

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

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Key words: *Speciation, Heavy metals, Sediments, Red Sea*

ABSTRACT

Total concentrations and chemical forms of heavy metals in sediment samples collected from the Gulf of Suez and the northern part of the Red Sea were collected and measured during January 2003 using flame 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, reflecting the high contribution of land-based activities in the northern part of the Gulf. Also, high percentage of heavy metals were found in the residual fraction (Cu = 78.61, Zn = 77.10 and Pb = 66.80%. While, the high percentage of Cd was found in the carbonate fraction (45.82%). Few or negligible percentages were recorded in the exchangeable fractions (Cu = 0.51, Zn = 1.57 and Pb = 1.74%), and undetectable concentration of Cd was obtained in the exchangeable fraction.

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 Fig. 1. Its 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 considerably increased in recent years through ships oil and refuse several industrial and domestic drainage in the northern part and 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 anti-fouling paints of ships, industrial wastes and to a less extent the municipal wastes. To assess the environmental impact of heavy metal inputs in 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 more fully identified on the basis of speciation measurements. The present study was performed to identify the specific fractions of heavy metals in sediment samples collected from the Gulf of Suez and the northern part of the Red Sea.

Two main factors have to be taken into account assessing the risk arise from a heavy metal-contaminated site; the total amount of the respective heavy metal and the chemical binding form of the heavy metal. Measurement of the total concentration of heavy metal provides inadequate information to allow us to assess the bioavailability and toxicity of that metal. Chemical speciation can be defined as the process of identifying and quantifying the different species, forms or phases present in a material. The species can be define (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). 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 over the various chemical compounds and minerals in sediment, which determine its behaviour in the environment and its remobilization ability.

MATERIALS AND METHODS

Sediment samples were collected from nine locations distributed along the Gulf of Suez and the northern part of the Red Sea using Van-Veen grab during January 2003

(Fig. 1). Grain size analysis (mechanical sieving method) was used for sediment samples to get $<20 \mu\text{m}$ fractions. Sequential extractions were performed on the frozen sub samples according to Tessier et al. (1979), where exchangeable fraction (F1) was extracted by MgCl_2 (pH 7) and NaOAc (pH 8.2), carbonates fraction (F2) was extracted by NaOAc (pH 3), Fe-Mn oxide fraction (F3) was extracted by $\text{NH}_4\text{OH.HCl}$ in HOAC and organic fraction (F4) was extracted by HNO_3 and H_2O_2 . Carbonate was determined according to Adams (1990). Organic matter was measured according to Jorgensen (1977).

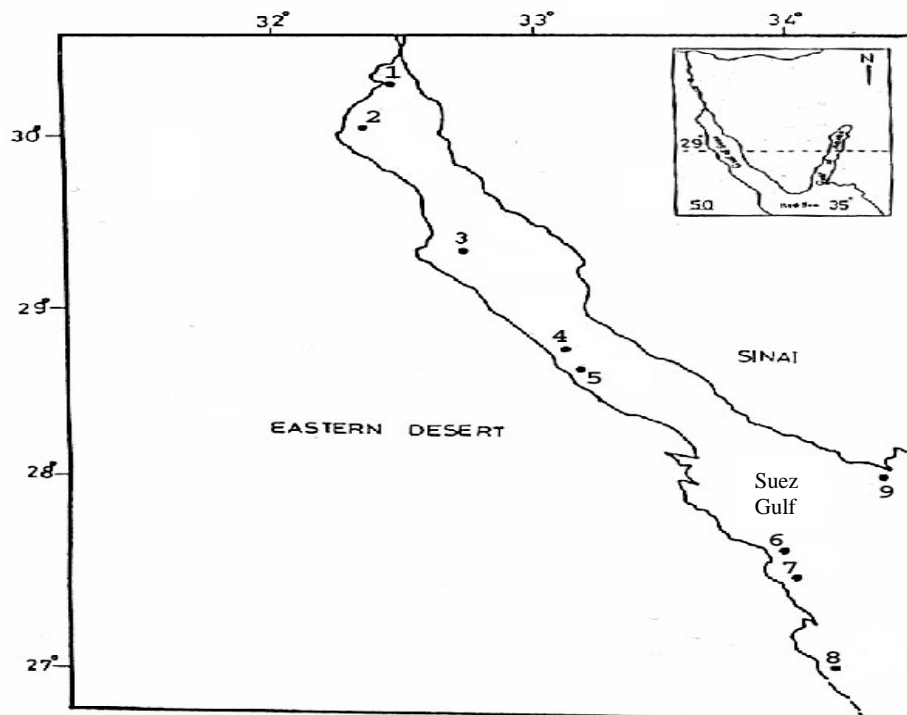


Fig. (1). Location of samples taken from the northern part of the Red Sea.
1. Adabiya, 2. Ain Sukhna, 3. Ras Zafarana, 4. Ras Gharib, 5. Ras Shukeir,
6. Hurghada, 7. Gifton, 8. Safaga and 9. Ras Mohamed.

