

CHEMICAL FORMS OF COPPER, ZINC, LEAD AND CADMIUM IN SEDIMENTS OF THE NORTHERN PART OF THE RED SEA, EGYPT

Mohamed A. Hamed

National Institute of Oceanography and Fisheries, Suez and Aqaba Gulfs Branch.

Email: drhamed64@yahoo.com

ABSTRACT: Total concentrations and chemical forms of heavy metals in sediment samples from the Gulf of Suez and the northern part of the Red Sea, collected during January 2003, were determined by atomic absorption spectrometry. Maximum concentrations of 49.56, 65.42, 33.52 and 3.52 $\mu\text{g/g}$ were recorded for total Cu, Zn, Pb and Cd respectively at Adabiya location. These may reflect the high contribution of land-based activities in the northern part of the Gulf. Also, high percentages of heavy metals were found in the residual fraction (Cu = 78.61, Zn = 77.10 and Pb = 66.80%) while a high percentage of Cd was found in the carbonate fraction (45.82%). However, few or negligible percentages were recorded in the exchangeable fractions (Cu = 0.51, Zn = 1.57 and Pb = 1.74%). Concentration of Cd in the exchangeable fraction was too low to be detected.

KEY WORDS: Speciation, Heavy metals, Sediments, Red Sea.

INTRODUCTION

The Gulf of Suez is relatively shallow and extends about 250 km south-southeast from Port Suez in the north (Lat. 29° 56' N) to Shadwan Island in the south (Lat. 27° 36' N) as shown in Figure. 1. It's width varies between 20 and 40 km and its depth throughout its axis is fairly constant with a mean depth of 45 m. The Gulf is bordered by high land, reaching close to the coast at many points. Pollution in the Gulf of Suez has increased considerably in recent years through ships' oil and refuse, industrial and domestic effluents and also due to the presence of many oil fields in the southern part of the Gulf.

Among the known pollutants, the most common and serious for the marine life of the northern part of the Red Sea are heavy metals from the anti-fouling paints of ships, industrial wastes and to a lesser extent the municipal wastes. In order to assess the environmental impact of heavy metals inputs into sediments of the northern part of the Red Sea, it is important to examine not only total metal concentration but also the chemical forms of these metals. The mobility and bioavailability of heavy metals can be identified through measuring different species of the heavy metals. The present study deals with the identity of the specific fractions of heavy metals in the sediment samples, collected from the Gulf of Suez and the northern part of the Red Sea.

Two main factors have to be considered while assessing the risk from a heavy metal-contaminated site: the total amount of the heavy metal and the chemical binding form of the heavy metal. Measurement of the total concentration only provides inadequate information to permit us to assess the bioavailability and toxicity of the metal. Chemical speciation can be defined as the process of identifying and quantifying the different species, forms, or phases present in a material.

Species can be defined (a) functionally e.g. "plant-available species" (b) operationally, according to the reagents or procedures used in their isolation or, most specifically, (c) as particular compound or oxidation states of an element (Saxby, 1973).

