TRACE METALS SPECIATION IN SEDIMENTS OF LAKE MANZALA, EGYPT

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ABSTRACT

Sediment samples were collected during summer, 2004 from Lake Manzala to determine the chemical association of trace metals (Fe, Mn, Cu, Zn, Pb, Cd, Co, Ni and Cr) in the lake sediments. Five fractions were extracted using sequential extraction techniques, which represent the major sedimentary phases including the exchangeable, carbonate, Fe-Mn oxides, organic fraction and residual metal. The results of metals speciation indicated that, the high proportion of trace metals were presented in the residual fraction which represents 50% of the total metals for Mn, Cu, Pb and reached to 73% of the total for Zn. The geochemical analysis of metal forms reflected the lithogenic origin of these metals in the study area.

The results also showed high percentage of Fe, Co, Ni and Cr in the organic fractions (40% of the total metal). High percentage of Cd was found in the carbonate fraction (32%). However, few percentages were recorded in the exchangeable fraction of Fe, Cu and Zn (< 1% of total content), while increased from 2 to 6% of total Mn, Cr, Co, Ni and reached to 6% for Pb and 12% for Cd. It is evident from the results that the sediments of Lake Manzala are highly polluted with Cd, Cr, Ni and Co, and the greater amount of these were found in the non-lithogeous origin (exchangeable, carbonate, oxides and organic materials).

Multivariate techniques of statistical analysis have been applied to a set of chemical forms of metals obtained by the analysis of Lake Manzala sediments. The correlation matrix and principal component analysis were performed to show the behavior of the nine metals in each fraction.

INTRODUCTION

Lake Manzala is the largest of the Nile Delta lagoons which is located at the coastal area of the Mediterranean sea of Egypt. It receives drainage water from several drains which serve as sources of pollution. Sediments act as both carriers and potential sources of contaminants in an aquatic environment. Anthropogenic activities, industrial and urban wastes as well as agriculture wastewater play an important role in influencing the pollution of the lake water and sediments.

Because the heavy metals can be either adsorbed onto sediments or accumulated by benthic organisms to a toxic level, the bioavailability and subsequent toxicity of the metals are dependent upon various kinds and amounts of the metals bound to the sediment matrices (Yu et al., 2001). Most studies are concerning with the total concentration of trace metals and few attempts have been done to evaluate the speciation of them.

One of the most widely applied for sequential extraction procedures was proposed more than 25 years ago by Tessier et al.(1979). It is now widely recognized that the toxicity and the mobility of trace metals are depending on their geochemical forms and on their binding state. The identification of the main binding sites and phase associations of trace metals in sediments helps in understanding geochemical processes and to evaluate the remobilization potential and the risks induced (Gleyzes et al., 2002).

Sequential extraction procedures are designed to isolate specific fractions of sediment by successively attacking the sample with chemical reagents and analysis the resulting supernatant (Krye et al., 2003).

A large number of researchers have used principal component analysis (PCA) in the evaluation of environmental data (Zitko, 1994; Soares et al., 1999; Rubio, 2000; El-Iskandarani et al., 2003). Multivariate data analysis techniques have been used in eco-toxicology (Sparks et al., 1999; De Bartolomeo et al., 2004). This technique explains the most relevant information about the relationships among the anthropogenic trace metal contamination of various environments.

The main objective of this study is to examine the sediment matrices and their binding fractions to trace metals (Fe, Mn, Zn, Cu, Cd, Pb, Cr, Co and Ni).

MATERIAL AND METHODS

1. Study area

Lake Manzala is the largest Nile Delta lagoon, has an area of about 670 km^2. The lake is connected with the Mediterranean sea through Boughaz El-Gamil, lying to the west of Port Said City. The lagoon is shallow with depth less than 1m and it is very important for fish production in Egypt. It lies between longitude 31° 45` and $32^{\circ}$ 15` and latitude 31° 00` and $31^{\circ}$ 35`N (Fig. 1).

2. Sampling and analysis

Twelve surface sediment samples were collected during summer, 2004 from Lake Manzala, covering the whole area under investigation (Fig. 1) by van veen grab sampler. Samples from each site were divided into two subsamples, then homogenized by mixing and kept in clean plastic containers. Samples were stored, frozen until analysis.

A sub-sample was taken to determine chemical and physical characteristics of the sediments such as grain size distribution, total organic matter and calcium carbonate contents. Wet sieving was carried out to define grain size distribution. The total organic carbon was determined as percentage loss of weight of dried sediment sample after ignition for 24 hours at 550°C (Dean, 1974).

The total concentrations of trace metals were determined according to Oregioni and Aston (1984); 0.2g of dried sample was digested using a mixture of nitric, perchloric and hydrofluoric acids in a previously cleaned and dried Teflon beaker, then evaporated to near dryness at 80°C. After complete digestion, the residue was transferred to 25 ml volumetric flask with 0.1 M HCl. The total concentrations of trace metals and their fractions were measured using A.A.S. (Perkin Elmer model 373).

The sequential extraction scheme of Tessier (1979) was performed (Fig. 2). In this procedure, bubbling nitrogen prior to contact with samples deoxygenated the chemical extracts of the first step. The tubes were closed with screw-caps during mechanical shaking and centrifugation. A chelator (10 mg EDTA) was added to the ammonium and sodium acetate extracts to prevent precipitation of metals during storage in the refrigerator. Acidification of these solutions were found to be inadequate due to precipitation of humic acids leached by the first two steps (Kersten & Forstner, 1987).

3. Quality control studies

Two natural samples were analyzed in duplicate in each of six batches of samples after spiking by a known concentration from the standard reference material. The same two natural samples were analyzed without spiking. The highest and lowest percentages of recovery for spiked samples were used to determine the accuracy. The results ranged between 90 and 110%, while precision was agreed to be within 10%. Table (1) illustrates the concentrations for different metals in the reference materials. The variation coefficients were 4.6% for Fe; 7.3% for Mn; 5.2% for Cu; 7.1% for Zn; 6.2 for Pb; 7.6% for Cd.

4. Statistical analysis

Correlation matrix and principal component analysis (PCA) were carried out on the data set of trace metals among the five fractions, to describe the behavior and the association of the metals in the present study.

RESULTS AND DISCUSSION

1. Chemical properties of the sediments

The relative percentage of organic matter , $CaCO_3$ and graine size distribution of Lake Manzala sediments are shown in Table 1a. The amounts of organic matter were relatively high in the sediment samples, its content ranged from 2.07%(Stations IX and XI) to 8.96% (station XII). The organic matter distribution is affected by its rate oxidation and the amount of wastewater drainage through the drains located in the southern part of the Lake. The carbonate content ranged between 15.7% at St. XI and 67.8% at St.IV. It is clear from the sediments analysis of the Lake that the levels of $CaCO_3$ were higher in the eastern and western regions. The sediments type was sandy loam at most stations and clay at stations X and XII. The lake sediments were mixed with shells and shells fragment which constitute significant part of the sediments

Tables (3-11) show the values of a total concentration of nine trace metals (Fe, Mn, Cu, Zn, Pb, Cd, Cr, Ni and Co) which were accumulated in the sediments of Lake Manzala. The levels of total trace metals in the sediments of the investigated area revealed significant variations. The values of these metals were in the range 9184-11828; 309-1627; 20-101; 275-491; 24-83; 1.3-2.5 , 28-93; 26-79 and 19-54 μg/g for Fe, Mn, Cu, Zn, Pb, Cd, Cr, Ni and Co;S respectively. It was considered that the average values of trace metals (Cr= 90, Ni= 68, Pb= 20, Cd= 0.3 in ppm) in shales materials as the background concentration for the sediment (El-Sokkary, 1990). It is clear that the sediment in the present

study contain high amounts of metals than those background values. This may be related to the wastewater discharged through the drains which are polluted with municipals, industrial effluents and agriculture wastewater.