RESULTS AND DISCUSSION

Gibbs (1973) suggested four groups of heavy metals associations in aquatic solid substances (including suspended matter as well as sediments). They can be characterized by the following bonding processes: 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 which may release metals from suspended particulate are desorption dissolution and oxidation of organic matter (Forstner and Wittmann, 1983).

Speciation of copper in sediments

Speciation of Cu in sediments collected from the northern part of the Red Sea are presented in Table 1 and Fig. 2. It is clear that the percentage of exchangeable fraction was small or negligible in comparison to 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

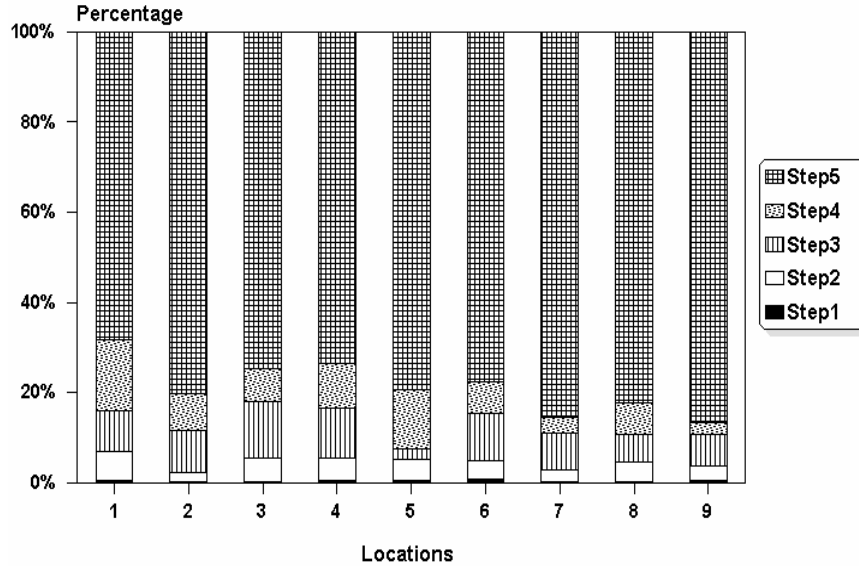
Ras Mohamed (location 9), [0.39, 0.41 and 0.34 $\mu\text{g/g}$, respectively] probably due to the decrease in total carbonate content in the sediment was recorded at these locations [2.7, 4.8 and 3.2%, respectively, Table 5]. Relatively high percentage of Cu in the carbonate fraction 3.22 $\mu\text{g/g}$ (6.5%) was recorded at Adabiya, and is attributed to the high content of carbonate with 17.9% at this area. 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.

Kuo and Baker (1983) and Leriche and Weir (1963) showed that copper is 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.

The organic fraction, F_4 of copper in the study area ranged between 0.28 $\mu\text{g/g}$ at Ras Mohamed and 7.73 $\mu\text{g/g}$ at Adabiya. The relatively high amounts of copper in organic fraction at Adabiya and Ras Shukeir (Table.5) are probably due to the relatively high contents of organic matter.

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

Fraction Location	Exchangeable		Carbonate		Fe-Mn oxide		Organic		Residual		Total
	Conc	%	Conc	%	Conc	%	Conc	%	Conc	%	
1.	0.30	0.60	3.22	6.50	4.41	8.90	7.73	15.60	33.90	68.40	49.56
2.	0.09	0.40	0.39	1.80	2.06	9.50	1.78	8.20	17.38	80.10	21.70
3.	1.05	0.20	1.39	5.20	2.33	12.40	2.01	7.50	20.05	74.70	26.84
4.	0.20	0.60	1.58	4.90	3.61	11.20	3.16	9.80	23.72	73.50	32.27
5.	0.29	0.70	1.91	4.60	0.91	2.20	5.51	13.30	32.82	79.20	41.44
6.	0.10	0.80	0.50	4.10	1.29	10.60	0.84	6.90	9.46	77.60	12.19
7.	0.05	0.30	0.41	2.50	1.37	8.30	0.59	3.60	14.07	85.30	16.50
8.	0.046	0.30	0.66	4.30	0.96	6.20	1.10	7.10	12.71	82.10	15.48
9.	0.074	0.70	0.34	3.20	0.73	6.90	0.28	2.60	9.20	86.60	10.62
Mean \pm SD	0.24 \pm 0.30	0.51 \pm 0.20	1.16 \pm 0.92	4.12 \pm 1.36	1.96 \pm 1.21	8.47 \pm 2.90	2.56 \pm 2.38	8.29 \pm 3.93	19.26 \pm 8.75	78.61 \pm 5.48	25.18 \pm 12.80



