Proc. Symp. Mar. Chem. in the Arab Region, Suez, April, 1991 : 99 - 112

Manganese, Iron, Coblt, Nickel and Zinc in the Eastern Harbour and El-Mex Bay Waters, (Alexandria)

By

Hosny I. Emara and M. A. Shriadah

National Institute of Oceanography, Alexandria, Egypt.

Abstract

The concentrations of manganese, iron, cobalt, nickel and zinc have been determined by atomic absorption spectrophotometry on 97 sea-water sample from 8 stations in the Eastern Harbour and 7 stations from El-Me Bay (Fig. 1) of Alexandria during the period from November 1987 to January 1989. Trace metals concentrations are scatterd in the ranges (0.14-30.7), (1.39-148.0), (nd-0.32), (0.09-1.43) and (2.02-320.7) ug.1^{-1} respectively.

The concentrations of trace metals in both areas are in the order zn > Fe > Mn > Ni > Co at the surface and near the bottom water. El-Mex Bay, the most industrialized area in Alexandria, showed higher levels of Mn, Co, Ni and Zn in the bottom water than in the surface water. On the other hand, with the exception of Zn, the surface water of the Eastern Harbour reflects higher values in comparison with the bottom water.

Generally, the Eastern Harbour reveals slightly higher levels of Fe, Co, Ni and zn than El-Mex Bay water.

Trace metals Mn, Fe and Zn distribution suggests a clockwise circulation pattern of fresh water discharging from Umoum drain, to El-Mex Bay. The Eastern Harbour which is polluted by sewage, showed a tendency to concentrate Fe and zn inside the harbour by 14 and 39% more than outside the barour, while Mn, Co and Ni showed nearly the same level.

The distribution of Zn showed a rate of decrease of 15.9 ug.1^{-1} km^{-1} in the Eastern Harbour and can be used as a good tracer for fresh water or sewage discharge.

The appearance of local high concentration for one metal by possible contamination does not necessarily correlate with high values for other metals, however, the relationships Fe-Mn (r=0.80) Fe-Zn (r=0.80), Mn-Zn (r=0.85) showed good correlation for the bottom water as well as for the surface water (Mn-Ni, r=0.80) of El-Mexx Bay. The western Harbour also showed good correlations between Fe and Co (r=0.83), Mn and Co (r=0.60) for the surface and bottom water respectively.

The present data show that the concentrations of trace metals compared to other regions in the world are higher, probably due to the increasing pollution from waste and domestic sewage.