2. Distribution of trace metals in the sediment matrices

The relative amounts of Fe among different phases of surface sediments are presented in Table 3 and Fig. 3. Iron fractionation analysis revealed that 55.53% of the total Fe occurred in the organic fraction and 39.56% in the residual fraction. Smaller fractions are exchangeable (0.22%), carbonate (0.11%) and 4.69% in the Fe- Mn oxide fraction.

The relatively high amounts of Fe in organic fraction at St. VII (62.20%) are perhaps due to the relatively high contents of organic matter (8.96%) as shown in Table 2. Data indicated that the percentage of exchangeable, carbonate and oxides fractions were few or in comparison to other fractions.

In the same context, the relative amounts of Mn in different phases of surface sediments samples collected from Lake Manzala are presented in Table 4 and Fig. 3. The residual fraction of Mn was 1051.79 µg/g (64.62%) at St. IX compared to 134.59µg/g (43.53%) at St. IV.

The high percent of residual fraction of Mn at St. IX 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).

The relative amounts of copper in different phases of surface sediments are presented in Table 5 and Fig.3. It is clear that the percentage of exchangeable fraction (F1) was few in comparison to other fractions. The percentage of Cu-carbonate fraction (F2) fluctuated between 4.44% at station III and 24.87% at station IV. Relatively high of Cu in the carbonate fraction at station IV may be due to the high content of carbonate with 67.80% at this location.

The Fe-Mn oxide fraction (F4) of Cu was in the range of 2.26 µg/g (17.85%) at St. VIII and 19.07 µg/g (25.48%) at St. II. Shuman (1979) stated that Cu is mainly associated with Fe-Mn oxides fraction in sandy soils. Kuo & Baker (1983) reported that Cu is highly bound to Mn oxides. The organic fraction of Cu was in the range 7.36 µg/g at St. VIII and 29.73 µg/g St. II.

High concentration of Cu in the organic fraction at stations I, II and III may be due to the sector El-Genkah and its water was affected mainly by industrial untreated sewage and agriculture effluents discharged from Bahr El-Bakar, Ramsis and Hodous drains.

The results also indicate that Cu is predominant in the residual fraction and ranged between 2.10 µg/g at St. IV and 57.39 µg/g at St. V. This is in accordance with Moussa (1984) who reported that, the chief source of Cu and Zn seems to be the lithogenic minerals.

The relative amounts of zinc among different phases of surface sediments are presented in Table 6 and Fig.4. It is clear that the percentage of exchangeable fraction (F1) was few in comparison to other fraction ranging between 2.59 µg/g at St. VIII and 5.34 µg/g at St. III.

The average values of zinc fractionation analyses revealed that 73.20%, 8.97%, 10.81%, 6.21% and 0.87% of the total zinc occurred in the residual, organic bound, oxide bound, carbonate bound and exchangeable bound, respectively. The Fe-Mn oxide fraction (F4) of zinc was in the range of 34.80 µg/g (8.42%) at St. VII and 52.05 µg/g (13.82%) at St. VI. Davis & Leckie (1973) reported that amorphous sesquioxides have greater ability to retain the heavy metals to their specific surface area. Zinc is absorbed by oxides as well as being occulded in the structure. The similarity between the atomic radius of Zn and Fe makes their exchange possible. The residual fraction of Zn reached a maximum of 363.94 µg/g (74.16%) at St. XII. This 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).

The relative amounts of lead among different phases of surface sediment are presented in Table 7 and Fig.4. It is clear that the distribution of Pb in the exchangeable fraction is limited to a few percent. Mahmoud (1994) showed that the percentage of exchangeable of Pb is few or negligible in sediment in comparison to other fractions. The distribution of Pb bound to carbonate was minimum at St. II (2.72µg/g; 6.84%) compared to a maximum of 10.02 µg/g (17.97%) recorded at St. XII. However, the percentage of oxide and organic fractions of Pb were in the range 2.76-15.60% and 14.58-31.25% respectively.

It is clear that the residual fraction Pb reached a maximum of 55.47 µg/g (66.67%) at St. VIII and a minimum of 9.15 µg/g (37.13%) at St. IV. Pardo et al. (1990) showed that the greater percentage of this fraction metal particulates means a smaller or less dangerous pollution effect. This inactive phase corresponds to a lattice bound metal, which can not be remobilized at least under normal polluting circumstances.

The relative amounts of Cd among different phases of surface sediment are presented in Table 8 and Fig. 4. Cadmium fractionation

analyses revealed that high average value of Cd, reached to 32.00% of the total Cd occurred in the carbonate fraction (F2) and 28.51% in the oxide fractions. Similar fractions are found in the exchangeable (12.31%), organic bound (12.41%) and the residual fraction (15.80%). The relatively high percentage of Cd occurred as carbonate fraction especially at stations XI and I (44.38 and 39.45%, respectively). This is in accordance with Förstner & Whittmann (1983) who stated that the occurrence of Cd in sediments is mainly related to the formation of $CdCO_3$. High percentage of Cd was recorded as Fe-Mn oxides fractions (F3), particularly at St. XII (52.23%). On the other hand, the organic fraction (F4) shows high percentage at St. II (24.86%). This is mainly related to affinity of cadmium to form CdS precipitate especially at this station which is affected by drainage water discharged from Bahr El-Bakar drain.

The amounts of Cr, Ni and Co among different phases of surface sediments are presented in Tables 9, 10 and 11, respectively. The relative percentage of these fractions is recorded in Fig. 5. Cr, Ni and Co fractionation revealed that relatively high percentage of the total Cr, Ni and Co occurred in the organic fractions (42.61, 39.00 and 37.53%, respectively) and residual fractions (29.36, 32.81 and 32.35% respectively). Smaller fractions are exchangeable 1.08, 3.04 and 2.79 for Cr, Ni and Co metals respectively.

Relatively high amounts of Cr and Co in the organic fractions (56.81 and 52.85%) were recorded at stations V and X, may be due to high amount of organic matter at these stations (6.31% for St. V and 5.86% for St. X).

3. Statistical analysis
3.1. Correlation Matrix

The behavior of the nine trance metals (Fe, Mn, Cu, Zn, Pb, Cd, Cr, Ni and Co) in the sedimentary five fractions could be known by performing correlation matrix (Tables 12 a-e).

As shown in Table 12, the correlation matrix of trace metals bounded to the exchangeable fraction revealed significant correlation between Cu-Exch. and Mn-Exch. (r= 0.59) and between Co-Exch and Pb-Exch (0.62). The results of carbonate fraction (Table 12b) showed significant correlation between Ni-Carb. with both Fe-Carb. (r= 0.59) and Zn-Carb. (r= 0.71). Also, significant correlation between Cd-carb. with both Co-Carb. (r= 0.56) and Cu-Carb. (r=-0.58). The correlation matrix of trace metal bounded to Fe-Mn oxide fraction (Table 12c) showed significant

relationship between Fe-Oxide and Cr-oxide (r= 0.67) and between Cu-oxide with both Cd-oxide (-0.64) and Ni-oxide (r= 0.60). In the organic fraction (Table 12d), the results showed significant correlation between Cu-OM with both Fe-OM and Cd-OM fraction (r= 0.62 and 0.76, respectively). The correlation between Cd-OM and Ni-OM was r= 0.77 and between Fe-OM and Mn-OM was r= 0.61. The correlation matrix of metals in the residual fraction (Table 12e) revealed significant correlation between Cd-Res and Zn-Res (r= -0.59) and between Co-Res and Cu-Res (r= 0.67).