Fig(2): The Sequential extraction results for copper.

Callender and Bower (1980) and Collier and Edmond (1984) stated that Cu is 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 is 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 is predominant in the residual fraction, F₅ and ranged between 9.20 µg/g at Ras Mohamed and 33.90 µg/g at Adabiya. This is in accordance with Moussa (1984) who reported that, the chief source of Cu and Zn seems to be the lithogenic minerals. It is observed from Table (1) that concentration of copper species are very high at Adabiya, which is associated with maximum content of carbonate and organic matter in sediment. This is affected by the invading water coming from the highly industrialized Suez Bay, where there are many sources of pollution. On the other hand, very low content of

different copper species was found at Ras Mohamed, which is considered as a protected area of low content of carbonate and organic matter in sediment.

Speciation of zinc in sediments

The relative amounts of zinc among different phases of surface sediments are presented in Table 2 and Fig. 3. Zinc fractionation analyses revealed that more than 77% of the total zinc occurred in the residual form.

Smaller fractions are exchangeable (1.57%), carbonate; oxide and organic bound 5.4, 7.38 and 7.89% respectively. The exchangeable zinc at Ras Zafarana and Adabiya (2.7 and 1.4%, respectively) showed higher values compared with lower one at Safaga (1.1%). This may be attributed to the effect of the fine grain size and organic matter content. Ras Zafarana and Adabiya have clay and organic matter contents of 26.29%, 16.7% and 20.35, 20.50%, respectively. On the other hand, Safaga had 8.70 and 9.2% of clay and organic matter contents, respectively.

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

Fraction Location	Exchangeable		Carbonate		Fe-Mn oxide		Organic		Residual		Total
	Conc.	%	Conc.	%	Conc.	%	Conc.	%	Conc.	%	
1.	0.92	1.40	6.28	9.60	1.83	2.80	7.59	11.60	48.67	74.40	65.42
2.	0.84	1.80	2.62	5.60	5.58	11.90	4.87	10.40	32.94	70.30	46.86
3.	0.93	2.70	2.91	8.50	4.52	13.20	3.15	9.20	20.79	60.65	34.28
4.	0.51	1.30	2.48	6.30	4.01	10.20	3.82	9.70	28.53	72.50	39.35
5.	0.76	1.50	4.76	9.40	1.27	2.50	5.57	11.00	38.28	75.60	50.64
6.	0.284	1.40	0.57	2.80	1.89	9.30	1.03	5.10	16.52	81.40	20.30
7.	0.32	1.70	0.52	2.80	1.56	8.40	1.22	6.60	14.93	80.50	18.55
8.	0.27	1.10	0.55	2.20	1.31	5.30	1.02	4.10	21.63	87.30	24.78
9.	0.163	1.20	0.19	1.40	0.38	2.80	0.45	3.30	12.42	91.30	13.60
Mean \pm SD	0.56 \pm 0.29	1.57 \pm 0.45	2.32 \pm 2.00	5.40 \pm 3.05	2.48 \pm 1.67	7.38 \pm 3.90	3.19 \pm 2.33	7.89 \pm 2.97	26.08 \pm 11.36	77.11 \pm 8.71	34.86 \pm 16.26