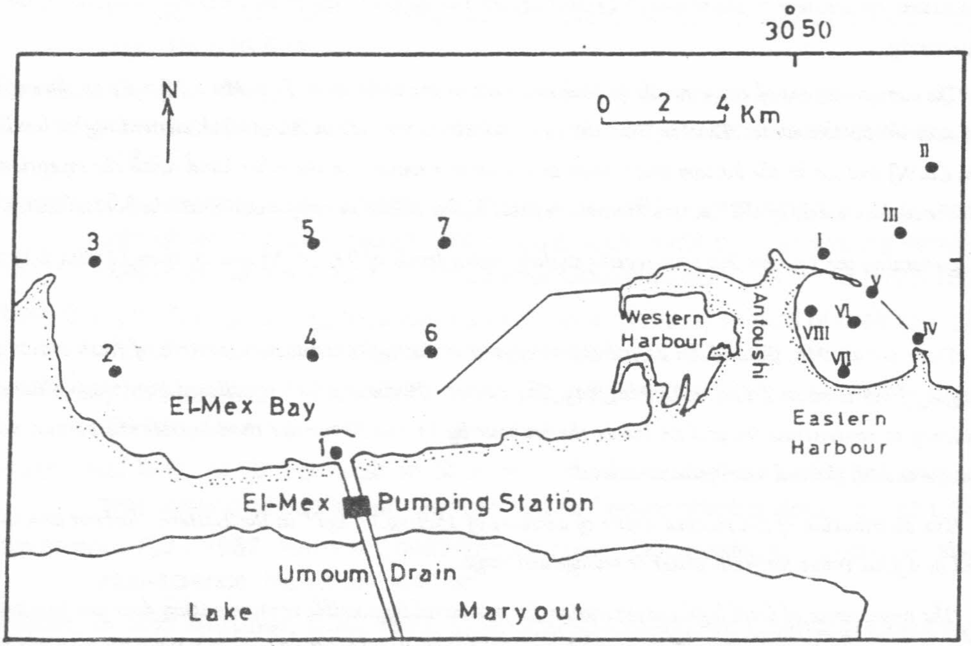

Fig. (1)

Area of investigation

Introduction

The eastern harbour (EH) is a semi-enclosed shallow bay (2-12 m). An average amount of 230,000 m^3 of wastes is discharged daily from a major outfall at Kayet Bey, in addition to 7 minor outfalls inside the harbour. At the northwestern edge of the harbour, there is a shipyard which gives additional source of trace metals to the harbour. El-Mex Bay, west of Alexandria city, is affected by brakish water (144-284 x 10^6 m^3/ month) from Umoum Drain. El-Mex Bay also receives directly industrial wastes from chloro-alkali plant, tanneries and slaughterhouse.

The bay is contaminated by petroleum products from El-Alamien oil field and from Suez-Mediterranean pipeline terminal (SUMED). The aim of the present study was to establish the levels of Mn, Fe, Co, Ni and Zn in this environment and the extent to which they are influenced by pollution from sewage, industrial and agriculural run-off.

Materials and Methods

Sea water samples were collected monthly (November 1987- September 1988) from 8 stations in the eastern harbour (EH) and bimonthly (January 1988-January 1989) from 7 stations in El-Mex (Fig.1). Surface and bottom water samples (2 liters) were filtered through a 0.45-um Millipore. Metals in the filtered sea water were preconcentrated using APDC-MIBK extraction procedure and back extraction into an acidic aqueous solution. Manganese was determined after the extraction of Mn oxinate into MIBK. The final acidic extracts were analyzed with a Varian (Model 1250) AA Spectrometer. The precision for replicate samples was between 5 and 10% of the lowest values determined in this study.

A detailed description of the method is given by Boniforti et, al., (1984). Dissolved oxygen, hydrogen sulphide and salinity were analysed according to Grasshoff (1976), and oxidizable organic matter by the method of Ellis et al. (1946).

Results and Discussion

The concentrations of trace metals studied Mn, Fe, Co, Ni and Zn in the eastern harbour (EH) and in El-Mex Bay are given in Table 1.

The concentrations in both areas are in the order Zn > Fe > Mn > Ni > Co at the surface and near the bottom waters. El-Mex Bay, the most industrialized area in Alexandria, Showed higher levels of Mn, Co, Ni, and Zn in the bottom water than in the surface water. On the other hand, with the exception of Zn, the surface water of the EH reflects higher values in comparison with the bottom water. Generally, the EH reveals higher levels of Fe (1.2 times), Zn (3.1 times) and Ni (1.4 times) than. El-Mex Bay waters.

Table (1) : Concentration of trace metals (ug. l^{-1}) in sea water samples of the eastern harbour and El-Mex Bay.

Sampling area		Manganese Range (Mean)	Iron Range (Mean)	Cobalt Range (Mean)	Nickel Range (Mean)	Zinc Range (Mean)
Eastern	S	0.28-5.54 (1.23)	5.82-96.2 (26.0)	nd-0.27 (0.07)	0.09-143 (0.55)	24.7-547.2 (162.4)
Harbour	B	0.14-5.40 (1.14)	5.00-69.9 (24.8)	nd-o.20 (0.05)	0.13-1.30 (0.47)	25.2861.5 (178.0)
El-Mex	S	0.14-30.7 (1.73)	1.39-148.1 (22.7)	nd-0.32(0.04)	0.09-1.25 (0.32)	2.02-195.7 (51.2)
Bay	B	0.14-27.0 (2.48)	1.39-119.0 (20.0)	nd-o.24 (0.05)	0.09-1.25 (0.40)	0.06-320.7 (59.7)

S: Surface; B: Bottom; nd: not detectable.

