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Chemical Fractionation of Copper and Manganese in the Sediment of Alexandria Two Bays, Egypt

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Abstract: EL-Mex and Abu-Kir bays are subjected to contaminations by several anthropogenic materials such as trace elements and other wastes. The distribution of total and different chemical forms of copper and manganese has been studied using sequential extraction techniques. Chemical analysis of the sediments show that, in Abu-Kir bay, cupper is bonded more with the residual and organic fractions and manganese with residual and carbonate fractions. In EL-Mex bay, cupper is enriched in the labile fractions (exchangeable, carbonate and oxides) and manganese with carbonate fraction. This means that, the mobility and bioavailability of cupper and manganese in EL-Mex bay is higher than that in Abu-Kir bay. This is mostly due to the more aeration in front of EL-Umum drain in EL-Mex bay which exposed more to the open sea action than that of Abu-Kir bay especially in front of Tabia outlet which represent a restricted region and depleted in oxygen content.

Key word: Heavy metal · Sequential extraction · Sediments

INTRODUCTION

Heavy metals are one of the serious pollutants in marine environment due their toxicity, persistence and bioaccumulation problems [1]. Trace metals derived from natural inputs and anthropogenic emissions are ubiquitous in global environment [2]. Sediments usually act as a sink for aquatic pollutants. Consequently, sediment-associated contaminates can influence the concentrations of trace metals in both the water column and biota if they are desorbed or become available to benthic organisms. One of the major problems that heavy metals cause with respect to their effects on aquatic organisms is their long biological half-life [3]. Metals in contaminated sediments may return to the sediment-water interface through diffusion [4], sediment re-suspension [5], or biological activity such as bioturbance [6]. Once at the sediment-water interface or in the water column, metals are more likely to be transported and to enter the food web. Therefore, in areas with heavy metal pollution, it is important to inventory the concentration and special distribution of each metal to evaluate the potential for remobilization, transport and biological uptake.

The total concentrations of heavy metals indicate the extent of contamination, but they provide little information about the forms in which heavy metals are present, or about their potential for mobility and bioavailability in the environment [7].

Metal speciation in sediments in different environments have been used by many authors in studies concerned with metal associations, mobilization, bioavailability, digenesis and pollution [8,9]. The potential mobility of heavy metals strongly depends on specific chemical forms of association [10].

Thus, multiple step methods, better know as sequential extractions after a useful tool for the deduction of in for motion about the various types of metal associations in sediments. They can also inform the chemical nature or potential mobility and bioavailability of a particular element, which consequently can offer a more realistic estimate of actual environmental impact [11,12].

The present study was performed the distribution of different chemical forms of copper and manganese for the surface sediments in the hot spots of EL-Mex and Abo-Kir bays to evaluate bioavailability and origin of these two metals.

Area of Study: Abu-Kir Bay (AKB) is one of the Mediterranean coastal bays. It is a shallow (mean depth 12 m) semi-circular bay, lies 36 km east of Alexandria city. The area of the bay is about 360 km^2 with shore line of about 50 km long. This bay receives a continuous run off (totally of about 5 million m^3 / d) mainly from three land-based sources (Fig. 1), namely from west to east Tabia pumping station (mainly industrial and agricultural waste waters), Maadia outlet (mainly agricultural

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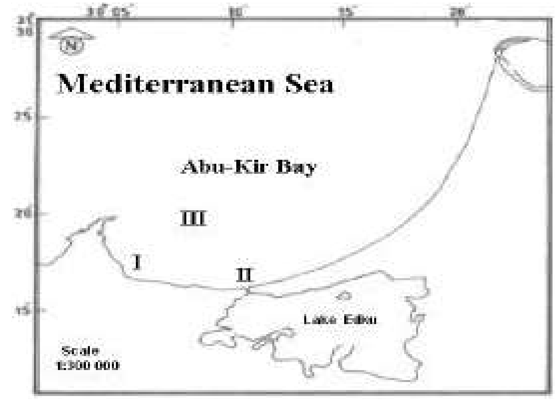