The carbonate-Zn fraction increased at Adabiya and Ras Shukeir (9.6 and 9.4% of total zinc) and the lowest value was (1.4%) recorded at Ras Mohamed. This result could be due to zinc precipitation as ZnCO_3 or $\text{Zn}_5[\text{CO}_3]_2[\text{OH}]_2$, which is due to high content of carbonate at Adabiya and Ras Shukeir (17.9% and 14.4%, respectively). While, carbonate content at Ras Mohamed was low 3.2%. The oxide-Zn fraction was in the range of 2.50% at Ras Shukeir and 13.20% at Ras Zafarana. Davis and Leckie (1978) reported that amorphous sesquioxides have greater ability to retain the heavy metal to their specific surface area. 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 lowest Zn concentration was recorded in the organic fraction with $0.45 \mu\text{g/g}$ (3.30%) at Ras Mohamed compared with $7.59 \mu\text{g/g}$ (11.60%) at Adabiya reflecting high content of organic matter at this area. The residual fraction of Zn was $12.42 \mu\text{g/g}$ (91.30%) at Ras Mohamed compared to $20.79 \mu\text{g/g}$ (60.65) at Ras Zafarana. The high percent of residual fraction of Zn at Ras Mohamed reflects the predominance of physical conditions such as sedimentation rate. This finding is similar to that given by Lyengar et al. (1981) and Shata et al. (1993).

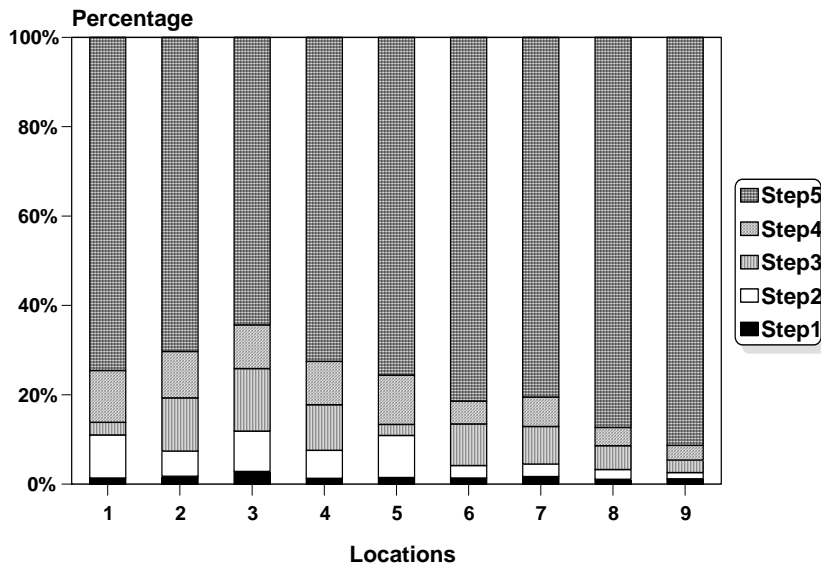
Speciation of lead in sediments

Speciation of lead in surface sediments are presented in Table 3 and Fig. 4. Lead fractionation analyses revealed that more than 63.17% of the total lead occurred in the residual form. Smaller fractions are exchangeable (1.55%), carbonate, oxide and organic bound 5.55%, 11.09 and 18.64% respectively.

The distribution of Pb in the exchangeable fraction is limited to a few percent which is similar to the results of Mahmoud (1994). The distribution of Pb bound to carbonate was minimum at Adabiya ($0.96 \mu\text{g/g}$, 2.85%) compared to a maximum of $1.12 \mu\text{g/g}$ (11.94%) recorded at Safaga, this form is not generally indicating that preferable even with high content of carbonate at Adabiya (17.9%).

The oxide-Pb fraction was in the range of $0.48 \mu\text{g/g}$ (2.45%) at Hurghada and $4.58 \mu\text{g/g}$ (13.66%) at Adabiya. The high percentage of amorphous iron oxide or reducible fraction of Pb (13.66%) at Adabiya and (13.43%) at Safaga reflect the mud nature of sediment at these locations. Iron is principally associated with silt-clay fractions; it is a mobile element, which is subjected to diagenetic remobilization as stated by Forstner and Wittmann (1983).

Also, high content of Pb bound to Fe oxides at Ras Zafarana (12.75%) and Ras



Fig(3): The Sequential extraction results for zinc.

Mohamed (11.09%) is mainly related to the precipitation of mineral Kaolin. This is in accordance with Carrol (1958) who stated that Fe exists in the form of oxides coating the fine particles and especially in clay minerals.

The concentration of organic bound fraction of Pb in sediments fluctuated between a minimum of 1.87 µg/g (8.32%) at Ras Gharib and maximum of 9.6 µg/g (28.64%) at Adabiya reflecting high concentration of organic matter at Adabiya (20.50%). Organic components of sediment act as ion exchange surface 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 F₅ reached a maximum of 18.70 µg/g (83.15%) at Ras Gharib and a minimum of 4.10 µg/g (63.17%) at Ras Mohamed. Pardo et al. (1990) showed that the greater percentage of this fraction of metal particulate means 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 polluting circumstances.

