

LEACHABLE AND TOTAL NINE HEAVY METALS IN MUDDY AND SANDY SEDIMENT COLLECTED FROM SUEZ GULF

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Keywords: Suez Gulf, Red Sea, Sediment, Heavy metals, Pollution.

ABSTRACT

The concentrations of nine heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in labile and total fractions of muddy and sandy sediment samples, collected from seven sites in Suez Gulf in April 1999, were determined in order to evaluate the pollution status of the Suez Gulf. Atomic Absorption Spectrophotometer (AAS) was used to determine the metal contents by means of using (SD-M-2/TM) certified reference material (National Research Council of Canada). The enrichment factors (EFs) were calculated for each element. EFs revealed that sediments were highly enriched by Cd, Co, and Pb, moderately enriched by Cu, Ni and Zn and slightly enriched by Cr and Mn. The concentrations of most studied metals in sediments were interpreted using the Effect Range-Low (ERL) and the Effect Range-Median (ERM) for all investigated locations. The levels of heavy metals pollution in mud and sand fractions were measured using the Index of Geoaccumulation (I_{geo}). Fe and Cr were in the unpolluted level and Co, Cu and Zn showed low polluted level whereas Pb and Mn exhibited low to moderate pollution level at most of the examined locations.

INTRODUCTION

The Suez Gulf is a narrow shallow water body covering an area of about 7,500 Km² and it has 11 Km as a proper transitional area at the Suez Bay-Gulf and the width increases to 19 Km at Ras Matarma and 45 Km at Ras Abu Zenima. The water depths of the Suez Gulf increase from 16 m southward the Suez Bay to 50-85 m towards the open Gulf.

The Suez Gulf is perhaps the most polluted area in the Red Sea and the main problem arises from oil pollution (Khaled *et al.* 2003; El-Sikaily *et al.* 2003 and 2004; El Nemr *et al.* 2004). The middle and southern parts of the Suez Gulf are under stress from extensive inshore and offshore oil production operations. The number of producing oil fields is 32, most of them lying offshore with a total production more than 2500 million barrels. The major industrial activities in the Suez Gulf are oil refineries, marketing,

storage and piping, fertilizers and chemicals, cement, thermal electric stations, ceramics, steel, shipyard, edible oils and fiberglass. At the south of the Suez Bay a large recreational area has been recently established at Ain Sukhna. In addition, the framework of the developing plan for the northern Suez Gulf, a huge port is established nearby. The sediments of Suez Gulf are comprised of disintegration products of coral reef framework builder (local production); rock fragments, quartz and feldspars, and carbonates pellets (Sneh and Friedman 1985).

Heavy metals are a group of metals that occur naturally, and most of them can be found in rocks and soil. Natural weathering of rocks and soil can break down and release them into aquatic environment. In addition to the geological weathering, human activities have also introduced large quantities of metals to the localized area of water bodies (Thompson *et al.* 1983). Heavy metals,

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contrary to most pollutants, are not biodegradable and undergo a global ecobiological cycle (Nurnberg 1984). It has long been demonstrated that, sediments can adsorb persistent and toxic chemicals to levels many times higher than its concentrations in the water column (DeIValls and Conradi 2000; DeIValls *et al.* 2002). Therefore, bottom sediments can serve as a reservoir for heavy metals and deserve special consideration in the planning and design of aquatic pollution research studies (Kishe and Machiwa 2003). One advantage of the use of sediment analysis, rather than water analysis, for evaluating the degree of contamination in aquatic medium, is that it gives a stable image over time compared with the huge temporal variability in levels of contaminants in water. Furthermore, concentrations of toxic elements are usually higher in sediment and therefore less possibility of contamination of samples during handling and processing, and the analytical methods are also less complex (Villares *et al.* 2003).

The present study aims to determine the concentrations of total and labile heavy metals in surface sediment as well as in the mud and sand fractions collected from Suez Gulf, Red Sea, and to study the pollution level of this area based on metal concentrations. The surface layer was chosen where this layer controls the exchange of metals between sediments and water and constitutes a reserve of metals to which benthic organisms are exposed. Additionally, to compare the concentration of heavy metals bound in the fine grained fraction (<0.063 mm) and the sand sized fraction (0.2 – 0.063 mm) of the sediment.

MATERIALS AND METHODS

Sampling

Sampling locations along Suez Gulf were selected to cover the expected polluted location due to industrial and other activities. Surface sediment (<5 cm) samples were

collected from seven sites during April 1999 (Fig. 1). Samples were transferred into polyethylene bags and stored in the laboratory at -20 °C until analysis. The sediment samples were dried in an oven at 105 °C to constant weight. From each dried sample collected at different zones at Suez Gulf, sand fraction (0.063 – 0.2 mm) was separated from mud fraction (<0.063 mm).

Grain Size Analysis

Grain Size Analysis was carried out using the conventional method (Folk 1954, Galehouse 1971). Raw samples were treated with 30% hydrogen peroxide to destroy the organic matter content, and about 100 g of washed quartered dried sample were placed in the topmost sieve and the entire column of sieves was shaken on a mechanical shaker (Betriebsanleitung vibration testing sieve mechanical machine Thyr 2) for 20 minutes. The sieve meshes give the glass intervals 2, 1, 0, 0.5, 0.2, 0.125 and 0.063 mm. These correspond to the Phi (Φ) classes of -1, 0, 1, 2, 3, 4, respectively (Table 1).

Determination of Total Heavy Metals

The determination of total heavy metals in sediments was measured by using the method described in UNEP/IAEA (1986). An exact weight of dry sample (about 0.2 g) of sediment was completely digested in Teflon Vessels using a mixture of HNO₃, HF and HClO₄ (3:2:1 v/v, 10 mL) (triplicate digestions were made for each sample). The final solution was diluted to 25 mL with distilled deionized water. All digested solutions were analyzed in triplicate by using Atomic Absorption Spectrophotometer (Spectr AA-10 plus Varian) working with an air/acetylene flame and D₂ background correction at optimum instrument operating conditions recommended by the manufacture. The results were expressed in µg/g dry weight. The absorption wavelength and detection limits were as follows: 228.8 nm and 0.006 µg/g for Cd; 240.7 nm and 0.009 µg/g for Co; 357.9 nm and 0.009 µg/g for Cr; 324.7 nm and 0.008 µg/g for Cu; 248.3 nm

and 0.007 $\mu\text{g/g}$ for Fe; 279.5 nm and 0.006 $\mu\text{g/g}$ for Mn; 232.0 nm and 0.009 $\mu\text{g/g}$ for Ni; 217.0 nm and 0.01 $\mu\text{g/g}$ for Pb; 213.9 nm and 0.004 $\mu\text{g/g}$ for Zn, respectively.

Determination of leachable heavy metals

An aliquot of 0.5 g of dry sediment was treated with an excess of 40 ml of 1N HCl at room temperature and shaken for two hours, centrifuging at 5000 rpm for 3 minutes (El Nemr 2003; Villares *et al.* 2003). The suspension was filtered on the nuclepore 0.4 μm polycarbonate filter, previously treated with 6M HCl and deionized water, then with 1M $\text{CH}_3\text{COONH}_4$ and finally with 100 mL deionized water (triplicate extractions were made for each sample).