Fig. 1: Map of sampling stations of Abu-Kir Bay

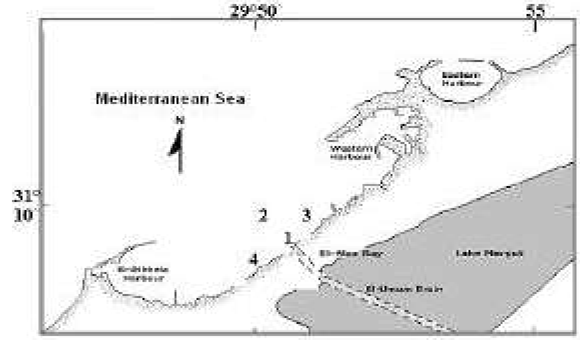


Fig. 2: Map of sampling stations of El-Mex Bay

drainage water) and Rosetta mouth (mainly river water).Many reefs, shoals and patches of foul ground could be found in the south west part of AKB. These ridges cause a rather limited water exchange with the open sea Faragallah [13].

El-Mex Bay is also one of the Mediterranean coastal bays, west of Alexandria city, extends for about 15 km between EL-Agamy headland to the west and the Western Harbour to the east (Fig. 1). Its area of about 19.4 km^2 and its volume of about 190×10^6 km^3.The bay receives a heavy load of waste water (2.4×10^9 m^3 l year) both directly from industrial outlets and indirectly from lake Maryout via EL-Mex pumping station (lies about one kilometer upstream on EL-Umum drain canal). This mainly agricultural drainage water collected by EL-Umum drain but also comprises the overflow lake Maryout.

MATERIALS AND METHODS

Sampling locations were selected during winter 2006 from the hot spots of the two bays. Two surface sediment samples from infront of Tabia outlet and Maadia opening besides offshore station were collected from AKB (Fig. 1). Also four surface sediment samples cover the area invicinty of El-Umum drain in EL-Mex bay were collected (Fig. 2).

The concentrations of total metals were measured using Flame-Atomic Absorption Spectrophotometer (AAS Perkin-Elmer Model 2380) after completely digested of sediment samples with mixture of concentrated HNO_3, HF and $HClO_4$ (3: 2: 1 v/v) (triplicate digestions were made for each sample) according to Oregioni and Aston [14].

For metal speciation, the technique based on Tesser *et al*. [15]; Engler *et al*. [16]; Pickering [17] and modified by Rifaat *et al*. [18], where fraction 1(F1), ion-exchanges sites and surface adsorption by using (1M ammonium acetate); fraction 2(F2), precipitated CO_3 ^{2}-and copercipitated amorphous hydrous oxides (acetic acid and 1N hydroxyl amine hydrochloride); fraction 3 (F3) copercipitated crystalline hydrous oxides (1N hydrochloric acid); fraction 4 (F4), co-ordinate to organic matter; (1:1 nitric and perchloric acid) and fraction 5(F5),occluded i.e. crystalline silicates and lattice components (HNO_3, HF and $HClO_4$) .

The accuracy and precision of the analytical procedures have been checked by analysis certified reference marine sediment (MESS-2 QMD 1-5), using four replicate sub samples. The standard deviation of the TCu was 0.827 and the recovery was 100.94%, standard deviation of the TMn was 182 and the recovery was 101.67%. While the standard deviations and coefficient of variety percentages for the five test fractions of Cu and Mn were shown in (Table 1).

Table 1: The results of the precision test sample in different metal forms

	Cu					Mn				
	F1	F2	F3	F4	F5	F1	F2	F3	F4	F5
	1.27	3.98	3.42	8.74	4.26	2.44	43	5.03	30.17	218.25
	1.11	4.11	3.2	8.01	3.86	1.99	41.02	4.72	28.07	222.11
	1.07	3.78	3.19	9.13	5.01	2.45	40.31	5.49	32.12	215
	1.32	4	2.99	8.33	4.05	2.11	45.12	4.81	30.97	216.75
mean	1.19	3.97	3.20	8.55	4.30	2.25	42.36	5.01	30.33	218.03
SD	0.12	0.14	0.18	0.49	0.50	0.23	2.16	0.34	1.71	3.03
CV%	10.16	3.46	5.49	5.70	11.73	10.38	5.10	6.86	5.63	1.39

CV% = SD /mean x 100

RESULTS AND DISCUSSION

Total Metals: Copper (Cu) is an essential element in the normal metabolism of plants, animals and human life, however in high levels, causes many diseases [19]. It is used in electrical equipments, alloys, antifouling paint for ship's hull, as an algeacide and wood preservative [20].