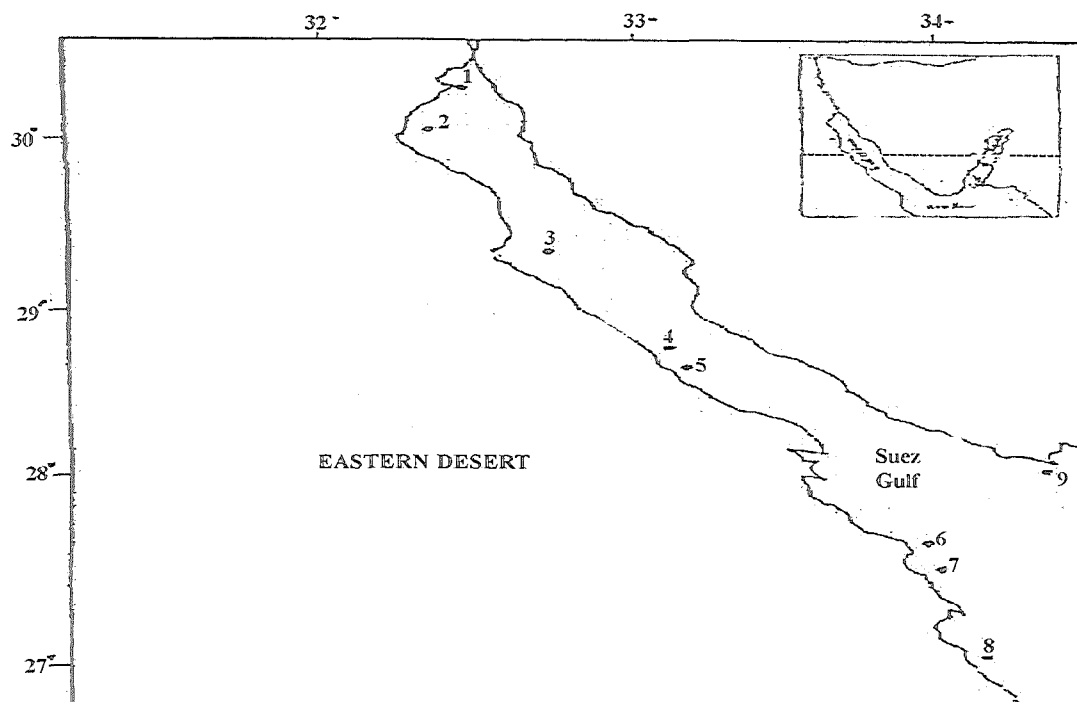


Fig. 1. Location of the samples taken from the northern part of the Red Sea, 1. Adabiya, 2. Ain Sukhna, 3. Ras Zafarana, 4. Ras Gharib, 5. Ras Shukeir, 6. Hurghada, 7. Gifton, 8. Safaga and 9. Ras Mohamed.

Therefore, it is desirable to have information on the potential availability of metals (whether toxic or essential) to biota under various environmental conditions (Carroll, 1958). Heavy metals are distributed among the various chemical compounds and minerals in sediments, which determine their behavior in the environment and their remobilization abilities.

MATERIALS AND METHODS

Sediment samples were collected, using Van-Veen grab, from nine locations along the Gulf of Suez and the northern part of the Red Sea during January 2003 (fig1). The sediments samples were mechanically sieved in order to get $<20 \mu\text{m}$ fractions. Sequential extractions were performed on the frozen sub samples according to the method of Tessier *et al.* (1979).

Carbonate was determined according to the procedures of Adams (1990). Organic matter was measured according to technique of Jorgensen (1977).

RESULTS AND DISCUSSION

Gibbs (1973) suggested four groups of heavy metals association in aquatic solid substances (including suspended matter as well as sediments). These can be characterized by the following bonding process: i) adsorptive bonding, ii) co-precipitation by hydrous iron and manganese oxides: iii) complexation by organic molecules and iv) incorporation in crystalline minerals. This categorization includes all main types, of metal associations in both natural and polluted water systems. The remobilization of metals from the sediments is caused mainly by three types of chemical changes in water: high salt concentrations, changes in the redox potential, and lowering of pH. The major processes that may release metals from suspended

particulate, are desorption, dissolution and oxidation of organic matter (Forstner and Wittmann, 1983).

Speciation of copper in sediments:

The relative amounts of Cu in different phases of surface sediment samples collected from the northern part of the Red Sea are presented in Table.1 and Figure 2. It is clear that the percentage in the exchangeable fraction (F_1) was low or negligible in comparison to the other fractions ranging between $0.046 \mu\text{g/g}$ at Safaga and $1.05 \mu\text{g/g}$ at Ras Zafarana. The carbonate-Cu fraction (F_2) decreased at Ain-Sukhna (location 2), Gifton (location 7) and Ras Mohamed (location 9), [0.39 , 0.41 and $0.34 \mu\text{g/g}$, respectively] perhaps because of the decrease in total carbonate content in the sediments at these locations [2.7 , 4.8 and 3.2% respectively, Table 5]. Relatively high amounts or percentage of Cu in the carbonate fraction $3.22 \mu\text{g/g}$ (6.5%) were found at Adabiya. This is the result of the high content of carbonate (17.9%) at Adabiya. The Fe-Mn oxide fraction, F_3 of copper was in the range of $0.73 \mu\text{g/g}$ at Ras Mohamed and $4.41 \mu\text{g/g}$ at Adabiya. Shuman (1979) showed that copper was mainly associated with Fe-Mn oxide fraction in sandy soils.

Table 1. Copper species, total concentration ($\mu\text{g/g}$), and percentages in sediment samples collected from the part of the Red Sea during January 2003.