The significant correlations between any two of trace metals binding fractions in the present study indicate that these metals may be discharged from the same source of pollution. The interpretation of the relationship between any two metals may be related to several main factors which are the stability constants of trace metal complexation reactions, the input of trace metals into water bodies; the quantities of ligand which refer to the binding sites (Tessier *et al.* 1985 ; Yu *et al.*, 2001).

3.2. Principal component analysis (PCA)

The principal component analysis in the present study was performed to obtain more information about the relationships among trace metals in the binding fractions. The PCA of the metals in the five binding fractions are shown in Table 13. In the case of exchangeable fraction, F1, four components have been extracted, they accounted for 78.5% of the variance in the original data (Table 13). The plot of loadings of the components were PC1, which associated with Cu, Mn and Ni, the PC_2 showed the polluted signal of Pb and Co, the PC_3 gives the signal of pollution by Cd and Cr and the finally PC_4 associated with Fe, Cu and Zn.

The principal component analysis of carbonate fraction(F2), was recorded in Table 13. Four components have been extracted, together they account for 81.8% of the variability in the original data. The PC_1 was associated with Cu, Cd and Co and the PC_2 was associated with Mn and Pb, while the PC_3 and PC_4 were associated with Fe, Cr, Zn and Ni, respectively.

The PCA was applied on the results of trace metals associated with the oxide-fraction (lithogenic form, F_3). Four components whose eigenvalues were higher than 1, accounted for a cumulative variance of 78.2% (Table 13), PC_1 represent 33.1% of the data variance was associated with Cu and Ni, PC_2 represented 18.9% of the variance was associated with Zn, while the PC_3 was 14.1% of the variance associated

with Fe, Zn and Cd and finally PC_4 (12% of the variance) associated with Mn, Pb, Cr and Co.

The plot of loading of the components in the organic fraction gives a distribution of the metals into three components. PC_1 was associated with Fe, Mn, Cu, Pb and Co; they are mainly related to the anthropogenic materials and reflect the complexing nature of the organic matter, seqarate group is formed by Cr, this is interpreted as an anthropogenic element that is not forming part of organo-metalic compounds (Rubio *et al.* 2000). PC_2 of this fraction showed the polluted signal of Cr, Cd and Ni and finally PC_3 gives the signal of pollution by Zn.

The application of PCA on the data of trace metals binding to the residual fraction (Table 13) explaining only the first three components (66.5% of the variance). The PC_1 of this fraction represent 30.5% of the variance and associated with Ni and Cr while PC_2 (20.6% of the variance) associated with Mn, Cu, Pb and Cd. On the other hand the PC_3 represent 15.4% of variance and associated with Fe, Cu and Zn.

CONCLUSION

Sequential extraction results have been proved to be useful to ·distinguish between anthropogenic and geochemical sources of most metal species in sediment. The high proportion of metals in the residual phase and the generally low levels of extractable metals indicate that the sediments were relatively unpolluted. It was concluded that the capacity of the sediment to function as a sink for heavy metals was sufficient. Redistribution phenomena during the extraction were not evaluated. The forgoing discussion implies the following points: i) high content of Cu, Zn, Pb and Mn are formed in the residual fractions reflecting geochemical origin, ii) the relatively high amount of Cr, Ni, Co and Fe in the organic fraction, iii) high content of Cd was found in the carbonate fraction and iv) high levels of Cu, Zn, Pb, Cr, Ni, Co, Fe and Mn in the three steps, F_1, F_2 and F_3 may be related to the non-lithogenous origin, indicating that these metals were incorporated into the mineral phase, and are therefore of natural geochemical origin.

REFERENCES

Adams, V. (1990). Water and Wastewater Examination Manual. Lewis publishers, USA, 2457 pp.

Brannon, J. M.; Engler, R. M.; Rose, J. R.; Hunt, P. G. and Smith, I. (1977). Dredged material research program. Technical Report D-76-7 Office, Chief of Engineers, U.S. Army, Washington, D.C. 20314pp.

Davis, J. A. and Leckie, J. O. (1978). Effect of adsorbed complexing ligands on trace metals uptake by hydrousoxides. Environ. Sci., Technol., 12: 1309-15.

Dean W. E. (1974). Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss ignition comparison with other methods J. Sedimentry Petrology, 44: 242.

DeBartolomeo, A.; Poletti, L.; Sanchini, G.; Sebastiani, B. and Morozzi, G. (2004). Relationship among parameters of Lake polluted sediments evaluated by multivariate statistical analysis. Chemosphere, 55: 1323-1329.

El-Iskandarani, M.; Nasr, S.; Okbah, M. and Jensen, A. (2003). Principal components analysis for quality assessment of the Mediterranean coastal water of Egypt,65 (2): 69-86.

Forstner, U. and. Wittmann, G. (1983). Metal pollution in the aquatic environment, springer Verlag Berlin Heidelberg, New York, Tokyo, 486 pp.

Gleyzes, C.; Tellier, S. and Astruc, M. (2002). Fractionation studies of trace elements in contaminated soils and sediments: a review of sequential extraction procedure. Trends in Analytical Chemistry, 21(6+7): 451-467.

Kersten, M. and Förstner, U. (1987). Effect of sample pretreatment on the reliability of solid speciation data of heavy metals: implications for the study of early digenetic processes. J. Marine Chemistry., 22: 299.

Krye, K. A.; Murray, R. W. and Murray, D. W. (2003). Elemental fractionation of Si, Al, Ti, Fe, Ca, Mn, P and Ba in five marine sedimentary reference materials: results from sequential extractions. Analytica chemica Acta, *487*: 117-128.

Kuo, S. and Baker, A. B. (1983). Distribution and forms of copper, zinc, cadmium, iron and manganese in soils near a copper smelter, J. Soil Sic., *135*: 101-9.

Layengar, S. S.; Martens, D.C. and Miller, W. P. (1981). Distribution and plant availability of soil zinc fractions. Soil Sci. Am. J., *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. Univ. 223 pp.

Moussa, A. A. (1984). Estimation of metal pollutant levels in sediments from Lake Borollos, J. Etud. Pollut. Cannes CIESM, *5:* 373-7.

Oregioni, B. and Aston, S. R. (1984). The determination of selected trace metals in marine sediments by flame atomic absorption spectrophotometry. IAEA. Monaco Laboratory Internal Report. UNEP, reference methods for marine pollution studies No. 38.

Pardo, R.; Barrado, E.; Perez, L. and Vega, M. (1990). Determination and speciation of trace metals in sediments of the Pisuerga Rive, Water Res.*24*: 337-343.

Rubio, B.; Nombela, M. A. and Vilas, F. (2000). Geochemistry of major and trace elements in sediments of the Ria de Vigo (NW Spain): an Assessment of metal pollution. Marine Pollution Bulletin. *40* (11):968-980.

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. Chemistry & Ecology, *8*: 89-103.

Shuman, L. M. (1979). Zinc, manganese, and copper in soil fractions, Soil Sci., *127*: 10-7.

Soares, H.M.V. M.; Boaventura, R. A. R.; Machado, A. A. S. C. and Esteves da silva, J. C. G. (1999). Sediments as monitors of heavy metal contamination in the Ave river basin (Portugal): multivariate analysis of data. Environ. Pollut., *105*: 311-323.