Speciation of cadmium in sediments

The results of the sequential extraction method of Cd are represented in Table 4 and Fig. 5. It is clear that no detectable concentration of Cd was obtained in exchangeable fraction. The relatively high percentage of Cd occurred as carbonate fraction was recorded at Adabiya, Ain Sukhna, Ras Zafarana and Hurghada (78.63, 57.05, 66.66 and 72.82% respectively).

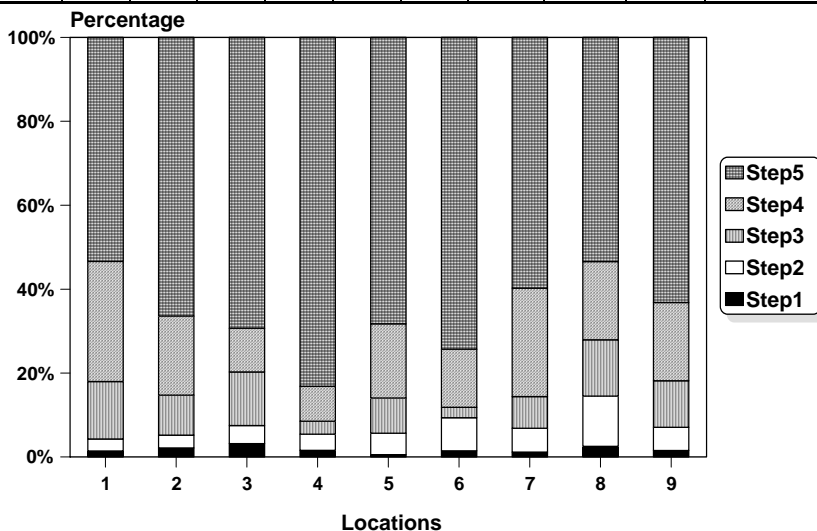
This is in accordance with Forstner and Wittmann (1983) who stated that, the occurrence of Cd in sediments is mainly related to the formation of CdCO₃. High percentage of Cd was recorded as Fe-Mn oxides fraction particularly at Ras Gharib, Ras Shukeir, Gifton, Safaga and Ras Mohamed (58.33, 66.92, 59.37, 60.18 and 54.22%, respectively). This reflect that at these locations, Cd is likely bounded to Fe-Mn oxides. On the other side, organic/sulphide fraction shows high percentage at Ain Sukhna (28.86%). This is mainly related to complexation reaction

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between the high content of organic matter precipitate especially at this location (15.1%) and the affinity of Cd to form CdS

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

Fraction Location	Exchangeable		Carbonate		Fe-Mn oxide		Organic			Residual		Total
	Conc	%	Conc	%	Conc	%	Conc	%	Conc	%		
1.	0.48	1.44	0.96	2.86	4.58	13.66	9.60	28.64	17.90	53.40	33.52	
2.	0.37	2.15	0.53	3.07	1.64	9.51	3.25	18.84	11.46	66.43	17.25	
3.	0.60	3.18	0.82	4.34	2.41	12.75	1.97	10.42	13.10	69.31	18.90	
4.	0.36	1.59	0.86	3.85	0.69	3.09	1.87	8.32	18.70	83.15	22.48	
5.	0.13	0.55	1.21	5.13	1.97	8.35	4.18	17.71	16.11	68.26	23.60	
6.	0.29	1.48	1.55	7.90	0.48	2.45	2.72	13.86	14.58	74.31	19.62	
7.	0.10	1.17	0.49	5.68	0.65	7.54	2.23	25.87	5.15	59.74	8.62	
8.	0.24	2.56	1.12	11.94	1.26	13.43	1.75	18.66	5.01	53.41	9.38	
9.	0.10	1.55	0.36	5.55	0.72	11.09	1.21	18.64	4.10	63.17	6.49	
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	17.76 \pm 8.10	



Fig(4): The Sequential extraction results for lead.