Fraction Location	F_1		F_2		F_3		F_4		F_5	
	Conc.	%	Conc.	%	Conc.	%	Conc.	%	Conc.	%
1. Adabiya	0.30	0.60	3.22	6.50	4.41	8.90	7.73	15.60	33.90	68.40
2. Ain Sukhna	0.09	0.40	0.39	1.80	2.06	9.50	1.78	8.20	17.38	80.10
3. Ras Zafarana	1.05	0.20	1.39	5.20	2.33	12.40	2.01	7.50	20.05	74.70
4. Ras Gharib	0.20	0.60	1.58	4.90	3.61	11.20	3.16	9.80	23.72	73.50
5. Ras Shukeir	0.29	0.70	1.91	4.60	0.91	2.20	5.51	13.30	32.82	79.20
6. Hurghada	0.10	0.80	0.50	4.10	1.29	10.60	0.84	6.90	9.46	77.60
7. Gifton	0.05	0.30	0.41	2.50	1.37	8.30	0.59	3.60	14.07	85.30
8. Safaga	0.046	0.30	0.66	4.30	0.96	6.20	1.10	7.10	12.71	82.10
9. Ras Mohamed	0.074	0.70	0.34	3.20	0.73	6.90	0.28	2.60	9.20	86.60
Mean \pm SD	0.24 ± 0.30	0.51 ± 0.20	1.16 ± 0.92	4.12 ± 1.36	1.96 ± 1.21	8.47 ± 2.90	2.56 ± 2.38	8.29 ± 3.93	19.26 ± 8.75	78.61 ± 5.48

(F_1 - Exchangeable, F_2 - Carbonate- cu, F_3 - Fe-Mn oxide, F_4 - Organic, F_5 - Residual).

Kuo and Baker (1983) and Leriche and Weir (1963) showed copper to be high in Mn-oxide fraction. Shuman (1979) found that the soils high in Fe-oxides had the highest copper in the Fe-oxide fraction because the copper was probably associated with these oxides by being occluded in the structure.

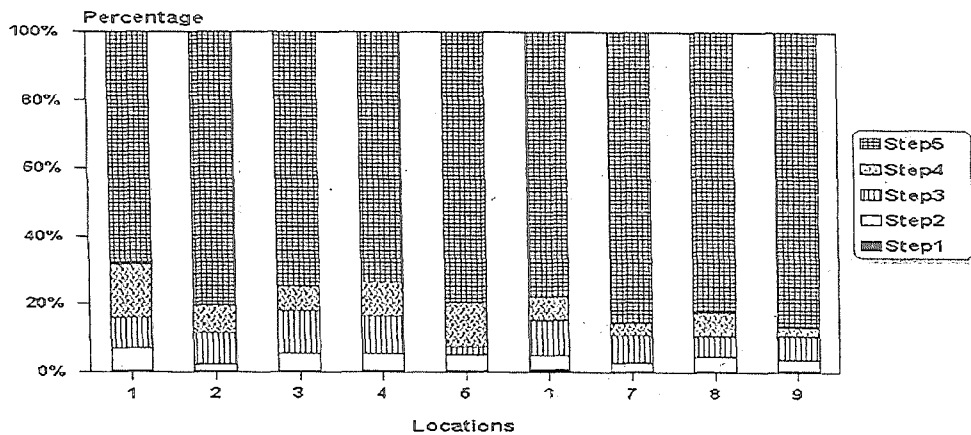


Fig. 2. The Sequential extraction results for copper.

The organic fraction (F_4) of copper in the study ranged between $0.28 \mu\text{g/g}$ at Ras Mohamed to $7.73 \mu\text{g/g}$ at Adabiya. The relatively high amounts of copper in the organic fractions at Adabiya and Ras Shukeir [7.73 and $5.51 \mu\text{g/g}$, respectively] are perhaps due to the relatively high contents of organic matter (20.5 and 17.4%, respectively) as shown in Table 5. Callender and Bower (1980) and Collier and Edmond (1984) stated that Cu was mainly transported to the sediment surface in association with a biogenic carrier phase. Chester *et al.* (1988) reported that 50% of the total copper in the surface water particulates was held in organic associations. When such material is deposited at the sediment surface, total copper undergoes phase transformations as the organic carriers are destroyed depending on the diagenetic environment of deposition such as dissolved oxygen.