Quality Assurance

To control accuracy and to determine the uncertainty of the heavy metals determination, every extraction batch a blank extraction and reference material (SD-M-2/TM) was included. Reference material was totally digested by $\text{HNO}_3/\text{HF}/\text{HClO}_4$ (3:2:1 v/v, 10 mL) solution. Analytical results of the quality control samples indicated a satisfactory performance of heavy metals determination within the range of certified values with 90.4 to 97.5 % recovery for all metals studied (Table 2). To prevent contamination, all used plastic laboratory were previously washed in diluted nitric acid and deionized water.

Table 1. Percentage of grain size distribution of sediment samples collected from Suez Gulf.

Station number	Sand %	Mud %	Gravel %
1	86.68	12.66	0.66
2	98.61	1.25	0.14
3	82.73	15.28	1.99
4	96.50	2.35	1.15
5	98.20	1.50	0.30
6	53.89	44.91	1.20
7	33.50	64.76	1.74

Table 2. Heavy metal concentrations $\mu\text{g/g}$ in reference materials analyzed together with Suez Gulf sediments.

Element	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Certified values	0.11	13.6	77.2	32.7	27.1	12.1	56.1	22.8	74.8
Found values	0.107	12.33	75.39	31.2	26.45	11.46	53.90	21.27	71.38
Recovery%	97.27	90.64	97.65	95.39	97.61	94.73	96.08	93.29	95.43

LEACHABLE AND TOTAL NINE HEAVY METALS IN MUDDY AND SANDY SEDIMENT COLLECTED FROM SUEZ GULF

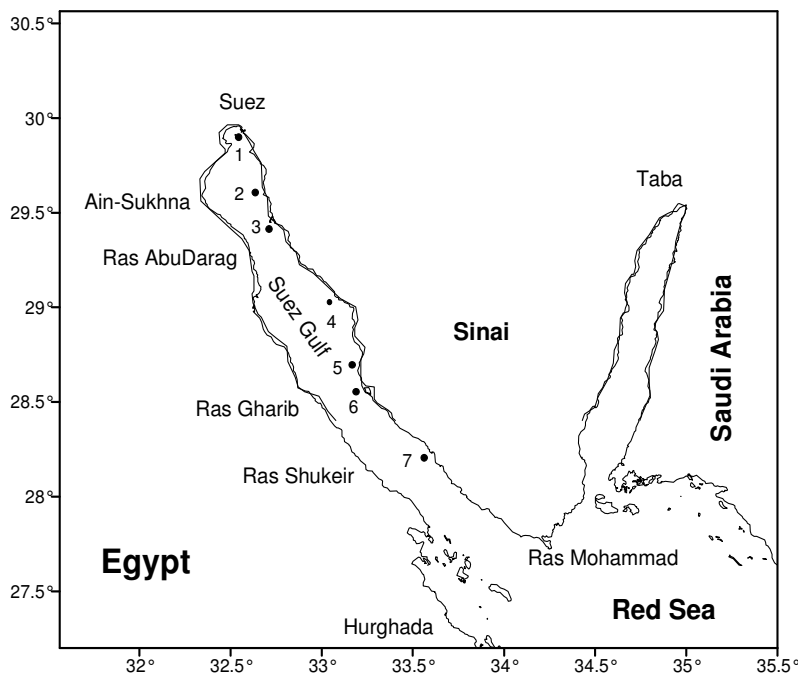


Fig. 1. Sampling locations

RESULTS AND DISCUSSION

Grain size distribution

A major problem occurring when sediment-based metal pollution resulting from different studies are used for comparative purposes is the non uniformity of the grain size of the analyzed fractions (Groot *et al.* 1982). The distribution percentages of mud (<63 μm) and sand (2 mm-63 μm) in Suez Gulf sediment collected from the location under investigation are summarized in Table 1. The sediments of the seven stations under study are generally sandy except station 7 which is muddy sand. Sand is generally of fine size (stations 2, 3, 4 and 6) or medium size fraction as in stations 1 and 5.

Heavy metals in sediment

The concentrations of total and labile heavy metals in total sediment at the seven locations under investigation are illustrated in Table 3 and Fig. 2. The concentration of heavy metals for were decreased in the order $\text{Fe} > \text{Mn} > \text{Pb} > \text{Zn} > \text{Ni} > \text{Co} \geq \text{Cu} > \text{Cr} > \text{Cd}$.

Cadmium can move between air and water and once reach the water; it will find its way into sediment. Tessier *et al.* (1980) reported that there was no interaction of Cd with organic matter but large amounts were found in exchangeable and carbonate fractions. The concentration of Cd in the present work fluctuated between 6.7 and 9.9 $\mu\text{g/g}$ dry wt with an average $8.16 \pm 1.2 \mu\text{g/g}$

dry wt in the total fractions and ranged between 1.9 to 5.45 $\mu\text{g/g}$ dry wt with an average value $3.72 \pm 1.06 \mu\text{g/g}$ dry wt in the labile fractions. The concentration of both total and labile fractions in the present study were higher than the Effect Range Low (ERL = $1.25 \mu\text{g/g}$ dry wt) but lower than the Effect Range Median (ERM = $9.65 \mu\text{g/g}$ dry wt) (Long *et al.* 1995) in most station.

The ratio (percentage) of the concentration of the metal in the labile fraction to the total concentration in the sediment has been used as a theoretical estimation for the relative importance of metal with anthropogenic origin (Carral *et al.* 1994). The labile fraction is usually defined as that exchangeable, carbonate-bound, iron and manganese oxide bound and organically bound fractions. The ratio between labile and total heavy metals may be referring to the anthropogenic input or the new input percentage (NIP). The NIP for Cd was ranged from 25.75 % at station 1 to 80.28 % at station 7 with a mean value of 46.72 %. The industrial activities at Suez Gulf (e.g. Ceramics, Thermal Electrical Stations, Fertilizers and Chemicals) besides the offshore oil fields at the south area of the Gulf explained the elevation of Cd concentration. El-Samara and Moussa (1995) reported similar finding.

The average concentrations of Co in both total and labile fractions of total sediment were 42.07 and 13.34 $\mu\text{g/g}$ dry wt, respectively. Station 6 recorded the highest value of total Co while the highest value of Co in the labile fraction was recorded at stations 3 and 7 (Fig. 2). The average extractability percentage of Co was 32.18 % indicating that the enrichment of Co in the studied locations may be due to the anthropogenic origin.

Station 3 in the present work recorded the highest values of Cr for both total and labile fractions (Fig. 2), while station 7 recorded the highest extractability percentage of Cr, which may be due to the offshore oil fields at this station. All sites in the present study exhibited concentrations lower than the

ERL ($81.5 \mu\text{g/g}$ dry wt). The total concentration of Cr in the present study was lower than that was observed in Danube river sediment ($64 \pm 6.5 \mu\text{g/g}$ dry wt) (Woitke *et al.* 2003) and Lake Kariba, Zimbabwe ($29.3 \pm 1.6 \mu\text{g/g}$ dry wt) (Berg and Kautsky, 1997).