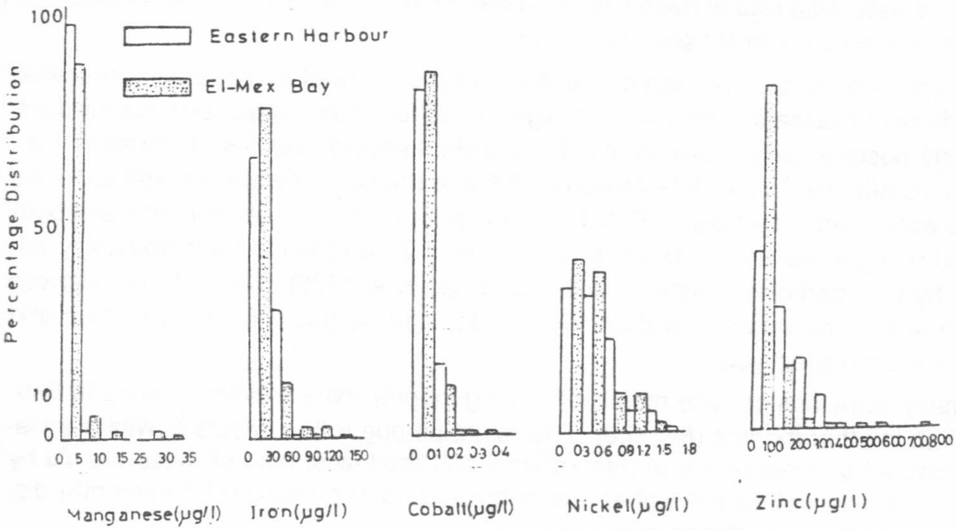

Fig. (2)

Percentage distribut of samples in ranges of defined concentration.

Percentage distribution of water samples in ranges of defined concentrations (Fig.2) showed that with the exception of Ni, 42-98% of the samples in the EH and 79-89% of El-Mex Bay exhibited low concentrations, while the very high concentrations represent insignificant portion (1%).

The elevated metal values at station VIII (EH) and stations 1,2 (El-Mex) are much less than that measured previously by El-Sayed and El-Sayed (1980) in the eastern harbour, and several orders of magnitude higher than values in the open Mediterranean waters (Bernhard, 1982) and are believed to be mainly due to sewage, industrial and agricultural runoff. The lowest levels for most of the elements were observed at stations II, III (EH) and station 6 in El-Mex Bay.

Trace metals Mn, Fe, Zn and salinity distribution (Fig 3) suggests a colckwise circulation pattern of fresh water discharging from Umoum drain to El-Mex Bay. The discharged brakish water and the industrial wastes resulted in a wide range of both trace metals and salinity (5,83-39.12) as well as stronger negative correlations (r = -0.63, -0.90) in El-Mex Bay compared with the EH (Fig.4).

The eastern harbour which is polluted by sewage, showed a tendency to concentrate Fe and Zn inside the harbour by 14% and 39% respectively more than outside the harbour, while Mn, Co and Ni showed nearly the same levels. The concentration of Zn showed a gradual decrease from 235.6 $ug.1^{-1}$ at station VIII to 140.4 $ug.1^{-1}$ at station II. The estimated rate of decrease of Zn was found to be 15.9 $ug.1^{-1}$ Km^{-1} which can be used as a good tracer for sewage discharge.

The appearance of local high concentration for one metal by possible contamination does not necessarily correlate with high values for other metals. Despite this fact, significant positive correlations were found between several couples of elements e.g., Fe-Mn (r=0.80), Fe-Zn (r=0.80), Mn-Zn (r=0.80) in the bottom water as well as in the surface water (Mn-Ni,r=0.80) of El-Mex. The high correlations between iron and both zinc and manganese are attributed to the ability of Zn and Mn to be increasingly adsorbed by iron particles (Kester, 1974; Duursma, et al.1975). The EH also showed good correlation between Fe and Co (r=0.83), Mn and Co (r=0.60) for the surface and bottom waters respectively.