Copper was predominant in the residual fraction, (F_5) and ranged between $9.20 \mu\text{g/g}$ at Ras Mohamed to $33.90 \mu\text{g/g}$ at Adabiya. This is in agreement with Moussa (1984) who reported that the chief source of Cu and Zn seemed to be the lithogenic minerals. It may be observed from Table 1. Copper species contents are very high at Adabiya, which is considered as having maximum contents of carbonate percentage and organic matter in the sediment samples. This part is affected by invading water coming from Suez Bay, where there are many sources of pollution, such as: domestic drainage of Suez City, industrial wastes from fertilizer company, the power station and oil refineries. In contrast, very low contents of different copper species were found at Ras Mohamed which is considered a protected area with low contents of carbonate and organic matter in sediment samples.

Speciation of zinc in sediments:

The relative amounts of zinc among different phases of surface sediments are presented in Table 2 and Figure 3. Zinc fractionation analyses revealed that more than 77% of the total zinc occurred in the residual form. Smaller fractions were exchangeable (1.57%), carbonate bound (5.4%), oxide bound (7.38%) and organic bound (7.89%).

Table 2. Zinc species, total concentration ($\mu\text{g/g}$), and percentages in sediment samples collected from the north the Red Sea during January 2003.

Location	F ₁		F ₂		F ₃		F ₄		F ₅	
	Conc.	%	Conc.	%	Conc.	%	Conc.	%	Conc.	%
1. Adabiya	0.92	1.40	6.28	9.60	1.83	2.80	7.59	11.60	48.67	74.40
2. Ain Sukhna	0.84	1.80	2.62	5.60	5.58	11.90	4.87	10.40	32.94	70.30
3. Ras Zafarana	0.93	2.70	2.91	8.50	4.52	13.20	3.15	9.20	20.79	60.65
4. Ras Gharib	0.51	1.30	2.48	6.30	4.01	10.20	3.82	9.70	28.53	72.50
5. Ras Shukeir	0.76	1.50	4.76	9.40	1.27	2.50	5.57	11.00	38.28	75.60
6. Hurghada	0.284	1.40	0.57	2.80	1.89	9.30	1.03	5.10	16.52	81.40
7. Gifton	0.32	1.70	0.52	2.80	1.56	8.40	1.22	6.60	14.93	80.50
8. Safaga	0.27	1.10	0.55	2.20	1.31	5.30	1.02	4.10	21.63	87.30
9. Ras Mohamed	0.163	1.20	0.19	1.40	0.38	2.80	0.45	3.30	12.42	91.30
Mean \pm SD	0.56 ± 0.29	1.57 ± 0.45	2.32 ± 2.00	5.40 ± 3.05	2.48 ± 1.67	7.38 ± 3.90	3.19 ± 2.33	7.89 ± 2.97	26.08 ± 11.36	77.11 ± 8.71

The exchangeable, F₁ zinc increased at Ras Zafarana and Adabiya (2.7 and 1.4%, respectively) and decreased at Safaga (1.1%). This may be the effect of the fine grain size and organic matter content at the latter site. Ras Zafarana and Adabiya have clay and organic matter contents of 26.29%, 16.7% and 20.35, 20.50%, respectively.

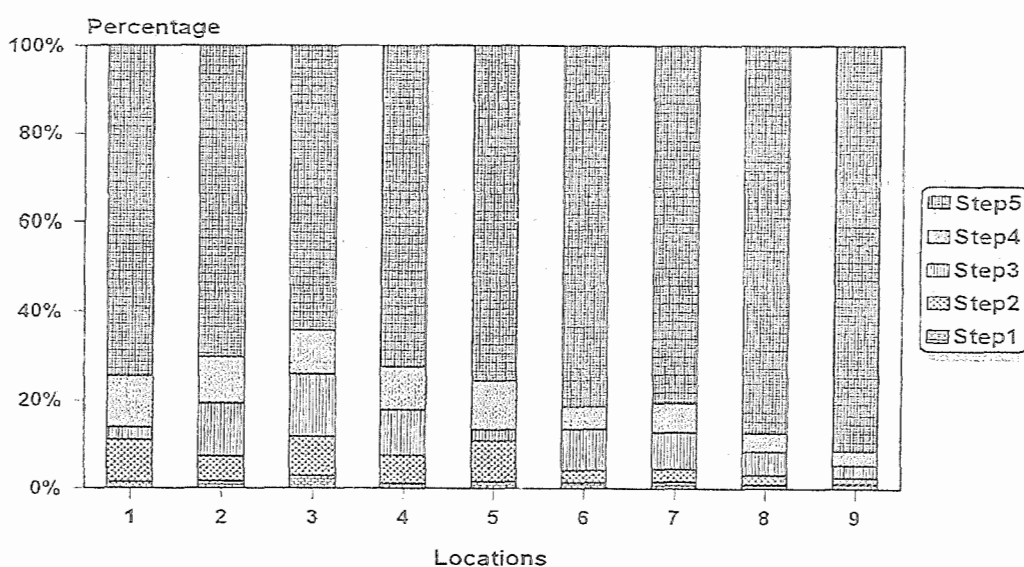


Fig. 3. The Sequential extraction results for zinc.