Sparks, T. M.; Scott, W. A. and Clarks, R. T. (1999). Traditional multivariate tenchniques: Potential for use in ecoloxicology. Environ. Toxicol. Cehm. *18* (2): 128-137.

Tessier, A.; Rapin, F. and Carignan, R. (1985). Trace metals in oxic lake sediments: possible adsorption onto iron oxyhydroxides. Geochim. Cosmochim. Acta. *47:* 1091-1098.

Tessier, A.; Gampbell, P. G. C. and Rissa, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem., *51*: 844-851.

Yu, K. C.; Tsai, L. J.; Chen, S. H. and Ho, S. T. (2001). Correlation analysis on binding behavior of heavy metals with sediment matrices. Wat. Res. *35* (10): 2417-2428.

Zitko, V. (1994). Principal component analysis in the evaluation of environmental data. Marine Pollution Bulletin. *28*: 718-722.

Table (1). The concentrations for trace metals (µg/g) in the references materials (MESS-3, National research of council of Canada).

Metal	Found	Certified
Iron	0.230 ± 0.02	0.236 ± 0.017
Manganese	328 ± 8.00	324 ± 12.0
Zinc	156 ± 10.10	159 ± 8.0
Copper	34.2 ± 2.53	33.9 ± 1.6
Lead	20.38 ± 0.85	21.10 ± 0.70
Cadmium	0.20 ± 0.08	0.24 ± 0.01
Chromium	107.0 ± 7.03	105.0 ± 4.0
Nickel	48.10 ± 3.10	46.9 ± 2.2
Cobalt	14.05 ± 1.80	14.4 ± 2.0

Table 2 : Organic matter, Ca CO₃ contents and graine size analysis of Lake Manzalah during summer ,2005

Stations	Organic Matter%	Ca CO3%	Graine Size Distribution %			Type of Sediments
			Sand	Silt	Clay	
I	2.41	18.20	25.20	29.50	35.30	Sandy Loam
II	2.41	26.40	4.80	48.50	46.70	Silt Loam
III	5.52	48.60	36.00	37.50	26.50	Clay Loam
IV	2.30	37.80	38.80	27.50	33.70	Clay Loam
V	6.31	25.20	53.00	32.80	14.20	Sandy Loam
VI	6.89	60.30	55.20	31.00	13.80	Sandy Loam
VII	8.96	65.80	53.40	30.60	16.00	Sandy Loam
VIII	8.28	54.20	59.20	25.50	15.30	Sandy Loam
IX	2.07	50.20	57.20	19.60	23.20	Sandy Loam
X	5.86	35.40	7.40	32.50	60.10	Clay
XI	2.87	15.70	25.30	29.20	35.50	Sandy Clay Loam
XII	4.83	65.30	7.20	28.00	64.80	Clay
Min.	2.07	15.70				
Max.	8.96	65.80				
Average	4.98	41.76				
SD	2.55					

Table3: Iron concentration (μg/g) in each fraction of Lake Manzalah sediments

Stations	Exchangeable	Carbonate form	Oxides form	Organic form	Residual form	Total
	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g
I	17.08	5.79	717.00	6272.12	4,570	11,582
II	25.08	5.68	727.34	6493.1	4,577	11,828
III	12.76	7.03	687.53	6555.16	4,098	11,360
IV	21.81	10.27	461.49	4392.92	4,298	9,184
V	20.32	35.98	724.96	6443.22	4,207	11,431
VI	10.31	14.05	465.73	5521	4,941	10,952
VII	31.01	7.56	193.11	5715.32	3,241	9,188
VIII	14.86	1.36	287.35	5758.34	3,740	9,802
IX	16.96	8.26	620.09	6114.36	4,074	10,834
X	23.31	7.94	584.09	6537.76	4,535	11,688
XI	65.44	15.60	372.33	6144.52	4,543	11,141
XII	6.91	9.16	440.17	6208.9	4,122	10,787
Average	24.16	11.86	514.40	5936.06	4,223	10,771
SD	18.09	10.55	191.04	705.78	513.52	969.96

Table4: Manganese concentration (μg/g) in each fraction of Lake Manzalah sediments

Stations	Exchangeable	Carbonate form	Oxides form	Organic form	Residual form	Total
	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g
I	28.87	156.85	148.83	75.69	503.91	914.15
II	37.43	167.73	184.6	97.7	525.54	1,013.00
III	30.64	182.76	184.77	59.1	543.61	1,000.00
IV	6.12	31.08	114.64	22.75	134.59	309.18
V	11.85	58.38	179.93	98.1	304.74	653
VI	15.52	154.07	106.09	97.24	409.16	782.08
VII	11.47	87.32	165.25	62.38	430.76	757.18
VIII	11.33	115.2	106.71	89.04	500.35	822.63
IX	23.58	199.41	259.84	93.08	1,051.79	1,627.70
X	12.59	75.76	153.3	87.52	415.56	744.73
XI	8.57	121.86	137.74	55.15	280.98	604.3
XII	4.84	52	47.35	85.16	286.53	475.88
Average	37.43	199.41	259.84	98.1	1,051.79	1,627.70
SD	12.44	62.6	68.28	26.24	225.86	329.49

Table 5: Copper concentration (µg/g) in each fraction of Lake Manzalah sediments

Stations	Exchangeable	Carbonate form	Oxides form	Organic form	Residual form	Total
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
I	0.71	8.10	17.01	23.13	49.30	98.25
II	0.43	7.61	19.07	29.73	43.98	100.82
III	0.42	4.03	16.24	27.20	42.85	90.74
IV	0.16	5.14	3.02	10.25	2.10	20.67
V	0.25	6.32	5.27	20.67	57.39	89.9
VI	0.18	6.79	2.76	10.24	36.12	56.09
VII	0.2	2.34	3.19	9.06	17.54	32.33
VIII	0.15	4.74	2.26	7.36	13.93	28.44
IX	0.23	3.56	3.38	9.09	20.18	36.44
X	0.41	4.36	2.65	19.69	28.07	55.18
XI	0.36	5.17	2.88	13.65	22.20	44.26
XII	0.31	7.45	3.97	10.08	15.50	37.31
Average	0.32	5.47	6.81	15.85	29.10	57.54
SD	0.15	1.72	6.21	7.51	16.01	28.23

Table 6: Zinc concentration (µg/g) in each fraction of Lake Manzalah sediments

Stations	Exchangeable	Carbonate form	Oxides form	Organic form	Residual form	Total
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
I	4.01	20.95	35.2	45.88	308.19	414.23
II	3.2	29.6	51	37.72	302.88	424.4
III	5.34	31.99	46.21	31.56	263.65	378.75
IV	2.6	22.89	47.03	27.42	174.98	274.92
V	3.56	32.52	35.62	21.12	274.56	367.38
VI	3.74	24.37	52.05	27.51	269.09	376.76
VII	3.4	12.25	34.8	25.88	336.82	413.15
VIII	2.59	20.73	41.13	39.14	298.24	401.83
IX	2.94	21.93	35.8	32.29	309.41	402.37
X	2.83	23.09	49.34	53.83	340.52	469.61
XI	3.41	28.37	35.74	44.71	337.84	450.07
XII	2.96	30.68	36.44	56.72	363.94	490.74
Average	3.47	24.58	41.94	37.26	294.22	402.13
SD	0.87	6.56	6.97	12.15	57.62	108.48