Monthly variations of trace metals showed generally more elevated values in February than in other months (Fig. 5,6). This might be due to the effects of winter agitation of bottom sediments rich in trace metals and the low uptake of these metals by phytoplankton as well as the higher rate of brakish water (208-284x10^6 m/month) discharging to El-Mex Bay during winter season.

The concentration of Fe and Mn in El-Mex Bay and Mn in the EH showed negative correlation with dissolved oxygen, indicating the tendency of these metals to increase in the less oxygenated bottom water (Fig.7). This condition may indicate the release of these metals from the bottom sediments in poorly oxygenated water that is characterized by the presence of HS ion and their adsorption in oxygenated waters. The enrichment of dissolved Fe and Mn in the anoxic bottom layer is well documented in areas characterized by the coexistence of oxygen and hydrogen sulphide (Kremling, 1983).

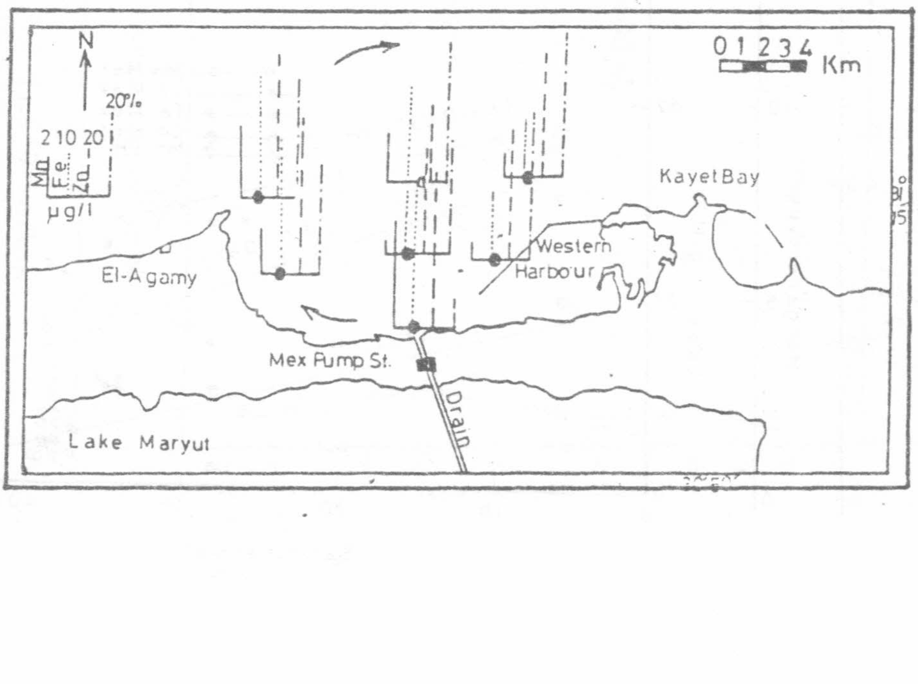

Fig. (3)

Distribution of mean concentrations of Mn, Fe, Zn (ug/L) and salinity in El-Mex Bay.

