygen intrusions in the western Black sea. Geochimica et Cosmochimica Acta., 69(9): 2241-2252.

Spencer, D.W. and Brever, P.G. 1971. Vertical Advection Diffusion and Redox Potentials as Controls on the Distribution of manganese and Other Trace Metals Dissolvend in Waters of the Black sea. J. Geophys. Res., 76: 5877-5892.

Stanev, E.V. 1990. Numerical Modelling of the Circulation and the Hydrogen Sulphide and Oxgen Distribution in the Black Sea. Deep Sea Research, 36: 1053-1065.

Tebo, M.N. 1991. Manganese (II) oxidation in the suboxic zone of the Black sea. Deep Sea Research., 38: 883-905.

TÜBİTAK, 1989. Ulusal Deniz Ölçme ve İzleme Programı Örnekleme ve Standart Yöntemler El Kitabı, Ankara, 49 pp.

Yemenicioglu, S., Erdoğan, S. and Tugrul, S. 2006. Distribution of dissolved forms of iron and manganese in the Black sea. Deep Sea Research II., 53: 1842-1855.

Yılmaz, A. 2002. Türkiye Denizlerinin Biyojeokimyası: Dağılımlar ve Dönüşümler. Turkish J. Eng. Env. Sci., 26: 219-235.