Table 7: Lead concentration (μg/g) in each fraction of Lake Manzalah sediments

Stations	Exchangeable	Carbonate form	Oxides form	Organic form	Residual form	Total
	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g
I	0.27	3.58	2.97	10.35	38.75	55.92
II	0.16	2.72	6.2	12.42	18.25	39.75
III	3.47	4.03	4.75	15.45	31.55	59.25
IV	1.65	4.11	3.36	6.37	9.15	24.64
V	2.11	6.47	8.94	14.38	32.22	64.12
VI	2.23	3.04	2.51	7.82	33.04	48.64
VII	1.68	8.83	5.4	9.5	26.36	51.77
VIII	1.77	9.1	2.3	14.56	55.47	83.2
IX	5.12	5.11	3.2	4.55	13.22	31.2
X	4.26	7.52	2.5	11.92	15.6	41.8
XI	2.71	5.02	3.6	5.3	17.23	33.86
XII	2.48	10.02	6.26	12.8	24.21	55.77
Average	2.37	5.88	4.52	10.39	27.12	49.84
SD	1.6	2.64	2.24	3.91	14.59	18.2

Table 8: Cadmium concentration (μg/g) in each fraction of Lake Manzalah sediments

Stations	Exchangeable	Carbonate form	Oxides form	Organic form	Residual form	Total
	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g
I	0.24	0.50	0.12	0.24	0.17	1.27
II	0.18	0.52	0.21	0.45	0.45	1.81
III	0.21	0.61	0.24	0.27	0.55	1.88
IV	0.22	0.57	0.35	0.23	0.31	1.68
V	0.23	0.46	0.74	0.18	0.37	1.98
VI	0.24	0.43	0.76	0.14	0.38	1.95
VII	0.19	0.64	0.50	0.22	0.09	1.64
VIII	0.14	0.35	0.63	0.09	0.44	1.65
IX	0.24	0.91	0.97	0.12	0.27	2.51
X	0.23	0.58	0.42	0.16	0.14	1.54
XI	0.18	0.65	0.28	0.20	0.15	1.46
XII	0.17	0.41	0.82	0.13	0.04	1.57
Average	0.21	0.55	0.50	0.20	0.28	1.75
SD	0.03	0.15	0.28	0.09	0.16	0.31748

Table 9: Chromium concentration (µg/g) in each fraction of Lake Manzalah sediments

Stations	Exchangeable	Carbonate form	Oxides form	Organic form	Residual form	Total
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
I	0.92	2.21	13.37	23.7	6.3	46.5
II	1.89	1.66	14.92	21.9	13.83	54.2
III	0.74	2.16	19.73	28.54	13.4	64.57
IV	0.61	1.61	7.57	15.05	3.56	28.4
V	2.16	2.34	16.09	41.8	11.19	73.58
VI	0.79	1.38	23.44	26.54	40.85	93
VII	1.06	1.86	13.86	34.51	31.89	83.18
VIII	1.38	1.33	12.2	23.44	32.48	70.83
IX	1.77	1.28	21.5	33.85	29.14	87.54
X	1.1	0.97	12.89	32.12	37.64	84.72
XI	0.6	1.51	21.59	41.52	27.86	93.08
XII	1.11	0.94	22.46	34.87	24.6	83.98
Average	1.21	1.61	16.47	29.62	22.65	70.36
SD	0.55	0.49	5.37	8.79	13.18	32.81

Table 10: Nickel concentration (µg/g) in each fraction of Lake Manzalah sediments

Stations	Exchangeable	Carbonate form	Oxides form	Organic form	Residual form	Total
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
I	2.18	2.57	10.72	29.11	24.92	69.5
II	1.8	11.09	12.6	30.47	22.89	78.85
III	0.86	3.44	8.53	22.41	38.16	73.4
IV	1.38	1.86	6.71	22.38	29.62	61.95
V	1.95	12.2	4.86	7.88	1.79	28.68
VI	0.94	1.5	4.37	18.03	17.06	41.9
VII	1.29	1.89	14.28	24.85	9.49	51.8
VIII	0.78	1.59	1.64	12.17	9.77	25.95
IX	1.32	2.46	5.79	14.15	4.58	28.3
X	1.53	1.89	4.93	16.47	24.43	49.25
XI	0.89	9.73	4.51	22.41	22.31	59.85
XII	0.83	7.55	5.82	14.44	12.56	41.2
Average	1.34	5.11	7.19	19.51	18.4	51.1
SD	0.5	4.69	4.1	7.45	11.81	18.98

Table 11: Cobalt concentration (µg/g) in each fraction of Lake Manzalah sediments

Stations	Exchangeable	Carbonate form	Oxides form	Organic form	Residual form	Total
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
I	0.32	2.01	3.2	8.11	23.71	37.35
II	0.59	3.5	4.11	16.08	30.4	54.68
III	0.88	3.98	5.8	17.31	14.66	42.63
IV	0.24	3.37	3.54	6.24	5.56	18.95
V	0.12	2.52	4.23	10.16	11.17	28.2
VI	0.12	2.26	3.36	15.94	12.3	33.98
VII	0.23	2.84	5.89	9.36	4.63	22.95
VIII	0.25	3.7	6.9	10.77	10.58	32.2
IX	1.42	4.47	7.43	14.76	2.52	30.6
X	2.44	2.03	6.64	24.38	10.64	46.13
XI	1.5	3.33	13.4	10.47	5.38	34.08
XII	2.2	1.31	7.2	· 9.88	5.94	26.53
Average	0.92	2.94	6.31	13.15	12.17	34.42
SD	0.87	1.02	3.26	5.71	9.19	11.23

Table (12). Correlation matrix of trace-metal bounded to a) Exchangeable b) Carbonate c) Fe-Mn oxides form d) Organic form e) Residual form; Manzalah Lake sediments (No. = 12, Significance at < 0.05)

a)	Fe-Exch	Mn-Exch	Cu-Exch	Zn-Exch	Pb-Exch	Cd-Exch	Cr-Exch	Ni-Exch	Co-Exch
Fe-Exch	1.00								
Mn-Exch		1.00							
Cu-Exch		0.59	1.00						
Zn-Exch				1.00					
Pb-Exch					1.00				
Cd-Exch						1.00			
Cr-Exch							1.00		
Ni-Exch								1.00	
Co-Exch					0.62				1.00

b)	Fe-Carb	Mn-Carb	Cu-Carb	Zn-Carb	Pb-Carb	Cd-Carb	Cr-Carb	Ni-Carb	Co-Carb
Fe-Carb	1.00								
Mn-Carb		1.00							
Cu-Carb			1.00						
Zn-Carb				1.00					
Pb-Carb					1.00				
Cd-Carb			-0.58			1.00			
Cr-Carb							1.00		
Ni-Carb	0.59			0.71				1.00	
Co-Carb						0.56			1.00

c)	Fe-Ox.	Mn-Ox.	Cu-Ox.	Zn-Ox.	Pb-Ox.	Cd-Ox.	Cr-Ox.	Ni-Ox.	Co-Ox.
Fe-Ox.	1.00								
Mn-Ox.		1.00							
Cu-Ox.			1.00						
Zn-Ox.				1.00					
Pb-Ox.					1.00				
Cd-Ox.			-0.64			1.00			
Cr-Ox.	0.67						1.00		
Ni-Ox.			0.60					1.00	
Co-Ox.									1.00

d)	Fe-OM	Mn-OM	Cu-OM	Zn-OM	Pb-OM	Cd-OM	Cr-OM	Ni-OM	Co-OM.
Fe-OM	1.00								
Mn-OM.	0.61	1.00							
Cu-OM	0.62		1.00						
Zn-OM				1.00					
Pb-OM					1.00				
Cd-OM			0.76			1.00			
Cr-OM							1.00		
Ni-OM						0.77		1.00	
Co-OM									1.00

e)	Fe-Res.	Mn-Res.	Cu-Res.	Zn-Res.	Pb-Res.	Cd-Res.	Cr-Res.	Ni-Res.	Co-Res.
Fe-Res.	1.00								
Mn-Res.		1.00							
Cu-Res.			1.00						
Zn-Res.				1.00					
Pb-Res.					1.00				
Cd-Res.				-0.59		1.00			
Cr-Res.							1.00		
Ni-Res.								1.00	
Co-Res.			0.67						1.00

Table (13): Loading of variables (9 metals) using PCA technique for the data set in the five fractions Lake Manzalah sediments.