On the contrary, Safaga had 8.70 and 9.2% of clay and organic matter contents, respectively. The carbonate-Zn fraction increased at Adabiya and Ras Shukeir (9.6 and 9.4% of total zinc). Whereas the lowest value was (1.4%) at Ras Mohamed. This result could be because of zinc precipitation as ZnCO_3 or $\text{Zn}_5[\text{CO}_3]_2[\text{OH}]_2$, which is due to the high content of carbonate at Adabiya and Ras Shukeir, (17.9% and 14.4%, respectively) whereas the carbonate content at Ras Mohamed was 3.2%.

The oxide-Zn fraction, (F₃) was in the range of 2.50% at Ras Shukeir and 13.20% at Ras Zafrana. Davis and Leckie (1978) reported that amorphous sesquioxides had greater ability to retain the heavy metal to their specific surface areas. Zinc is absorbed by oxides as well as being occluded in the structure. The similarity between the atomic radius of Zn and Fe makes their exchange possible.

The lower Zn concentration was recorded in the organic fraction (F₄) with 0.45 μ g/g (3.30%) at Ras Mohamed compared to 7.59 μ g/g (11.60%) at Adabiya, which reflected the high content of organic matter at Adabiya (20.50%).

The residual fraction, (F₅) of Zn was 12.42 μ g/g (91.30%) at Ras Mohamed compared with 20.79 μ g/g (60.65) at Ras Zafarana. The high percent of the residual fraction of Zn (91.30%) at Ras Mohammed reflected the predominance of physical conditions such as sediments rate. This finding is similar to that given by Lyengar *et al.*: (1981) and Shata *et al.* (1993).

Speciation of lead in sediments:

The relative amounts of lead among different phases of surface sediments are presented in Table 3, and Figure 4. Lead fractionation analyses revealed that more than 63.17% of the total lead occurred in the residual form, (F₅) Smaller fractions were exchangeable, (F₁), (1.55 %), carbonate bound (5.55%), oxide bound (11.09%) and organic bound (18.64%).

Table 3. Lead species, total concentration (μ g/g), and percentages in sediment samples collected from the northern part of the Red Sea during January 2003.

Fraction	F ₁		F ₂		F ₃		F ₄		F ₅	
	Conc.	%	Conc.	%	Conc.	%	Conc.	%	Conc.	%
Adabiya	0.48	1.44	0.96	2.86	4.58	13.66	9.60	28.64	17.90	53.40
Ain Sukhna	0.37	2.15	0.53	3.07	1.64	9.51	3.25	18.84	11.46	66.43
Ras Zafarana	0.60	3.18	0.82	4.34	2.41	12.75	1.97	10.42	13.10	69.31
Ras Gharib	0.36	1.59	0.86	3.85	0.69	3.09	1.87	8.32	18.70	83.15
Ras Shukeir	0.13	0.55	1.21	5.13	1.97	8.35	4.18	17.71	16.11	68.26
Hurghada	0.29	1.48	1.55	7.90	0.48	2.45	2.72	13.86	14.58	74.31
Gifton	0.10	1.17	0.49	5.68	0.65	7.54	2.23	25.87	5.15	59.74
Safaga	0.24	2.56	1.12	11.94	1.26	13.43	1.75	18.66	5.01	53.41
Ras Mohamed	0.10	1.55	0.36	5.55	0.72	11.09	1.21	18.64	4.10	63.17
Mean \pm SD	0.30 \pm 0.16	1.74 \pm 0.74	0.88 \pm 0.36	5.59 \pm 2.67	1.60 \pm 1.23	9.10 \pm 3.95	3.20 \pm 2.41	17.88 \pm 6.19	11.79 \pm 5.40	65.69 \pm 9.09

It is clear that distribution of Pb in the exchangeable fractions is limited to a few percentage points. Mahmoud (1994) showed that the percentage of exchangeable fraction of Pb is low or negligible in sediments in comparison to other fractions. The distribution of Pb bound to carbonate (F₂) was minimum at Adabiya (0.96% μ g/g, 2.85%) compared to a maximum of 1.12 μ g/g (11.94%) recorded at Safaga. This means that this form is not generally preferable even with high contents of carbonate at Adabiya (17.9%).