Copper is sorbed rapidly to sediment, resulting in high residue levels. Most copper in particles is either as a constituent of mineral phases or adsorbed to oxide surfaces or organic matters depending on the type of clay-sediment, pH, competing cations and the presence of ligands and Fe/Mn oxides; formation of copper sulfide can be particularly important in anoxic sediment (Di Toro *et al.* 1990). Desorption from sediments into the bulk water depends on pH, salinity and the presence of natural and or synthetic chelating agents (ICME 1995). The concentration of Cu ranged from 15.89 to 123.07 $\mu\text{g/g}$ dry wt in total fraction and from 9.03 to 15.62 $\mu\text{g/g}$ dry wt in labile fraction. All sites showed Cu concentrations lower than the ERL ($34 \mu\text{g/g}$ dry wt) for both labile and total fractions except stations 1 and 2 for the total and labile fractions, but lower the ERM ($270 \mu\text{g/g}$ dry wt). Cu concentration in the present work was comparable with data obtained for Danube River by Woitke *et al.* (2003) and with that was obtained for Galveston Bay, USA by Park and Presley (1997). However, it was higher than that recorded for Mwanza Gulf, Tanzania by Kishe and Machiwa (2003) ($21.6 \pm 2.4 \mu\text{g/g}$ dry wt) and Lake Kariba, Zimbabwe (16.1 ± 0.8 $21.6 \pm 2.4 \mu\text{g/g}$ dry wt).

The concentration of Fe in the total sediments fluctuated between 333.1 and 12428 $\mu\text{g/g}$ dry wt with an average value 4104 $\mu\text{g/g}$ dry wt while it ranged from 17.9 to 1529 $\mu\text{g/g}$ dry wt with an average value 490 $\mu\text{g/g}$ dry wt in the labile fraction. The mean percentage extractability was 11.14% indicating that the enrichment of Fe in the studied locations was of the natural origin.

The tendency of soluble manganese compounds to adsorb into sediments can be highly variable, depending mainly on the cation exchange capacity and the organic

composition (Garrison *et al.* 1995). In a recent study for the distribution of soluble Mn between ionic and complex form in saturated sediment as affected by pH, Mn was associated with only the smallest size range under all pH reflect its ionic nature (Ngiam and Lim 2001). In the current study, Station 3 recorded the highest values for both total and labile fractions while stations 4 and 6 recorded the highest values of extractability percentage (Table 3).

The concentration of Ni in total sediment fluctuated from 44.86 to 77.84 $\mu\text{g/g}$ dry wt and from 17.54 to 39.83 $\mu\text{g/g}$ dry wt in total and labile fractions, respectively. The high extractability percentage recorded at stations 3 and 7 (60.98 and 75.01 %, respectively) indicating a new input of Ni, which might be attributed to the cement manufactory and the oil refineries as well as the thermal electric stations and the sewage discharged into this area (El-Samara and Moussa 1995). Nickel concentration in the total fractions showed a higher value over ERM (51.6 $\mu\text{g/g}$ dry wt) at all locations except station 4 which had a lower value. Nickel may be deposited into the sediment by various processes such as precipitation, complex addition, adsorption on clay particles, and via uptake by biota. Because of the microbial activity or changes in physical and chemical parameters, including pH, ionic strength, and particle concentration, sorption processes may be reversed leading to release of nickel from the sediment into water column (Di Toro *et al.* 1986).

Coastal waters may receive significant inputs of Pb from industry, sewage sludge, domestic waste water and the combustion of fossil fuels (Fergusson, 1990). Sorption of lead by sediment is correlated to the organic content, the grain size and the anthropogenic pollution (Huang and Lin 2003; Muniz *et al.* 2004). The concentrations of Pb fluctuated from 71.48 to 99.81 and from 35.18 to 41.82 $\mu\text{g/g}$ dry wt in total and labile fractions, respectively. Labile fraction exhibited lower values than the ERL (46.7 $\mu\text{g/g}$ dry wt) at all studied locations, however, total fractions

recorded higher values than ERL but still much lower than the ERM (218.5 $\mu\text{g/g}$ dry wt). Total Pb concentrations were within the range (23.7-129.0 $\mu\text{g/g}$ dry wt) recorded by Park and Presley (1997) in Galveston Bay sediment in USA. The high extractability percentages of Pb recorded in most stations under study indicated a new input in Suez Gulf, which probably was due to the domestic and industrial effluents as well as the atmospheric deposition besides the contribution of Pb from the use of leaded petrol in outboard boat engines and the oil refineries in this area. Previous studies have also indicated elevated levels of heavy metals in aquatic systems receiving effluents from urban areas, domestic and untreated sewage (Kishe and Machiwa 2003; El-Nemr 2003).

The concentration of zinc in sediment is related to particle size, mineralogy and input sources and its biological effects in sediment are not related to total concentrations. The binding of zinc by sulfide, organic matter and metal oxides should be taken into account (Allen 1996). As consequence of adsorption to organic substances and other inorganic minerals, zinc is precipitated from waters and thus it is enriched in sediments. Removal of Zn from water and its incorporation into sediments can take place by adsorption on hydrous oxide of Fe, Mn and clay. Overall, the organic matter play an important role in the incorporation of metals in the sediment in addition to detrital and clay minerals rather than anthropogenic inputs (Krupadam *et al.* 2003). The concentration of Zn in total fraction fluctuated between 33.46 to 95.3 $\mu\text{g/g}$ dry wt with an average value 69.15 $\mu\text{g/g}$ dry wt. The extractability percentage ranged from 25.48 to 56.19 % indicating a new input in all stations. All locations in the present work showed a lower value than ERL (150 $\mu\text{g/g}$ dry wt) for both total and labile fractions.

Enrichment factors

For better estimation of anthropogenic input, an enrichment factor was calculated for each metal by dividing its ratio to the