Excheangeable.	Variables	PC1	PC2	PC3	PC4
	Fe	0.128	0.059	0.365	0.587
	Mn	-0.486	0.107	0.011	-0.053
	Cu	-0.433	0.311	0.191	0.373
	Zn	-0.322	0.369	0.319	-0.388
	Pb	0.267	0.512	-0.423	-0.1
	Cd	-0.292	0.305	-0.348	-0.175
	Cr	-0.159	-0.341	-0.562	0.146
	Ni	-0.47	-0.172	-0.25	0.347
	Co	0.231	0.501	-0.224	0.425
	Eigenvalue	2.718	1.693	1.457	1.198
	%Variance	30.199	18.82	16.191	13.312
	Cumulative	30.199	49.018	65.209	78.521
	%Variance				
Carbonate Form	Variables	PC1	PC2	PC3	PC4
	Fe	0.328	0.196	0.424	-0.323
	Mn	-0.339	0.413	-0.269	0.025
	Cu	0.452	0.267	-0.374	0.129
	Zn	0.282	0.317	-0.112	-0.642
	Pb	0.092	-0.543	0.347	-0.086
	Cd	-0.451	0.185	0.279	0.025
•	Cr	0.125	0.308	0.557	0.019
	Ni	0.202	0.369	0.268	0.62
	Co	-0.474	0.24	0.124	-0.269
	Eigenvalue	2.673	2.115	1.442	1.129
	%Variance	29.701	23.501	16.016	12.549
	Cumulative	29.701	53.202	69.22	81.769
	%Variance				
Oxides Form	Variables	PC1	PC2	PC3	PC4
	Fe	0.399	-0.257	0.445	0.137
	Mn	0.231	-0.389	0.059	0.323
	Cu	0.519	-0.089	-0.009	0.197
	Zn	0.171	0.449	0.519	0.108
	Pb	0.151	-0.484	-0.086	-0.531
	Cd	-0.377	-0.302	0.375	-0.354
	Cr	-0.205	-0.451	0.281	0.306
	Ni	0.407	-0.089	-0.436	-0.123
	Co	-0.341	-0.192	-0.335	0.557
	Eigenvalue	2.979	1.704	1.27	1.081
	%Variance	33.098	18.93	14.115	12.012
	Cumulative	33.098	52.028	66.143	78.155
	%Variance				

Table 13(Continued)

Organic Form	Variables	PC1	PC2	PC3	PC4
	Fe	0.539	-0.102	0.083	
	Mn	0.365	-0.291	-0.149	
	Cu	0.435	0.356	-0.143	
	Zn	0.205	-0.076	0.805	
	Pb	0.364	-0.013	-0.415	
	Cd	0.199	0.548	-0.112	
	Cr	0.164	-0.392	0.04	
	Ni	0.016	0.56	0.288	
	Co	0.382	-0.072	0.182	
	Eigenvalue	2.98	2.559	1.048	
	%Variance	33.112	28.43	11.646	
	Cumulative	33.112	61.543	73.188	
	%Variance				
Residual Form	Variables	PC1	PC2	PC3	
	Fe	0.539	-0.102	0.083	
	Mn	0.365	-0.291	-0.149	
	Cu	0.435	0.356	-0.143	
	Zn	0.205	-0.076	0.805	
	Pb	0.364	-0.013	-0.415	
	Cd	0.199	0.548	-0.112	
	Cr	0.164	-0.392	0.04	
	Ni	0.016	0.56	0.288	
	Co	0.382	-0.072	0.182	
	Eigenvalue	2.98	2.559	1.048	
	%Variance	33.112	28.43	11.646	
	Cumulative	33.112	61.543	73.188	
	%Variance				