The oxide Pb fraction, (F₃) was in the range of 0.48 μ g/g (2.45%) at Hurghada and, 4.58 μ g/g (13.66%) at Adabiya.

The high percentages of amorphous iron oxide or reducible fraction of Pb (13.66%) at Adabiya and (13.43%) at Safaga reflect the muddy nature of sediments at these locations. Iron is principally associated with silt-clay fractions; it is a mobile element that is subjected to

diagenetic remobilization as started by Forstner and Wittmann (1983). Also, high contents of Pb bound to (F_3) at Ras Zafarana (12.75%) and Ras Mohamed (11.09%) are mainly related to the precipitation of mineral Kaolin. This is in accordance with Carroll (1958) who stated the Fe existed in the form of oxides coating the fine particles and especially in clay minerals.

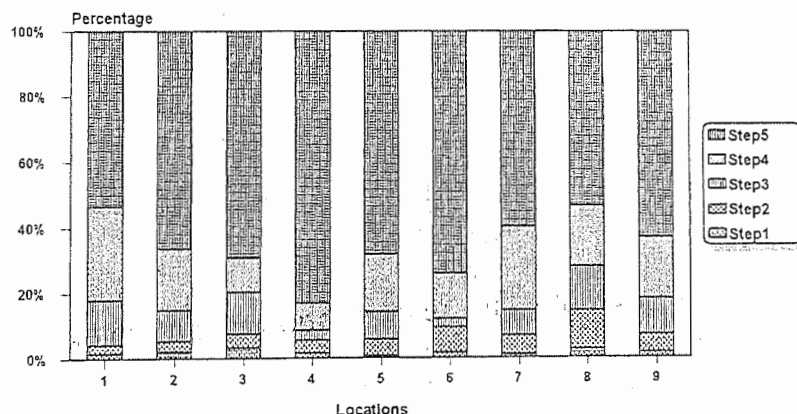


Fig. 4. The Sequential extraction results for lead.

The concentration of organic bound fraction (F_4) of Pb in sediments fluctuated between $1.87 \mu\text{g/g}$ (8.32%) at RasGharib and $9.6 \mu\text{g/g}$ (28.64%) at Adabiya. This may be attributed to the high concentration of organic matter at Adabiya (20.50%). Organic components of sediments act as ion exchange surfaces and may adsorb heavy metals. Also, bacteria and periphyton may accumulate trace metals from the water column and effectively concentrate them in the sediment.

It is clear that the residual fraction, of Pb (F_5) reached a maximum of $18.70 \mu\text{g/g}$ (83.15%) at Ras Gharib and a minimum of $4.10 \mu\text{g/g}$ (63.17%) at Ras Mohamed. Parrdo *et al.* (1990) showed that the greater percentage of this fraction of metal particulate meant a smaller or less dangerous pollution effect. This is because this inactive phase corresponds to a lattice bound metal, which cannot be remobilized at least under normal pollution circumstances.

Speciation of cadmium in sediments:

The results of the sequential extraction method of Cd are represented in Table 4 and Figure 5. It is clear that no detectable concentration of Cd was obtained in the exchangeable fraction (F_1). A relatively high percentage of Cd occurred as the carbonate fraction, F_2 especially at Adabiya, Ain Sukhna, Ras Zafarana and Hurghada (78.63, 57.05, 66.66 and 72.82% respectively). This is in accordance with Forstner and Wittmann (1983) who stated that, the occurrence of Cd in sediments was mainly related to the formation of CdCO_3 . High percentage of Cd was recorded as the Fe-Mn oxides fraction (F_3) particularly at Ras Gharib, Ras Shukeir, Gifton, Safaga and Ras Mohamed (58.33, 66.92, 59.37, 60.18 and 54.22%, respectively). This indicates that at these locations, Cd is likely bounded to Fe-Mn oxides. In contrast, the organic/sulphide fraction (F_4) showed a high percentage at Ain Sukhna (28.86%).

This is mainly related to complexation reaction between the high content of organic matter (15.1%) and the affinity of Cd to forms CdS precipitate especially at this location.

Table 4. Cadmium species, total concentration (μ g/g), and percentages in sediment samples collected from the northe part of the Red Sea during January 2003.