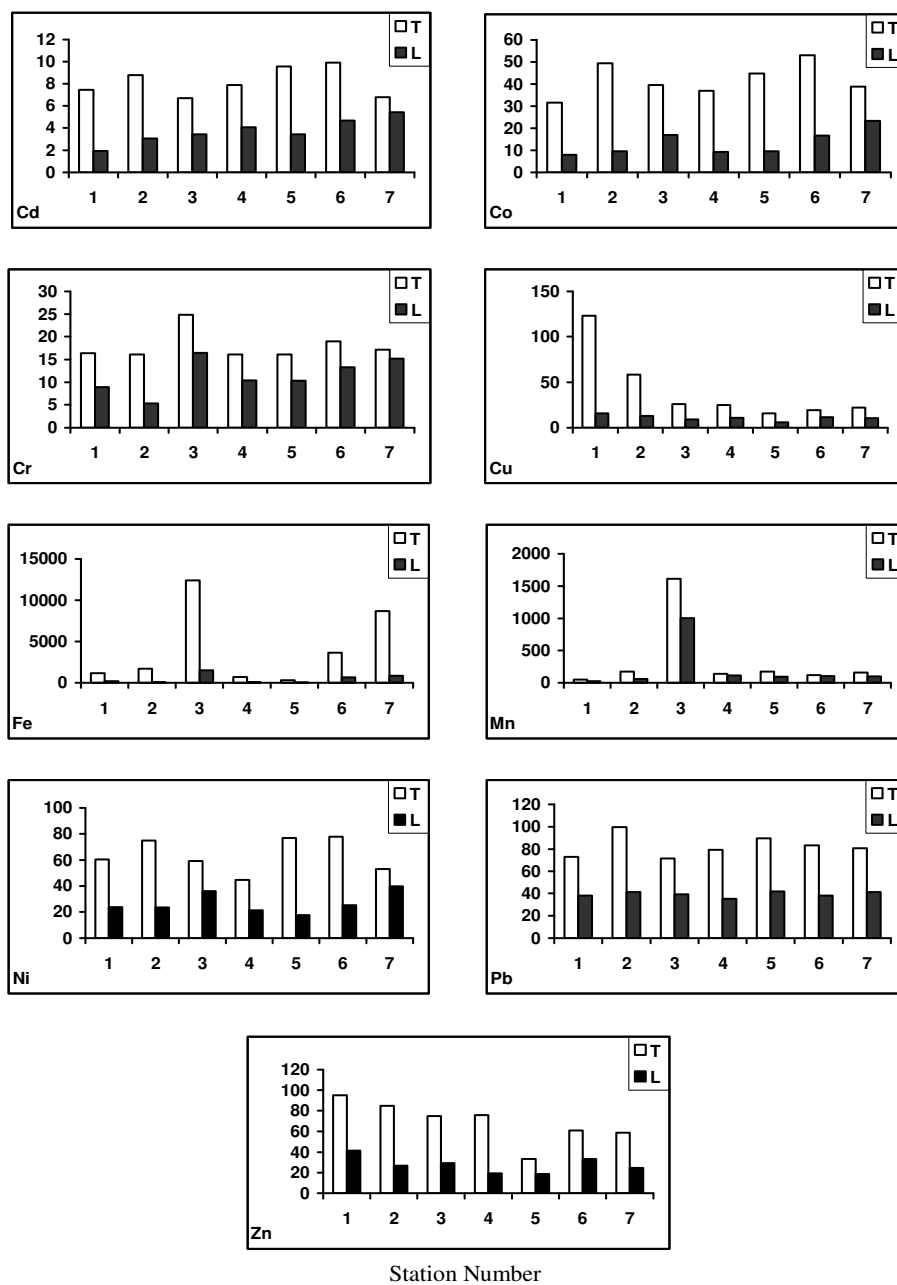


Fig. 2. Concentration of heavy metals in total (T) and labile (L) fractions in sediment.

LEACHABLE AND TOTAL NINE HEAVY METALS IN MUDDY AND SANDY SEDIMENT COLLECTED FROM SUEZ GULF

Table 3. Total (T), leachable (L) and leachable percentage (%L) of metal concentrations ($\mu\text{g/g}$ dry wt) in total sediment of Suez Gulf.

Metal species	Station number								
	1	2	3	4	5	6	7	Mean	\pm S.D.
T	7.45	8.80	6.70	7.89	9.56	9.91	6.79	8.16	1.20
Cd L	1.92	3.07	3.44	4.08	3.42	4.68	5.45	3.72	1.06
%L	25.75	34.92	51.38	51.69	35.8	47.21	80.28	46.72	16.35
T	31.73	49.43	39.62	36.97	44.83	53.08	38.83	42.07	6.89
Co L	7.96	9.55	16.99	9.32	9.55	16.62	23.36	13.34	5.32
%L	25.09	19.33	42.87	25.21	21.31	31.31	60.16	32.18	13.52
T	16.38	16.07	24.81	16.08	16.07	19.00	17.10	17.93	2.98
Cr L	8.94	5.30	16.44	10.42	10.32	13.26	15.18	11.41	3.56
%L	54.61	32.96	66.26	64.84	64.22	69.75	88.8	63.06	15.58
T	123.07	58.42	26.00	24.8	15.89	18.99	22.02	41.31	35.86
Cu L	15.62	12.83	9.03	10.93	5.83	11.42	10.48	10.88	2.82
%L	12.69	21.96	34.75	44.06	36.68	60.17	47.58	36.84	14.74
T	1164.3	1714.1	12428	726	333.1	3671.9	8690.1	4104.0	4317.7
Fe L	202	82.10	1528.9	75.3	17.9	653.1	870.8	490.0	520.3
%L	17.35	4.79	12.30	10.38	5.37	17.79	10.02	11.14	4.77
T	49.80	176.2	1616.0	136.8	177.3	117.4	162.4	348	519.3
Mn L	26.8	61.60	1005.1	114.4	97.50	102	101.1	215.5	323.6
%L	53.8	34.97	62.19	83.62	55.01	86.82	62.23	62.66	16.59
T	60.32	75.02	59.17	44.86	76.97	77.84	53.10	63.9	11.97
Ni L	23.74	23.47	36.08	21.38	17.54	25.3	39.83	26.76	7.50
%L	39.36	31.28	60.98	47.66	22.79	32.5	75.01	44.23	17.02
T	73.13	99.81	71.48	79.28	89.67	83.35	80.72	82.49	9.06
Pb L	38.36	41.33	39.15	35.18	41.82	38.1	41.08	39.29	2.17
%L	52.46	41.40	54.78	44.38	46.64	45.71	50.89	48.04	4.44
T	95.30	84.92	74.84	75.73	33.46	60.92	58.85	69.15	18.73
Zn L	41.45	27.05	29.37	19.29	18.80	33.33	24.78	27.73	7.39
%L	43.49	31.86	39.24	25.48	56.19	54.71	42.11	41.87	10.34

normalizing element by the same ratio found in the chosen baseline. The enrichment factors (EFs) for each element were calculated from the formulae (Sinex and Wright 1988; Grant and Middleton 1990):

$$EF = (\text{Metal} / \text{Fe})_{\text{sample}} / (\text{Metal} / \text{Fe})_{\text{crust}}$$

The values for the earth crust are obtained from Martin and Meybeck (1979) and represent the average composition of the surficial rocks exposed to weathering. Because of natural mineralogical differences of the sediment and the analytical uncertainty, only sediments with an EF greater than 2 were considered to be as enriched (Angelidis and Aloupi 1997; Liaghati *et al.* 2003).

The EFs calculated for sediments at studied locations revealed that they were highly enriched in Cd. The EFs varied from 9.7 at station 3 to 516.5 at station 5 (Table 4). Sediment samples were enriched in Co and Pb in most of studied locations. Cr and Mn were enriched only at station 5 by EFs 2.4 and 2.7, respectively. Cause of enrichment may be related to the land use in this area as mentioned previously. Stations 1, 2, 4, and 5 are enriched by Cu, Ni and Pb while stations 1, 4, 5 are enriched by Zn indicating that the pollution of these metals may be due to anthropogenic origin from the same sources of pollution.

Heavy metals in mud and sand fractions

Total and labile heavy metals in mud and sand fractions in the collected samples from surface sediments of Suez Gulf are given in Tables 5 and 6 respectively. The concentration of measured metals were in the sequence of Fe > Mn > Pb > Zn > Ni > Cu > Co > Cr > Cd and Fe > Mn > Pb > Zn > Ni > Co > Cr ≥ Cu > Cd for the total and labile fractions in sand. Whereas, they were in the next sequences in mud Fe > Mn > Zn > Pb > Cu > Ni > Co > Cr > Cd and Fe > Mn > Zn ≥ Pb > Ni > Cu > Co > Cr > Cd for total and labile fractions, respectively. The ratios between heavy metal concentrations in muddy and sandy sediments for both labile

and total fractions along Suez Gulf were higher than 1 (Table 7). This indicates that more heavy metals were bound in the silt and clay fraction than the sand-sized fraction of the sediments. Previous workers stated that the clay fraction is very important substrate for the metal attachment, and metal concentrations tended to increase from sand to silt (up to two-fold increase), whereas the increase from silt to clay averages four to five fold in estuarine sediments (Deely and Fergusson 1994; Liaghati *et al.* 2003). The metal adsorption capacity was in the order of sand < silt < clay, due to the increases in surface areas as particle size decreased from sand to clay (Haque and Subramanian 1982).