CONCLUSION

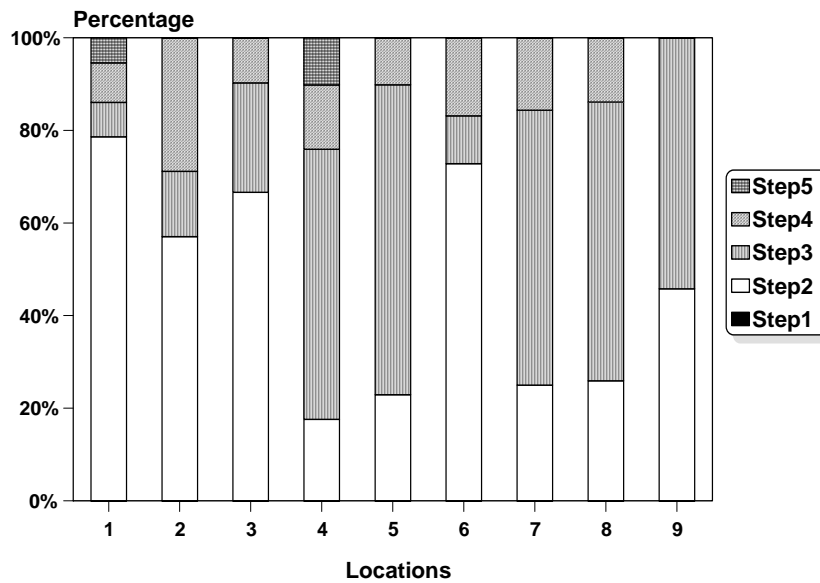
Sequential extraction results proved useful to distinguish between anthropogenic and geochemical sources of most metal species in sediments. The forgoing discussion implies the following points: i) High content of Cu, Zn and Pb are formed in the residual fraction reflecting geochemical origin. ii) Relatively high amounts of Cu, Zn and Cd in carbonate fraction with low 6.50, 9.60 and

high 78.63% respectively were recorded at Adabiya. This is due to the high content of carbonate (17.9%), iii) The relatively high amount of Cu, Zn and Pb in the organic fraction (15.60, 11.60 and 28.64%) were recorded respectively at Adabiya, may be due to high amount of organic matter found in the sediment iv) Generally, the percentages of Cu, Zn and Pb in the exchangeable fraction is limited to a few percent, while Cd, showed undetectable concentration 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.

Table (4).Cadmium species, total concentration ($\mu\text{g/g}$), and percentages in sediment samples collected from the northern part of the Red Sea during January 2003.

Fraction Location	Exchangeable		Carbonate		Fe-Mn oxide		Organic		Residual		Total
	Conc	%	Conc	%	Conc	%	Conc	%	Conc	%	
1.	-	-	2.76	78.63	0.26	7.41	0.30	8.55	0.19	5.41	3.51
2.	-	-	0.85	57.05	0.21	14.09	0.43	28.86	-	-	1.49
3.	-	-	1.09	66.66	0.39	23.64	0.16	9.76	-	-	1.65
4.	-	-	0.38	17.59	1.26	58.33	0.30	13.89	0.22	10.18	2.16
5.	-	-	0.61	22.93	1.78	66.92	0.27	10.15	-	-	2.66
6.	-	-	1.34	72.82	0.19	10.33	0.31	16.85	-	-	1.84
7.	-	-	0.32	25.0	0.76	59.37	0.20	15.63	-	-	1.25
8.	-	-	0.28	25.93	0.65	60.18	0.15	13.89	-	-	1.08
9.	-	-	0.38	45.78	0.45	54.22	-	-	-	-	0.83
Mean \pm SD	-	-	0.89 \pm 0.75	45.82 \pm 22.40	0.66 \pm 0.51	39.39 \pm 23.39	0.27 \pm 0.09	14.70 \pm 6.02	0.21 \pm 0.02	7.80 \pm 2.38	1.83 \pm 0.79



Fig(5): 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.

Parameter Location	Depth m	Carbonate %	Organic matter %
1. Adabiya	16	17.9	20.50
2. Ain Sukhna	50	2.7	15.10
3. Ras Zafarana	55	13.5	16.70
4. Ras Gharib	56	11.6	13.20
5. Ras Shukeir	65	14.4	17.40
6. Hurghada	76	9.3	7.90
7. Gifton	82	4.8	6.30
8. Safaga	82	8.7	9.20
9. Ras Mohamed	40	3.2	4.36

From the above mentioned results, it can conclude that the capacity of the sediment act as a sink for heavy metals was sufficient to indicate its pollution extend. Also, speciation of heavy metals and their effect on bioavailability are critical to understand the ecotoxicology. Further, this information is also crucial for development of polices concerning the use and disposal of toxic material in the environment.

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