Manganese (Mn) is the 11th element in terms of abundance in the earth crust [37]. Oxidized forms of Mn are very reactive and have a strong capacity for adsorption of trace metals and play an important role as both an electron donor and acceptor in redox processes of aquatic environments [21].

Generally, the concentrations of total copper (T-Cu) in EL-Mex bay are more than that in Abu-Kir bay (Fig. 3), but the reverse is observed for total manganese (T-Mn).

In Abu-Kir bay, the distributions of T-Cu and T-Mn are mostly have the same manner (r=0.98), where the two metals in front of Maadia opening (St.II) has the highest levels 42.32 and 768.60 µg/g for T-Cu and T-Mn, respectively and decrease west ward to reach 22.13 and 438.08 µg/g infront of Tabia outlet (St.I) which decrease again to the lowest levels 20.51 and 317.82 µg/g at the off shore station (St.III). Khaled [22] observed that, the high concentration of T-Cu was found infront of Maadia opening and respect that to the precipitation of copper from antifouling ship paints into the sediments. Faragallah [13] pointed out that, the relative depletion of T-Mn in the sediment in front of Tabia outlet implies its partial migration to the overlying euxinic waters, where it is most of the times are oxygen depleted and bear H_2S.

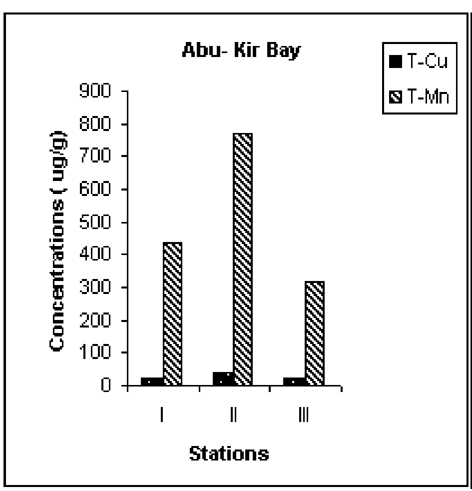
In EL-Mex bay, the distribution of the two metals are mostly reverse to each other (r=-0.53), where the concentration of T-Cu increase (101.08 µg/g) east of El-Umum drain (St.3) and decrease in front and west ward of it (<93.0 µg/g). But in the case of T-Mn, the high levels (185.34 and 181.00 µg/g) are detected infront and west of EL-Umum drain and decrease seaward (142.93 µg/g) and eastward (165 µg/g)

The average concentrations of T-Mn (512 and 169 µg/g in Abu-Kir and El-Mex bays respectively) are higher than that recorded in the Eastern Harbour (104.84 µg/g) by Al-Dughim [23] and in sandy sediments of Suez Gulf (115.54 µg/g) by EL-Nemer *et al.* [24]. The average concentration of T-Cu by Al-Dughim in the Eastern Harbour (33.44 µg/g) and in the sandy sediments of Suez Gulf by EL-Nemer *et al* (33.20 µg/g) is lower than recorded in the present study in EL-Mex Bay (90.96 µg/g) and higher than that in Abu-Kir bay (28.32 µg/g).

In general, in Abu-Kir bay the total concentration of Cu was elevated lower the Effect Range-Low (ERL) value (34µg/g) except st. II higher than ERL value. While, in El-Max bay the concentrations of Cu were higher than ERL value but lower than Effect Range-Median (ERM) value (270 µg/g) [25,26].