The heavy metals pollution levels in mud and sand fractions was measured using the Index of Geoaccumulation (I_{geo}) introduced by Muller (1981), which consists of six grades. The highest grade reflects 100 fold metal concentration relative to background values.

$$I_{\text{geo}} = \log_2 [C_n / (1.5 \times B_n)]$$

Where C_n is the measured concentration of the element n in sediment sample and B_n is the background concentration of the element n. The factor 1.5 is used because of possible variations of the background data to lithogenic effects. Samples were divided into six groups: unpolluted ($I_{\text{geo}} < 1$), very low polluted ($1 < I_{\text{geo}} < 2$), low polluted ($2 < I_{\text{geo}} < 3$), moderately polluted ($3 < I_{\text{geo}} < 4$), highly polluted ($4 < I_{\text{geo}} < 5$), and very highly polluted ($I_{\text{geo}} > 5$) (Ruiz *et al.* 1998).

The concentration of total Co in sand was ranged from 30.7 to 44.9 with a mean value 39.1 $\mu\text{g/g}$ dry wt while it fluctuated between 34.36 and 62.6 in mud fractions. The majority of the samples fall in the low polluted ($2 < I_{\text{geo}} < 3$) except stations 1 and 7 in mud fractions, and station 1 in sand fraction which fall in very low polluted level (Table 8). The total and labile concentrations of the Co in sand fractions in the present study recorded high levels compared to that recorded by Villares *et al.* (2003) for sandy sediments of NW Spain. The extractability

percentages of Co indicated a new input where they are fluctuated between 21.19 to 63.43 % in sand and from 27.55 to 76.07 % in mud fractions.

The mean value of total and labile Cr concentrations in sand fractions recorded in the present study was 16.42 and 10.22 $\mu\text{g/g}$ dry wt. The extractability percentage of Cr ranged from 40.4 to 82.3 %, indicating that over than 50 % of Cr detected in Suez Gulf was a new input. The average concentration of total Cr in sandy fraction was very low compared to that reported in Danube river ($64 \pm 12.3 \mu\text{g/g}$) (Woike *et al.* 2003) but comparable to that recorded in NW Spain ($14.4 \pm 10.48 \mu\text{g/g}$) (Villares *et al.* 2003). In the investigated area, both sand and mud fractions have been shown to be unpolluted with Cr element where $I_{\text{geo}} < 1$ in both of mud and sand fractions.

The mean concentration of total Cu in mud fractions was 80.1 $\mu\text{g/g}$ and recorded its highest value at station 1 (125.7 $\mu\text{g/g}$) and its lowest value at station 6 (20 $\mu\text{g/g}$). The percentage extractability of Cu was 39.3 % indicating a new input of Cu. The concentration of copper in the present work was five times higher than that reported by Villares *et al.* (2003) in NW Spain for total sandy sediment and double of its labile fractions, While Cu levels in both sand and mud fractions were comparable with that reported by Ruiz (2001) from SW Spain. The index of accumulation ($I_{\text{geo}} < 1$) indicates unpolluted level for stations 3, 4, 5, 6 and 7 in sand fraction as well as stations 6 and 7 for mud fractions while it indicates low polluted level for station 1 in sand fractions as well as stations 1, 2, 4 and 5 in mud fractions.

The distribution of total and labile Fe in both mud and sand fractions exhibited a similar trend (Tables 5 and 6), where station 3 recorded the highest value and station 4 recorded the lowest value. The extractability percentage of iron was very low (10.52 % for sand and 13.99 % for mud fractions) compared to all metals studied in this work, which indicate a natural origin of Fe at the studied location. The I_{geo} of Fe was almost

zero, which indicates unpolluted locations by Fe.

The extractability percentage of Mn was ranged from 48.8 to 84.6 % in sand and 57.8 to 89.05 % in mud fractions, indicating a new input of Mn. All sandy samples under investigation fall in the unpolluted level ($I_{\text{geo}} < 1$) except station 3 falls in very low polluted level ($2 < I_{\text{geo}} < 3$). Index of accumulation for mud fractions exhibits fluctuation between moderate pollution level at station 5 and very low pollution level at station 3, while the other stations are unpolluted locations by Mn.

The total and labile Ni in mud fractions fluctuated from 59 to 86.21 and 29.2 to 46.4 $\mu\text{g/g}$ dry wt, respectively, while it ranged in sandy sediment from 44.8 to 77.1 and 17.5 to 35.2 $\mu\text{g/g}$ dry wt for total and labile fractions, respectively. The mean extractability percentage was 43.2 % for sand fractions and 50.9 % for mud fractions indicating a new input of Ni in both mud and sand fractions.

The area under investigation displays Pb loadings with low to moderate polluted samples in most locations. The concentrations of Pb in the studied sand samples were fall in the range of 69.79 to 89.8 $\mu\text{g/g}$ dry wt with I_{geo} between 2 and 4 (Tables 6 and 8). The total and labile Pb concentrations in mud fractions fluctuated between 88.9 to 109.8 and 38.5 to 64.9 $\mu\text{g/g}$ dry wt, respectively indicating a new input pollution as shown in Table 5. The mean recorded values of total and labile Pb in the present work were double of that were reported for NW Spain by Villares *et al.* 2003.

The highest value of total and labile Zn concentration in both sandy and muddy sediment was observed at station 1. The I_{geo} indicates unpolluted level for all studied muddy samples except for stations 1 and 4, which exhibited very low polluted level, while sandy sediment showed a very low polluted level for all studied locations.

Normalization

It is well established that trace metals may be introduced to coastal environments by

both natural process and human activities within the catchments or adjacent to the coast (Rubio *et al.* 2000; Preda and Cox 2000; Ruiz 2001). Coastal sediments are contaminated by less than 5 % by weight with organic materials, which are regarded as a metal carrier such as Cd and Hg, however, due to its low abundance it is not usually considered as major contributor to total metal levels (Loring 1991). Inorganic detritus is composed mainly of a limited number of silicate minerals such as quartz, feldspar, micas and clay minerals and small amounts of metal oxides and sulphide phases. Carbonate and quartz have very low concentrations of Fe (generally <0.2 %) and trace metals. In contrast, clay minerals have concentrations of Fe and trace metals which are 20 to 50 times higher than carbonate and quartz (Kouadio and Trefry 1987; Krumgalz 1989). Therefore, natural variations in metal concentrations have often been related to the grain size effect. To composite for this natural variability, metal concentrations were normalized. This procedure can be done by calculating the ratio of natural concentrations to that of a normalizing factor whose concentration is not affected by anthropogenic processes (Daskalakis and O'Connor 1995). Two broad categories have been well established: granulometric and geochemical. Loring (1991) considered the geochemical normalization of trace metals to be better than granulometric methods,

because it compensates for both the granulometric and mineralogical variations. Iron is widely used as normalized of heavy metal concentrations (Rule 1986; Pardue *et al.* 1988; Baptista Neto *et al.* 2000, El-Sikaily *et al.* 2004). Iron is abundant in the earth's crust and is scarcely influenced by anthropogenic inputs, especially compared with the naturally occurring high levels of this element (Moore 1991).

To obtain a better understanding of normalization, a comparison between absolute and normalized metal contents respect to Fe was made. Total ratio of metal/iron (Me/Fe) in sediment and sand fractions (Figs. 3 and 5) shows similar trend for Cd, Co, Cr, Pb and Ni where station 5 recorded the highest value. On the other hand, the ratio of Me/Fe in mud fraction was high at stations 4 and 5 for all metals under investigation except Mn which recorded its highest value at station 5 (Fig. 4). The comparison between absolute and normalized values in sediments shows different trend and therefore in sandy samples, as the metal concentrations decreases, Me/Fe increases (as shown for station 5) therefore, a lower absolute metal content does not necessarily demonstrate lower normalized values and vice versa. Overall, comparison based on the absolute concentration of different elements alone could be misleading especially when the sediment samples are highly heterogeneous.