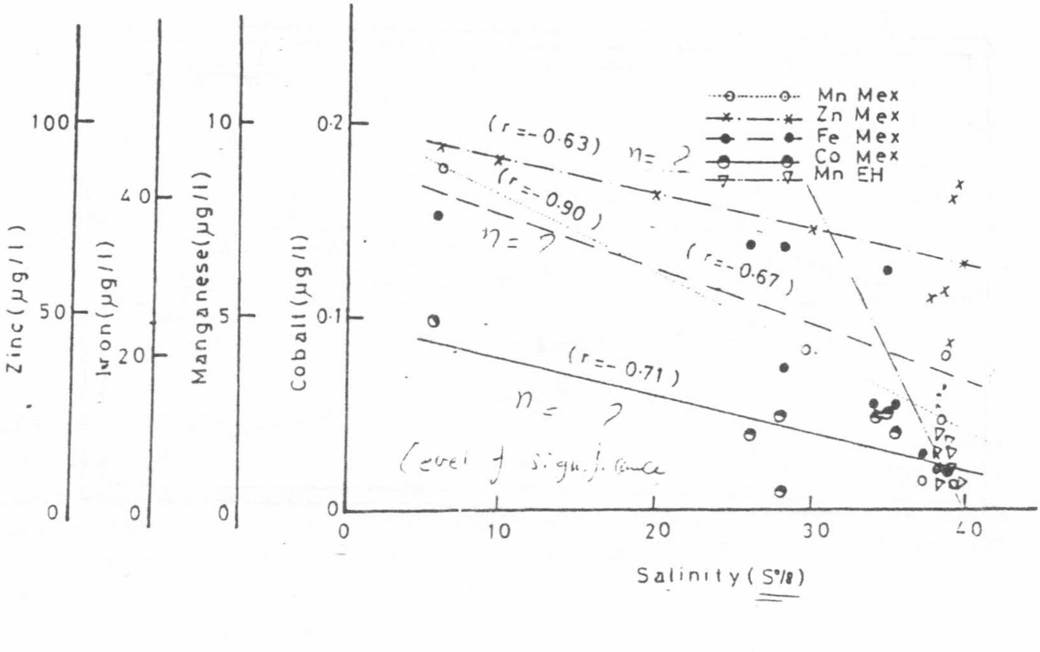

Fig. (4)

Salinity-Trace Metals relationships in the investigated area.

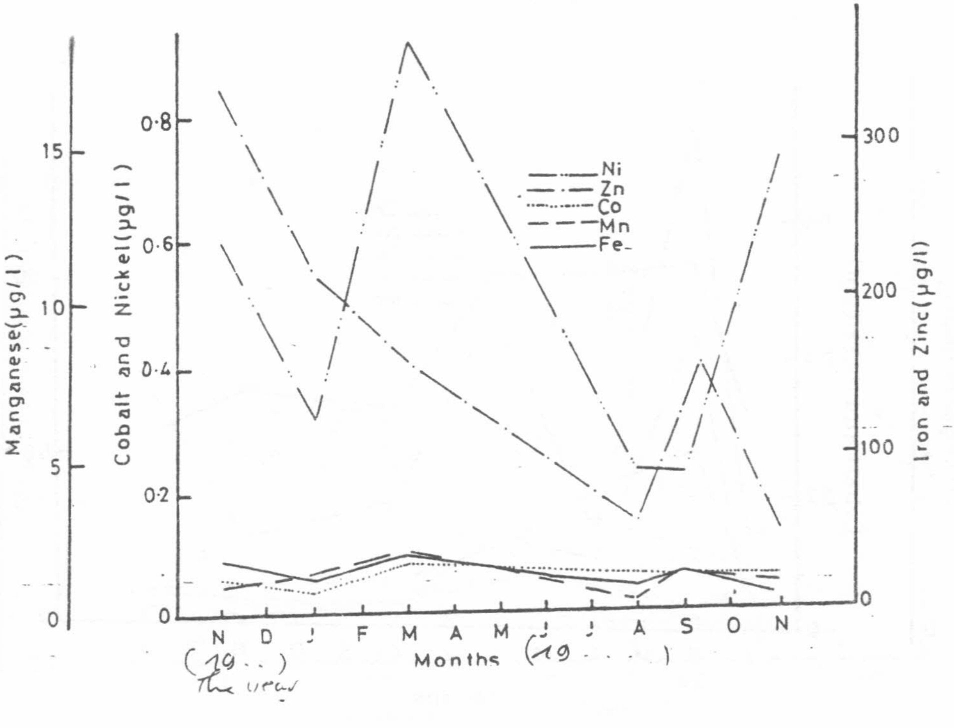

Fig. (5)

Monthly variations of Mn, Fe, Co, Ni and Zn in the eastern harbour.