Location	F ₁		F ₂		F ₃		F ₄		F ₅	
	Conc.	%	Conc.	%	Conc.	%	Conc.	%	Conc.	%
1. Adabiya	-	-	2.76	78.63	0.26	7.41	0.30	8.55	0.19	5.41
2. Ain Sukhna	-	-	0.85	57.05	0.21	14.09	0.43	28.86	-	-
3. Ras Zafarana	-	-	1.09	66.66	0.39	23.64	0.16	9.76	-	-
4. Ras Gharib	-	-	0.38	17.59	1.26	58.33	0.30	13.89	0.22	10.18
5. Ras Shukeir	-	-	0.61	22.93	1.78	66.92	0.27	10.15	-	-
6. Hurghada	-	-	1.34	72.82	0.19	10.33	0.31	16.85	-	-
7. Gifton	-	-	0.32	25.0	0.76	59.37	0.20	15.63	-	-
8. Safaga	-	-	0.28	25.93	0.65	60.18	0.15	13.89	-	-
9. Ras Mohamed	-	-	0.38	45.78	0.45	54.22	-	-	-	-
Mean \pm SD	-	-	0.89 ± 0.75	45.82 ± 22.40	0.66 ± 0.51	39.39 ± 23.39	0.27 ± 0.09	14.70 ± 6.02	0.21 ± 0.02	7.80 ± 2.38

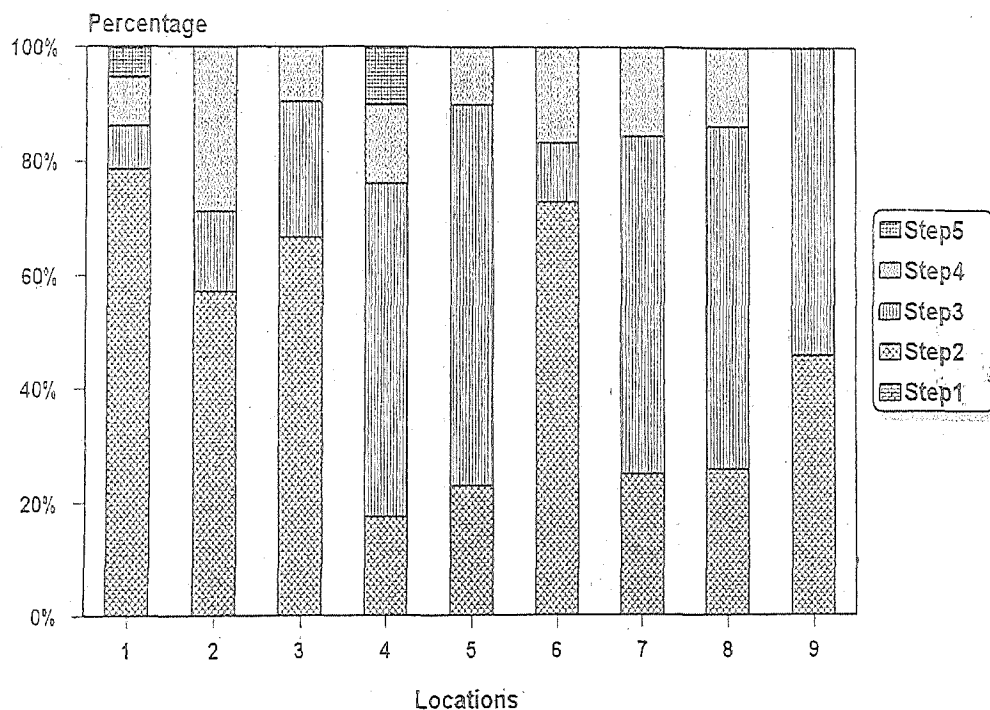


Fig5. The sequential extraction results for cadmium.

Table 5. Depth, carbonate and organic matter percentages in sediment samples collected from the northern part of the Red Sea during January 2003.