Table 4. Enrichment factors (EFs) of total heavy metals of Suez Gulf sediments.

Station number	Enrichment Factor							
	Cd	Co	Cr	Pb	Zn	Cu	Ni	Mn
1	115.238	7.547	0.713	14.132	2.320	11.892	3.806	0.214
2	92.381	7.986	0.475	13.102	1.404	3.834	3.216	0.514
3	9.702	0.883	0.101	1.294	0.171	0.235	0.350	0.650
4	195.614	14.102	1.123	24.571	2.957	3.844	4.539	0.942
5	516.515	37.273	2.446	60.572	2.848	5.366	16.978	2.661
6	48.573	4.003	0.262	5.108	0.470	0.582	1.557	0.160
7	14.062	1.237	0.100	2.090	0.192	0.285	0.449	0.093

LEACHABLE AND TOTAL NINE HEAVY METALS IN MUDDY AND SANDY SEDIMENT COLLECTED FROM SUEZ GULF

Table 5. Total (T), leachable (L) and leachable percentage (%L) of metal concentrations ($\mu\text{g/g}$ dry wt) in mud fraction of Suez Gulf sediments.

Metal species	Station number								Mean	\pm S.D.
	1	2	3	4	5	6	7			
Cd	T	11.67	9.02	9.96	8.49	12.20	10.61	7.43	9.91	1.72
	L	3.41	5.11	5.46	5.11	6.48	5.11	6.36	5.29	1.02
	%L	29.23	56.72	54.79	60.26	53.10	48.21	85.71	55.43	16.77
Co	T	40.67	55.46	59.15	51.76	51.79	62.55	34.36	52.25	7.75
	L	11.88	19.01	26.14	14.26	19.01	20.02	26.14	19.50	5.39
	%L	29.22	34.28	44.20	27.55	36.71	32.01	76.07	37.56	10.90
Cr	T	19.29	33.07	39.27	22.51	18.60	22.48	20.67	25.13	7.89
	L	14.46	16.08	19.29	16.54	16.08	18.60	19.22	17.18	1.87
	%L	74.97	48.61	49.12	73.47	86.42	82.76	92.97	72.62	17.52
Cu	T	125.71	99.99	61.87	104.42	124.26	20.00	24.28	80.07	44.86
	L	81.27	59.03	11.43	46.75	50.29	13.20	13.01	39.28	27.32
	%L	64.65	59.04	18.47	44.77	40.48	66.03	53.57	49.57	16.72
Fe	T	3244.53	8848.59	14798	2556.3	4032.5	7390.62	11306.5	7453.87	4548.62
	L	994.85	1065.07	2017.2	247.22	174.71	1356.74	1047.44	986.18	634.42
	%L	30.66	12.04	13.63	9.67	4.33	18.36	9.26	13.99	8.52
Mn	T	83.26	952.95	1705.26	230.93	2651.7	190.37	183.58	856.87	986.43
	L	61.14	681.15	1405.95	182.56	1978	169.53	106.11	654.78	755.68
	%L	73.43	71.48	82.39	79.05	74.59	89.05	57.80	75.40	9.82
Ni	T	72.60	77.14	67.86	63.53	81.67	86.21	58.99	72.57	9.82
	L	29.17	35.00	43.75	32.25	32.09	32.18	46.37	35.83	6.57
	%L	40.18	45.38	64.48	50.77	39.29	37.32	78.62	50.86	15.37
Pb	T	99.79	109.77	89.82	88.91	99.8	89.81	96.85	96.39	7.58
	L	64.91	51.32	44.91	38.50	53.05	43.67	44.90	48.75	8.630
	%L	65.05	46.75	50.00	43.30	53.15	48.62	46.36	50.46	7.14
Zn	T	231.02	102.06	86.55	127.58	63.79	64.48	64.14	105.66	60.21
	L	109.54	61.68	35.94	40.76	33.26	37.01	24.67	48.98	29.00
	%L	47.41	60.44	41.52	31.95	52.13	57.4	38.47	47.05	10.36

Table 6. Total (T), leachable (L) and leachable percentage (%L) of metal concentrations ($\mu\text{g/g}$ dry wt) in sand fraction of Suez Gulf sediments.

Metal species	Station number							Mean	\pm S.D.	
	1	2	3	4	5	6	7			
Cd	T	6.90	7.98	6.26	7.96	9.55	9.01	6.48	7.73	1.26
	L	1.73	3.07	3.09	4.09	3.41	4.43	4.77	3.51	1.03
	%L	25.06	38.44	49.39	51.42	35.72	49.17	73.68	46.13	15.37
Co	T	30.67	44.36	36.97	36.97	44.86	46.36	33.72	39.13	6.09
	L	7.51	9.51	15.39	9.26	9.51	14.26	21.39	12.40	4.89
	%L	24.48	21.43	41.63	25.05	21.19	30.76	63.43	32.57	15.35
Cr	T	16.08	12.86	22.74	16.08	15.97	16.51	14.67	16.42	3.06
	L	8.27	5.20	16.08	10.34	10.33	9.27	12.08	10.22	3.36
	%L	51.43	40.44	70.71	64.28	64.65	56.14	82.32	61.42	13.60
Cu	T	111.40	48.85	20.00	42.99	54.28	17.57	20.85	45.13	32.85
	L	16.54	12.34	8.67	9.80	5.20	10.41	8.55	10.22	3.54
	%L	14.85	25.25	43.36	22.81	9.59	59.24	40.98	30.87	17.65
Fe	T	869.33	818.59	12289.62	686.12	277.60	654.62	6783.93	3197.12	4617.14
	L	86.52	70.22	1451.11	70.23	17.24	104.56	737.50	362.48	541.36
	%L	9.95	8.58	11.81	10.24	6.21	15.97	10.87	10.52	3.01
Mn	T	45.25	79.59	1338.40	135.76	1048.38	59.30	143.58	407.18	544.79
	L	22.07	54.17	938.39	113.35	831.13	50.15	98.30	301.08	401.09
	%L	48.77	68.06	70.11	83.49	79.28	84.58	68.47	71.82	12.34
Ni	T	58.99	68.06	58.97	44.84	77.14	72.59	49.91	61.50	11.80
	L	23.34	23.50	35.21	21.25	17.50	20.42	35.00	25.17	7.08
	%L	39.56	34.53	59.71	47.40	22.69	28.13	70.13	43.16	17.09
Pb	T	69.79	89.82	69.81	79.84	89.80	79.83	69.86	78.39	8.99
	L	38.29	37.89	38.49	35.50	42.08	34.50	38.50	37.89	2.44
	%L	54.86	42.19	55.14	44.46	46.87	43.21	55.11	48.83	5.97
Zn	T	76.20	75.51	74.48	75.17	33.10	58.27	54.83	63.94	16.27
	L	31.94	26.82	28.43	18.91	18.77	31.11	25.21	25.88	5.34
	%L	41.91	35.52	38.17	25.15	56.71	53.38	45.98	42.40	10.81

LEACHABLE AND TOTAL NINE HEAVY METALS IN MUDDY AND SANDY SEDIMENT COLLECTED FROM SUEZ GULF

Table 7. Ratio between heavy metal concentration in mud and that in sand of Suez Gulf sediments.