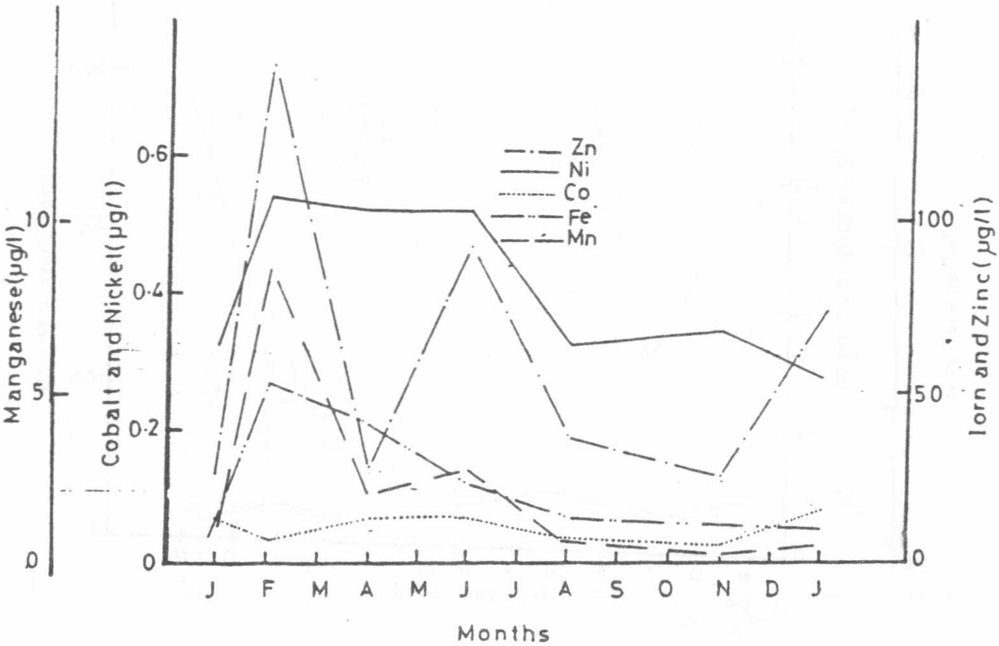

Fig. (6)

Monthly variations of Mn, Fe, Co, Ni and Zn in El-Mex Bay.

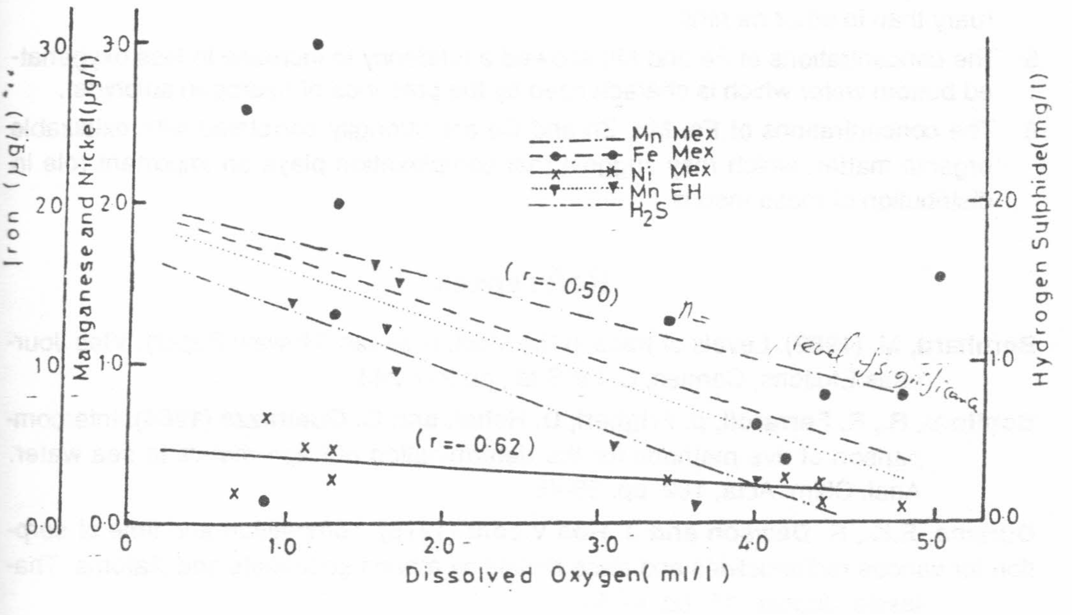

Fig. (7)

Dissolved oxygen-Trace Metals and Hydrogen Sulphide relationships in the investigated area.