Figure I: Locations of Sediment Sampling.
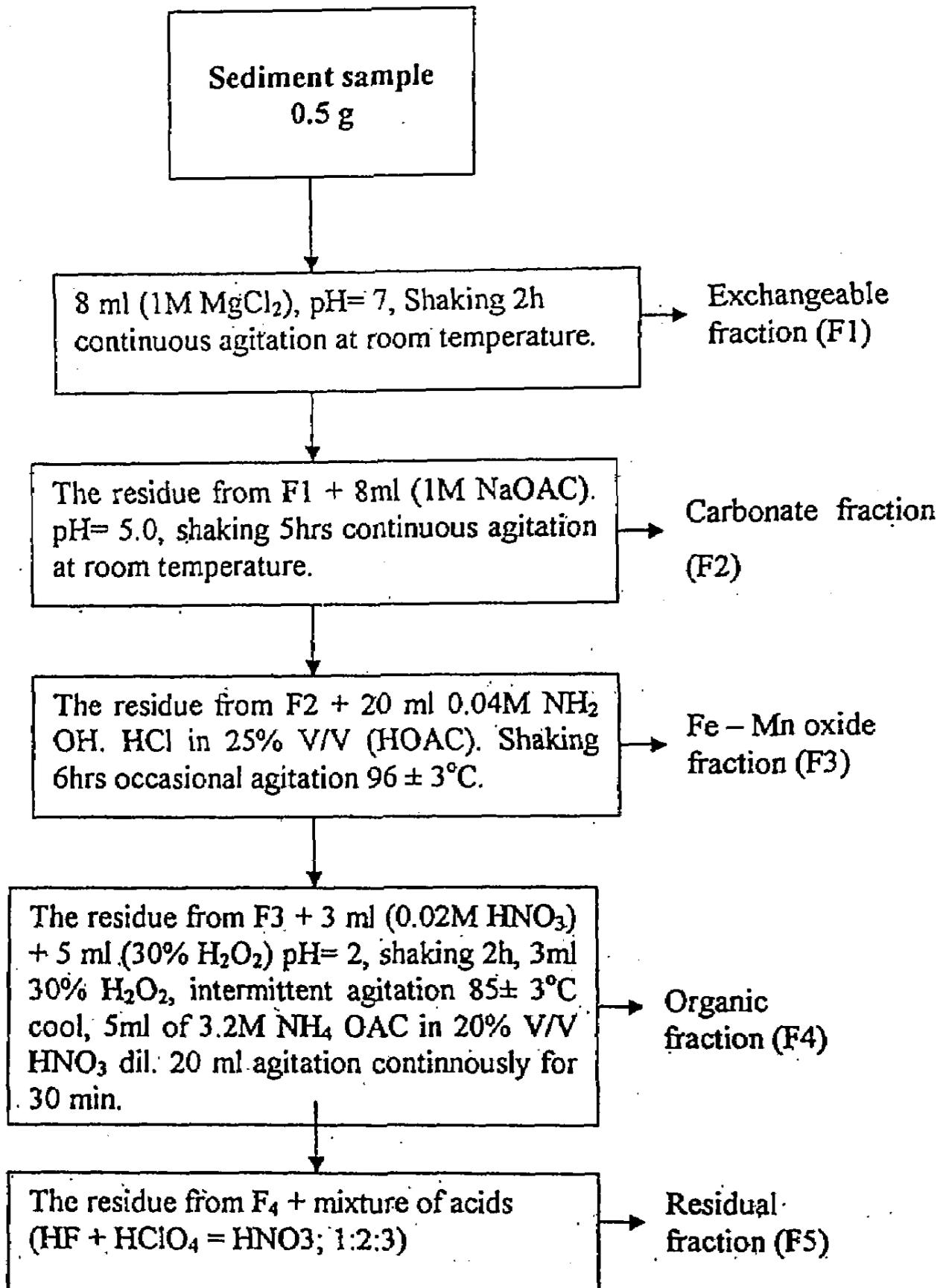
Fig. 2. Schematic diagram of sequential extraction procedure for trace metals (Tessier *et al.*, 1979).
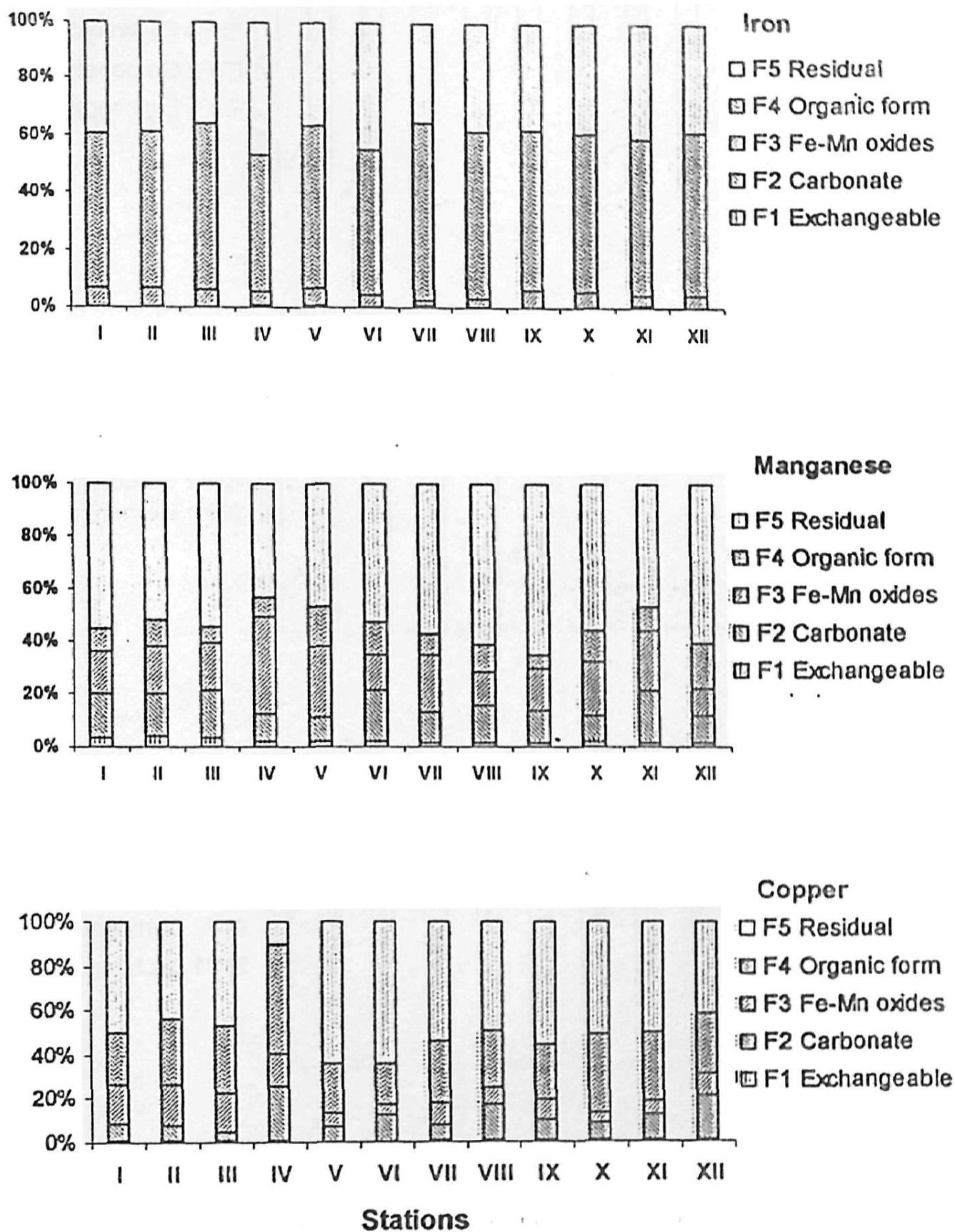
Figure 3. percentage of Fe, Mn and Cu in the five fractions to the total concentration of Lake Manzalah sediments