Station number	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
	Total fraction								
1	1.69	1.33	1.20	1.13	3.73	1.84	1.23	1.43	3.03
2	1.13	1.25	2.57	2.05	10.81	11.97	1.13	1.22	1.35
3	1.59	1.60	1.73	3.09	1.20	1.27	1.15	1.29	1.16
4	1.07	1.40	1.40	2.43	3.73	1.70	1.42	1.11	1.70
5	1.28	1.15	1.16	2.29	14.53	2.53	1.06	1.11	1.93
6	1.18	1.35	1.36	1.14	11.29	3.21	1.19	1.13	1.11
7	1.15	1.32	1.41	1.16	1.67	1.28	1.18	1.39	1.17
	Labile fraction								
1	1.97	1.58	1.75	4.91	11.50	2.77	1.25	1.70	3.43
2	1.67	2.00	3.09	4.79	15.17	12.57	1.49	1.35	2.30
3	1.76	1.70	1.20	1.32	1.39	1.50	1.24	1.17	1.26
4	1.25	1.54	1.60	4.77	3.52	1.61	1.52	1.08	2.16
5	1.90	2.00	1.56	9.67	10.13	2.38	1.83	1.26	1.77
6	1.15	1.40	2.01	1.27	12.98	3.38	1.58	1.27	1.19
7	1.33	1.22	1.59	1.52	1.42	1.08	1.32	1.17	0.98

Table 8. Index of Geoaccumulation (I_{geo}) for mud and sand fractions according to background levels for different grain sizes.

Station number	Co		Cr		Cu		Fe		Mn		Pb		Zn	
	Mud	Sand	Mud	Sand	Mud	Sand	Mud	Sand	Mud	Sand	Mud	Sand	Mud	Sand
1	1.76	1.77	0.00	0.25	2.51	2.69	0.00	0.00	0.00	0.00	2.15	3.54	1.98	1.67
2	2.21	2.30	0.07	0.00	2.36	1.33	0.00	0.00	0.56	0.00	2.29	3.90	0.80	1.65
3	2.30	2.04	0.32	0.75	1.67	0.04	0.00	0.00	1.40	2.45	2.00	3.54	0.57	1.63
4	2.11	2.04	0.00	0.25	2.42	0.24	0.00	0.00	0.00	0.00	1.98	3.73	1.12	1.65
5	2.11	2.32	0.00	0.25	2.67	0.67	0.00	0.00	3.75	0.00	2.15	4.90	0.12	1.88
6	2.38	2.37	0.00	0.29	0.04	0.00	0.00	0.00	0.00	0.00	2.00	3.73	0.00	1.43
7	1.49	2.30	0.00	0.12	0.32	0.10	0.00	0.00	0.00	0.00	2.11	3.54	0.00	1.42

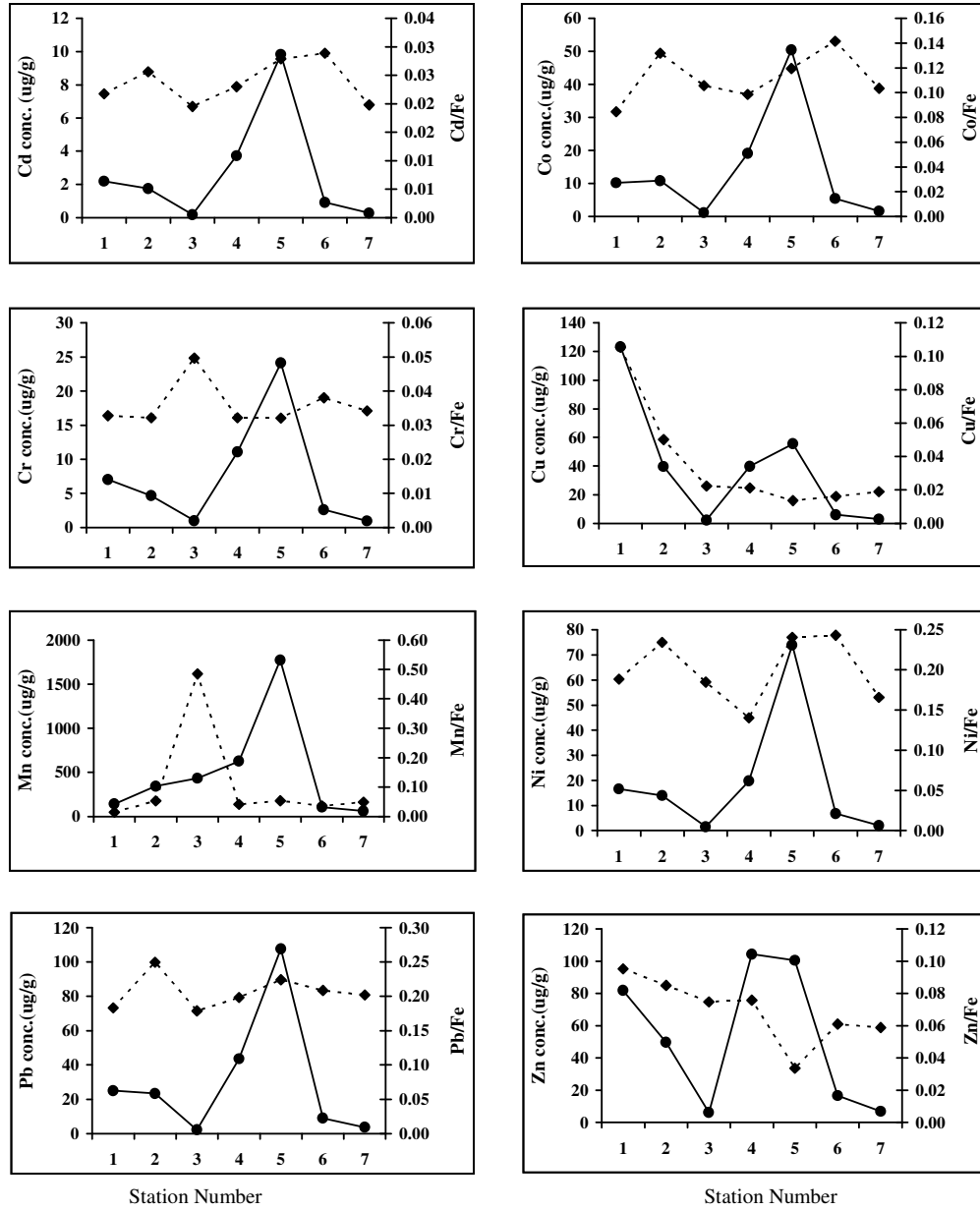


Fig. 3. Concentration of heavy metals and Me/Fe ratio in sediment fractions of Suez Gulf (Note: broken line for absolute concentration, solid line for Me/Fe).