Fractionation of Copper and Manganese

Abu-kir Bay Sediments: Generally, the Cu associations with different fractions in front of Tabia outlet (St .I) and Maadia opening (St .II) follow the order: organic > residual > Fe-Mn oxide > carbonate > exchangeable, while the off shore station (St. III) follow the order: organic > Fe-Mn oxide > residual > carbonate > exchangeable



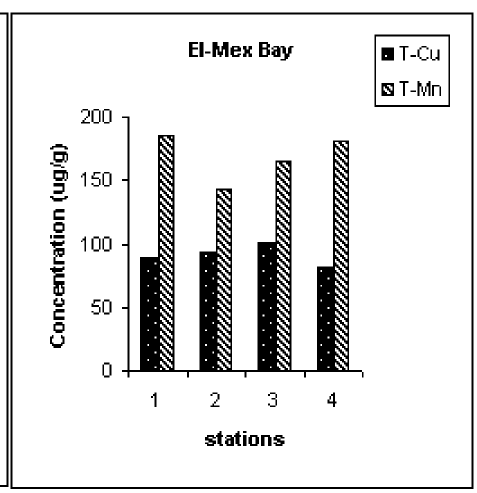


Fig. 3: The concentrations of total copper (T-Cu) and total manganese (T-Mn) in Abu-Kir and El-Mex bays

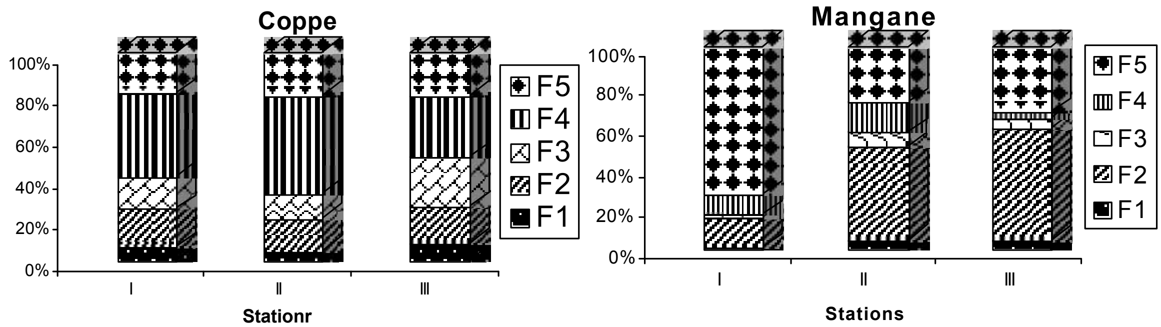


Fig. 4: The distribution of the percentage of different fractions of copper and manganese in Abu-Kir bay

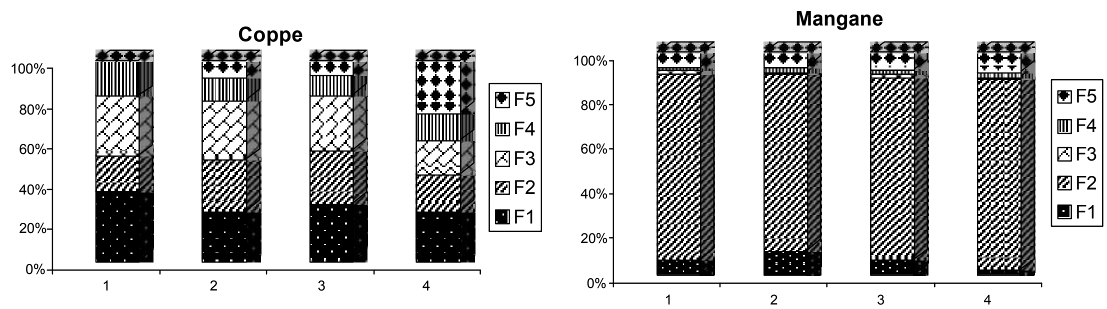


Fig. 5: The distribution of the percentage of different fractions of copper and manganese in El-Mex bay

(Fig.4). The high Cu concentrations in the organic and residual fractions in front of the outlets may indicate that Cu in the sediment of AKB is less mobile [27]. Cu in F2 (about 17.5%) the most labile; hence it may be available for uptake by biota. According to Forstner and Witt man [28], higher concentrations of metals in F2 could be regarded as pollution indicator.