Location	Parameter		
	Depth (m)	Carbonate %	Organic matter %
1	16	17.9	20.50
2	50	2.7	15.10
3	55	13.5	16.70
4	56	11.6	13.20
5	65	14.4	17.40
6	76	9.3	7.90
7	82	4.8	6.30
8	82	8.7	9.20
9	40	3.2	4.36

CONCLUSION:

Sequential extraction results proved useful to distinguish between anthropogenic and geochemical sources of most metal species in the sediments. The foregoing discussion implies the following points: i) High content of Cu, Zn and Pb are formed in the residual fraction reflecting geochemical origin; ii) Relatively high amounts of Cu, Zn and Cd in the carbonate fraction with 6.50, 9.60 and 78.63% respectively were recorded at Adabiya. This is because of the high content of carbonate (17.9%); iii) The relatively high amounts of Cu, Zn and Pb in the organic fraction (15.60, 11.60 and 28.64%) were recorded respectively at Adabiya, and may be due to high amount of organic matter found in the sediments there (20.50%); iv) Generally, the percentages of Cu, Zn and Pb in the exchangeable fraction were limited to a few percent, but for, Cd, not detectable in the exchangeable fraction; v) Low levels of Cu, Zn and Pb species were extracted in the first three steps, indicating that these metals were from anthropogenic origin i.e. allochthonous. From the above cited results, it can be concluded that the capacity of the sediment to act as a sink for heavy metals was sufficient to indicate its pollution extent. Speciation of heavy metals and their effect on bioavailability are critical to understanding ecotoxicology. Further this information is also crucial for the development of policies concerning the use and disposal of toxic materials in the environment.

REFERENCES

- Adams, V. 1990. Water and wastewater examination manual Lewis Publishers, USA, 2457 p.
- Callander, E., and C.J. Bower,. 1980. Manganese and copper geochemistry, of interstitial fluids from manganese nodule-rich sediments of the north-eastern equatorial Pacific Ocean. *American Journal of Science*, 280: 1063-96.
- Carroll, D. 1958. Role of clay minerals in the transportation of iron, *Geochimica Cosmochimica Acta*, 14: 1-27.
- Chester, R. A Thomas, F.J. Lin, A.S Basaham,. and G Jacinto, 1988. The solid state speciation of copper in surface water particulates and oceanic sediments. *Marine Chemistry*, 24: 261-92.
- Colliar, R. and Edmond, J.M. 1984. The trace element geochemistry of marine biogenic particulate matter. *Oceanography Programme* 13: 113 99.
- Davis, J.A. and Leckie, J.O. 1978. Effect of adsorbed complexing ligands on trace metal uptake by hydrous oxides. *Environmental Science and Technology*, 12: 1309-15.

- Forstner, U. and Wittmann, G. 1983. Metal pollution in the aquatic environment, Springer Verlag Berlin Heidelberg, New York, Tokyo, 486 p.
- Gibbs, R. 1973. Mechanism of trace metal transport in rivers. *Science*, 180: 71-73.
- Gupta, S.K. and Chen, K.V. 1975. Partitioning of trace metals in selective chemical fractions of near shore sediments. *Environmental Research Letters*, 10:129-58.
- Jorgensen, B.B. 1977. The sulfur cycle of a coastal marine sediments (Limfjorden, Denmark). *Limnology and Oceanography*, 22: 814-831.
- Kuo, S. and Baker, A.B. 1983. Distribution and forms of copper, zinc, cadmium, iron and manganese in soils near a copper smelter. *Soil Science*, 135: 101-9.
- Lerich, H.H. and Weir, A.H. 1963. A method of studying trace elements in soil fractions. *Journal of Soil Science*, 14: 225-35.
- Lyengar, S.S., Martens, D.C. and Miller, W.P. 1981. Distribution and plant availability of soil zinc fractions. *Soil Science society of America Journal*, 45: 735-9.
- Mahmoud, W.M.A. 1994. Chemical investigation on lead in the western harbour of Alexandria. M. Sc. Thesis, Faculty of Science, Alex. University, 223 p.
- Moussa, A.A. 1984. Estimation of metal pollutant levels in sediment from Lake Borollos, *Journess d' Etudes Pollutions Cannes CIESM*, 5, 373-7.
- Pardo, E., Perez, L. and Vega, M. 1990. Determination and speciation of trace metals in sediments of the Pisuerga River, *Water Resources Research*, 373-379.
- Saxby, J.D. 1973. Diagenesis of metal-organic complexes in sediments. Formation of metal sulphides from cysteine complexes, *Chemical Geology*, 12: 241-288.
- Shata, M.A., El-Deek, M.S. and Okbah, M.A. 1993. Fractionation of Mn, Fe, Zn and Cu in sediments of Khor Kalabsha Lake Nasser, Egypt *Chemical Ecology*, 8: 89-103.
- Shuman, L.M. 1979. Zinc, manganese, and copper in soil fractions, *Soil Science*, 127: 10-17.
- Tessier, A., Campbell, P.G.C. and Rissa, M. 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*, 51: 844-51.

(Received: 23 June, 2006)