LEACHABLE AND TOTAL NINE HEAVY METALS IN MUDDY AND SANDY SEDIMENT COLLECTED FROM SUEZ GULF

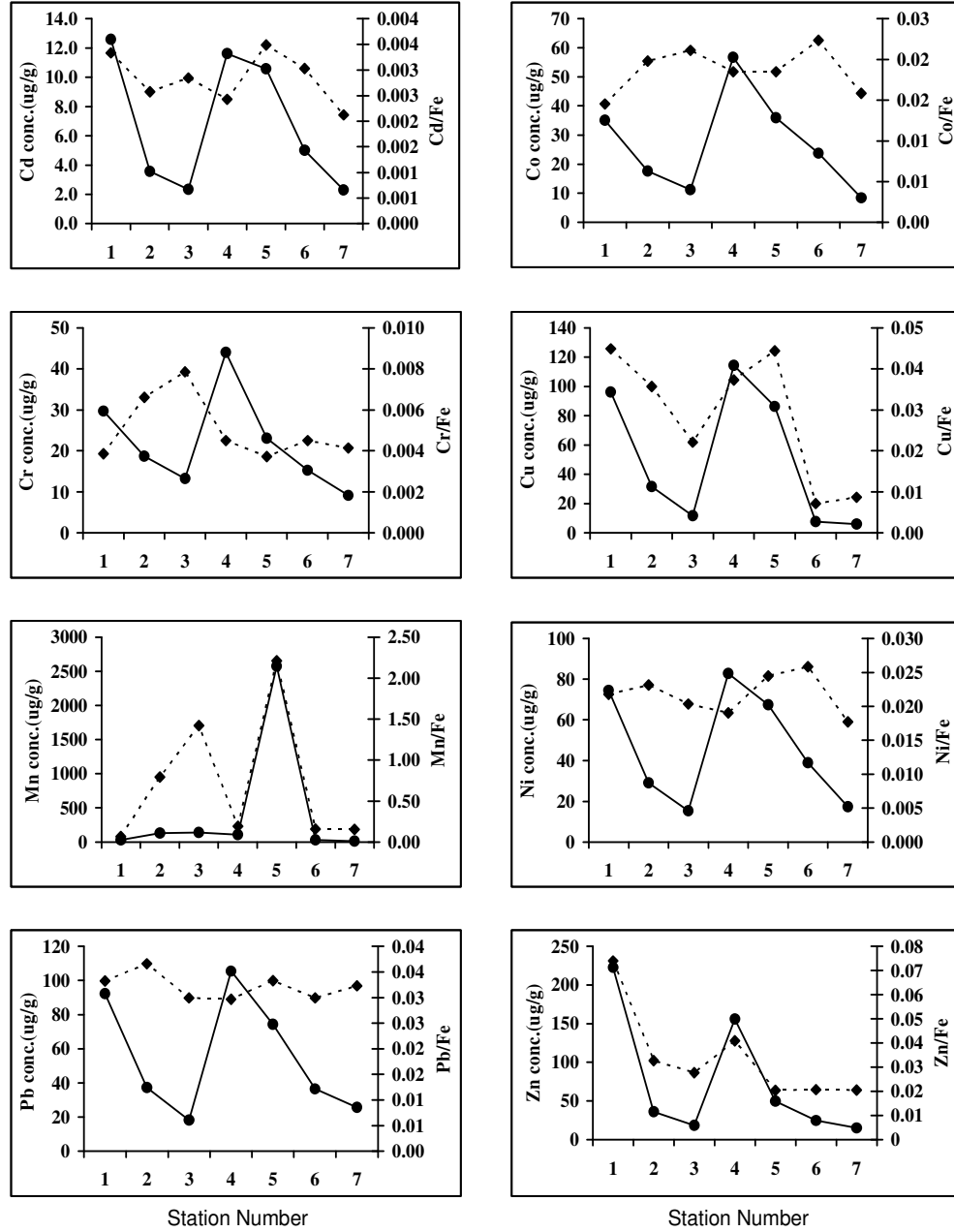


Fig. 4. Concentration of heavy metals and Me/Fe ratio in mud fractions of Suez Gulf (Note: broken line for absolute concentration, solid line for Me/Fe).

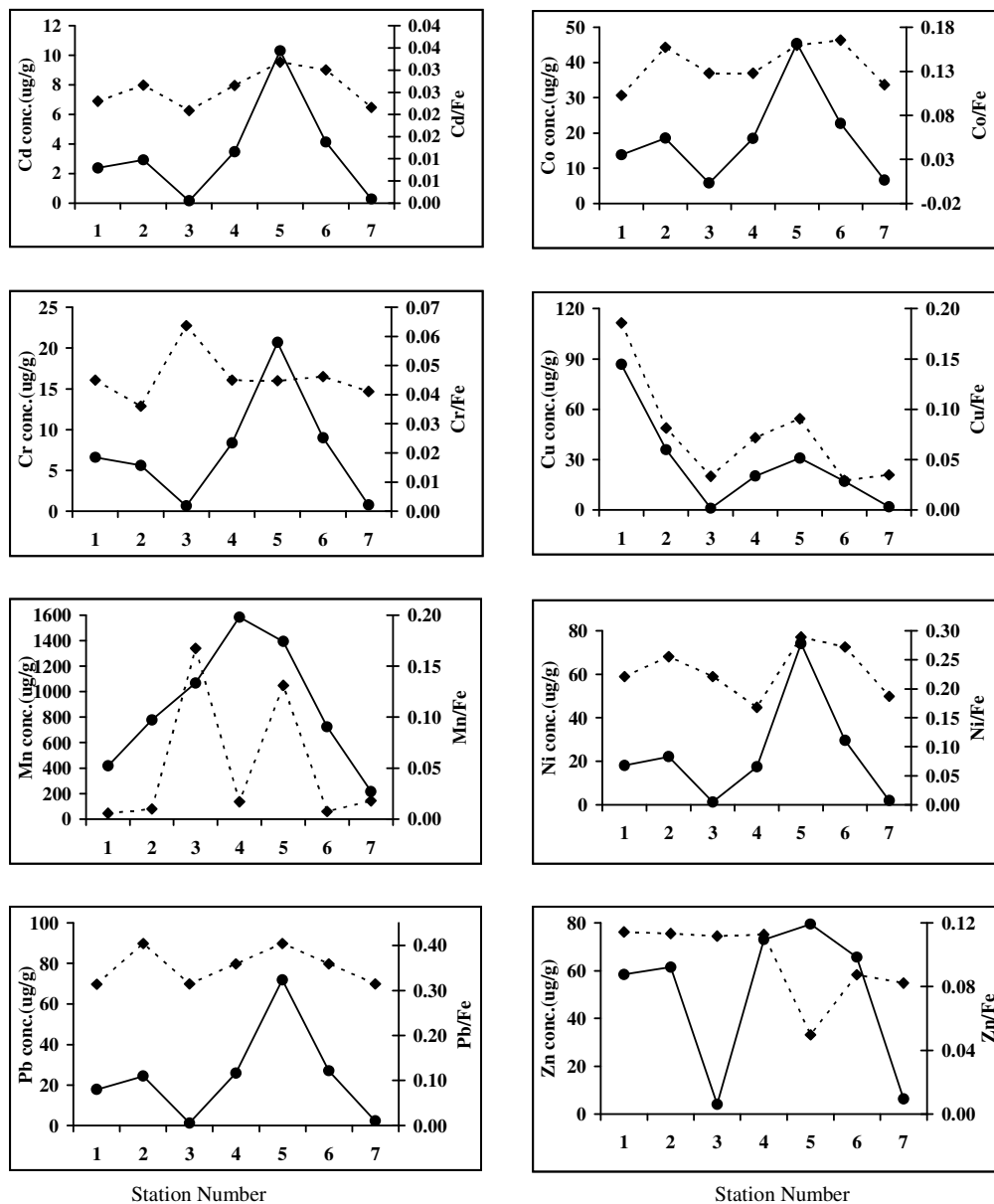


Fig. 5. Concentration of heavy metals and Me/Fe ratio in sand fractions of Suez Gulf (Note: broken line for absolute concentration, solid line for Me/Fe).

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