Nickel showed analogous behaviour, however, this metal does not change its oxidation state under reducing condition (Kremling, 1983).

The concentrations of Fe and Mn, and to a less extent Zn and Co are stronglly correlated with oxidizable organic matter (r=0.88,0.95 0.66, 0.62) in El-Mex Bay than in the EH. This is attributed to the higher (1.3 times) organic matter content of the bay (Emara et. al. 1990) and which may suggest that complexation plays an important role in distribution of these metals (Samuel and Phillips, 1988).

Conclusions

The conclusions which can be drawn from the present study may be summarized as follows:

1- The eastern harbour reflects higher levels of Fe, Zn and Ni than El-Mex Bay water.

2- Salinity and trace metals Mn, Fe, Zn distribution suggest a clockwise circulation pattern of brakish water discharging to El-Mex bay.

3- The distribution of Zn in EH showed that this metal can be used as a good tracer for sewage discharge.

4- Monthly variations of trace metals showed generally more elevated values in February than in other months.

5- The concentrations of Fe and Mn showed a tendency to increase in less oxygenated bottom water which is characterized by the presence of hydrogen sulphide .

6- The concentrations of Fe, Mn, Zn and Co are stronglly correlated with oxidizable organic matter, which may suggest that complexation plays an important role in distribution of these metals.

References

Bernhard, M. (1982). Levels of trace in the Mediterranean (Review Paper). Vles Journees Efutions, Cannes, C. I.E.S.M., pp 237-243.

Bonifortl, R., R. Ferraroli, p. Frigllerl, D. Heltal, and G. Quelrazza (1984). Intercomparison of five methods for the determination of trace metals in sea water. Anal. Chim. Acta, 162, pp. 33-46.

Dursma, E.K., R. Dawson and J. Ros Vlcent (1975). competition and time of sorption for various radionuclides and trace metals by marine sediments and diatoms. Thalassia Jugosl., 11, pp. 47-51.

Ellis, M. M., B. A. Westafall and D.M. Ellis (1946). Determination of water quality. U.S.Dep. Int. Fish and Wildlife service, Resarch Report No. 9, 122. pp.

El-Sayed, M.A., M. Kh. El-Sayed (1980). Levels of heavy metals in the surface water of a semi-enclosed basin along the Egyptian Mediterranean coast. Ves Journees Etud. pollutions, Cagliari, C.I.E.S.M., pp. 223-228.

Emara, H.I., M.A. Shrladah, Th. H. Mahmoud and M.S. El-Deek. (1990). Effects of sewage and industrial wastes on the chemical characteristics of the eastern harbour and El-Mex Bay waters of Alexandria, Egypt. Paper presented to the International Conference on Marine Coastal Eutrophication, Bologna, 21-24 March 1990. pp. 773-784 EL sevier.

Grasshoff, K. (1976). Methods of sea water analysis. Verlag. Chemic 317 pp.

Kester, D. R. (1974). Chemical behavior of trace metals in the ocean. Maritimes, 11, pp. 14-18.

Kremling, K. (1983). The behavior of Zn, Cd, Cu, Ni, Co, Fe, and Mn in anoxic Baltic waters. Marine chemistry, 13, pp. 87-108.

Samuel, N. L. and D. J. H. Phillips (1988). Distribution, variability, and impacts of trace elements in San Francisco Bay. Marine Pollution Bulletin, Vol. 19, No. 9, pp. 413-425.