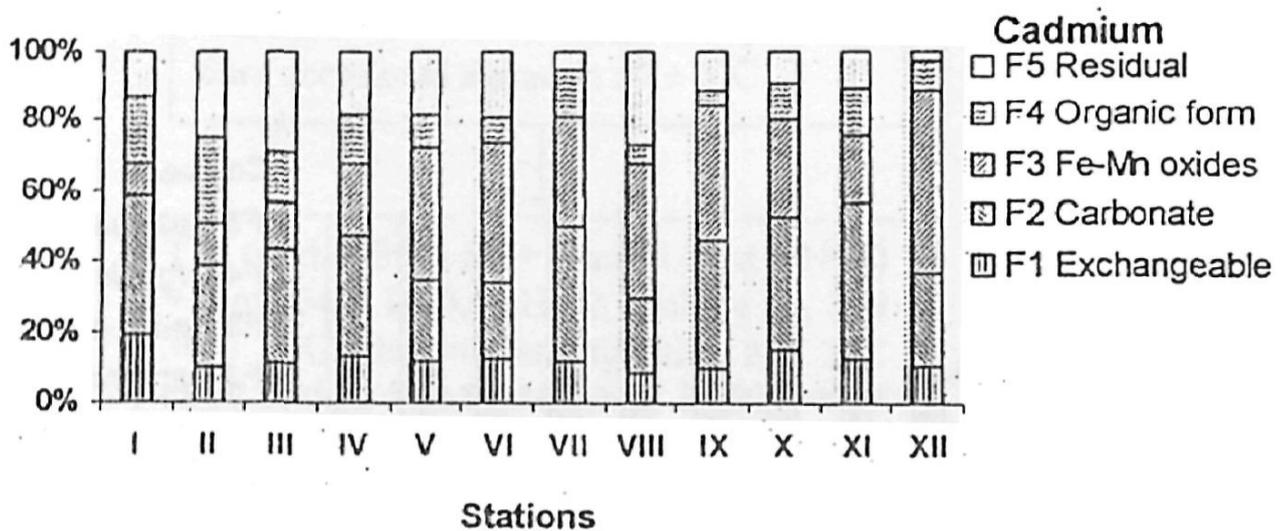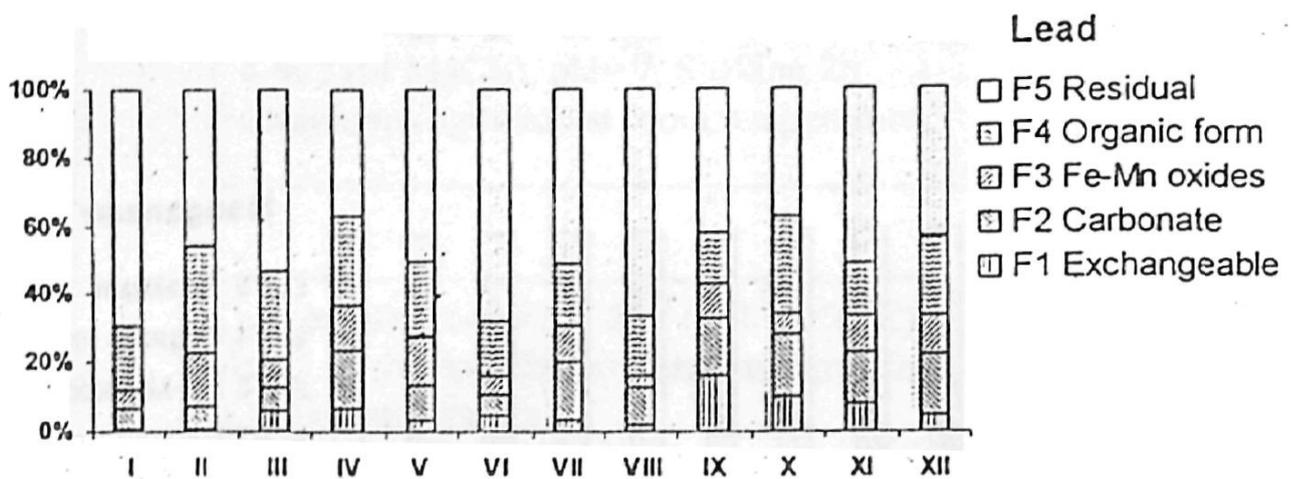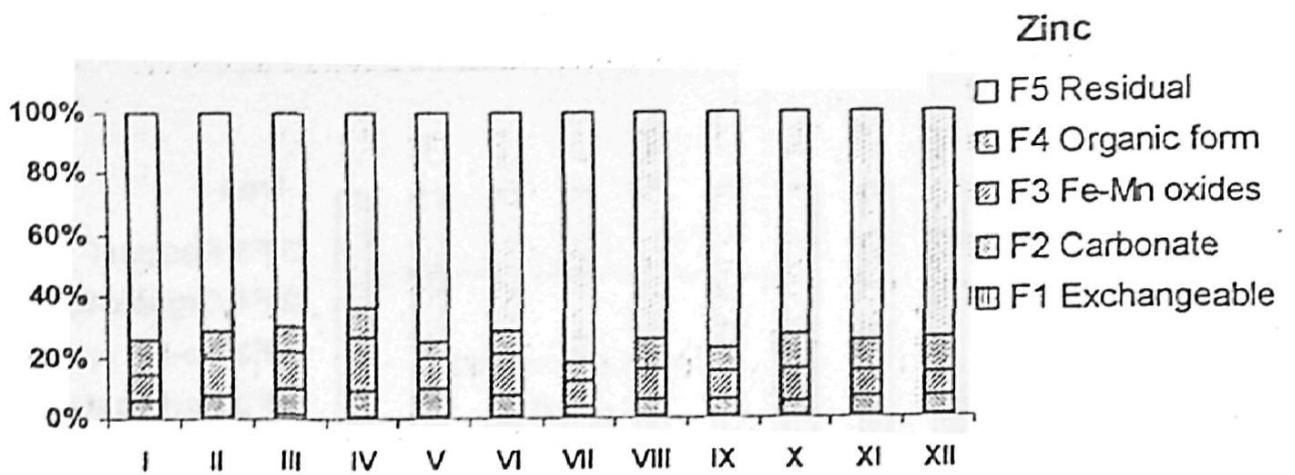
Figure 4. percentage of Zn and Cd in the five fractions to the total concentration of Lake Manzalah sediments
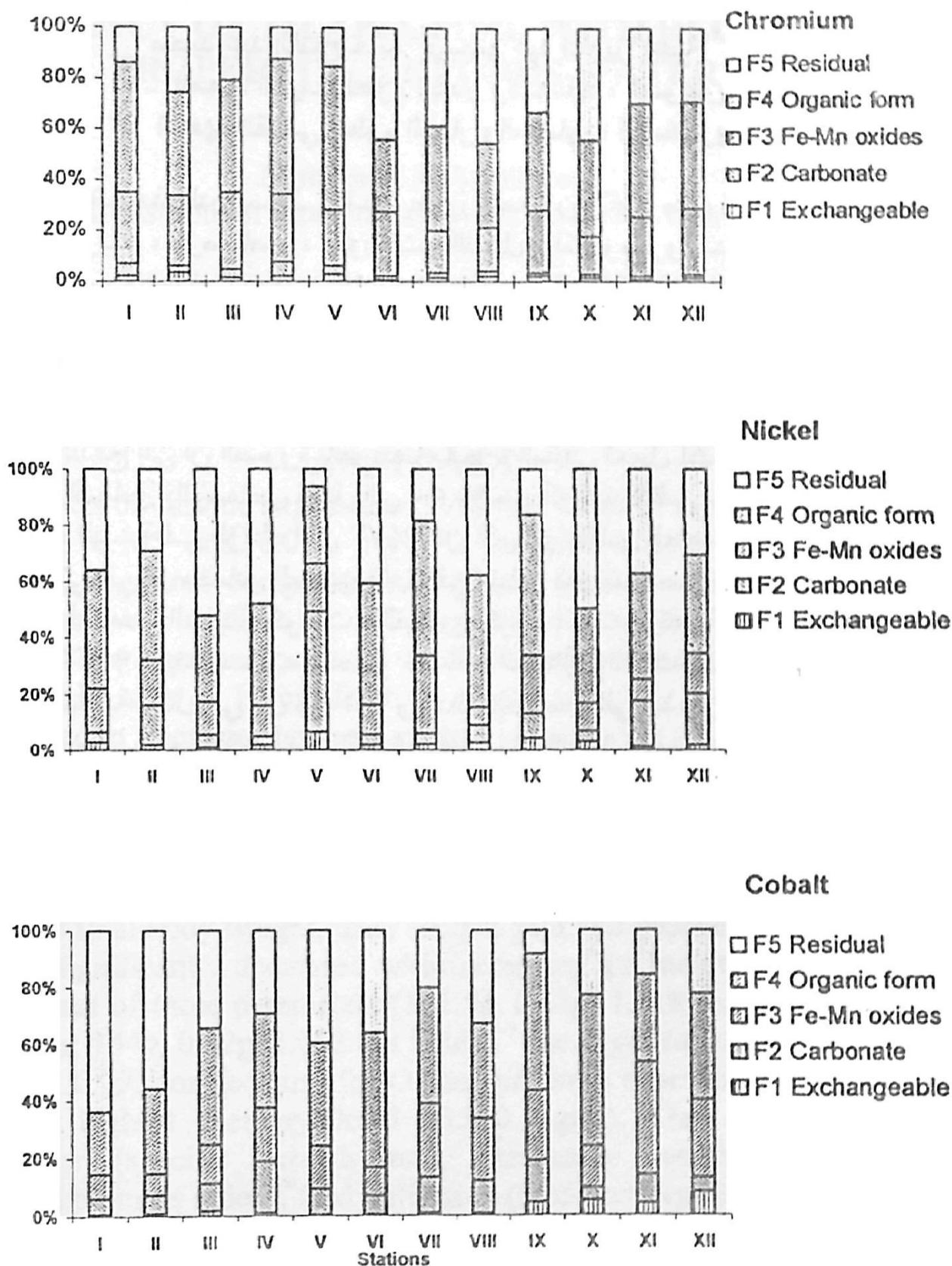
Figure 5. Percentage of Cr, Ni and Co in the five fractions to the total concentration
Lake Manzalah sediments