Copper could easily form complexes with organic matter, due to the stability copper constant of organic-Cu compounds. Li *et al*. [27] and Ramos *et al*. [29] reported significantly high concentration of Cu associated with organic matter in the sediments. Also, Callener and Bower [30] and collier and Edmond [31] stated that Cu is mainly transported to the sediment surface in association with a biogenic

carrier phase. Chester *et al*. [32] reported that 50% of the total copper in the surface water particulates is held in organic associations. When such material is deposited at the sediment surface, total copper undergoes phase transformation as the organic carriers are destroyed depending on the digenetic environment of deposition such as dissolved oxygen. Under oxidizing conditions at the sediments-water interface, most of the organic carrier phase of Cu is mobilized, releasing Cu into the dissolved phase.

Some of this Cu migrates downward and is incorporated into sediment.

But most of it is recycled back into water-column [33]. However, under oxygen-depleted condition at the sediment-water interface, relatively large amounts of organic carriers can be incorporated in the sediment, thus retaining some of their associated Cu.

The order of abundance of the chemical Mn-phases wasF2>F5>F4>F3>F1 for stations II and III, while station I about 73% of the total Mn was bound to the residual fraction (F5).

It is clear that the percentage of manganese is enriched in the carbonate amorphous oxides fraction especially in front of Maadia opening (St.II) and the off shore station (St.III) (Fig. 4). The method of fractionation used here does not distinguish metals in the carbonate and amorphous oxides forms. The statistical analysis of the chemical data was successfully applied to determine the possible association. Thus the insignificant association of Mn and total carbonate (r= 0.48) in the studied sediment show that manganese is principally present as amorphous oxides rather than carbonate. This is in accordant with Rifaat [18] for Nile Delta sediments.This indicate that Mn come from anthropogenic sources, which increased Potential Mn mobility and Bioavailability.

The dominance of the residual fraction for Mn in the sediment for st. I (in front of Tabia oulet) may be attributed to most of Mn at this station come from the parent material of geological origin.

El-Max Bay Sediment: Figure5 indicate that, Copper in all surface sediment, except St. 4 was associated with exchangeable fractions (F1) together with the precipitated oxide fraction (F3).

According to Abd El-Azim and El-Moselhy [34], Yuan *et al*. [35] and Dassenakis *et al*. [36], the concentration of F1 is coincided with the anthropogenic impact on the aquatic environment. Accordingly, it could be concluded that El-Max bay is under the effect of anthropogenic, industrial waste discharges, reflecting its high level pollution .In station 4 (west of EL-Umum drain), the total Cu was associated with residual fraction and the exchangeable fraction (25 % for each).

As shown in (Fig. 4), most of Mn (>80 %) was present in carbonate fraction (F2) in all stations of EL-Mex bay.The residual fraction (F5) was the next most important fraction for Mn (about 7%), followed by exchangeable (F1) fraction (about 6%). The crystalline hydrous oxide (F3) and organic (F4) fractions were found in minor concentrations (< 2.5 %).

The relatively recent precipitation of Mn is deduced from the low percentage of crystalline manganese oxide relative to the amorphous manganese oxide in the sediment of El-Max bay. Also, it indicates that this metal was from anthropogenic origin i.e. allochthonous.

More Mn was associated with the non residual fraction, which increase potential Mn mobility and bioavailability.

CONCLUSION

- The metals contamination in sediment of studied locations may be anthropogenic origin with the exception of some local anomalies.
- Total copper and total manganese has mostly the same distribution in Abu-Kir bay, while the reverse is observed in El-Mex bay.
- Copper-bond to organic and residual forms is mostly dominant in front of AKB outlets. This means, this refractory Cu is difficult to return under the natural conditions to the overlying water. The reverse is observed in front of EL-Umum drain in EL-Mex bay where Cu is more associated with exchangeable fraction together with the precipitated oxide fraction.
- Manganese in EL-Mex bay was associated with the non residual fractions (mostly carbonate), means increase potential Mn mobility and bioavailability. This manner is less abundance in front of the AKB outlets especially Tabia outlet.
- Generally, the mobility and bioavailability of cupper and manganese in EL-Mex bay is higher than that in Abu/Kir bay. This is mostly due to the more aeration in front of EL-Umum drain in EL-Mex bay which exposed more to the open sea action than that of Abu-Kir bay especially in front of Tabia outlet which represent restricted region and depleted in oxygen content.

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