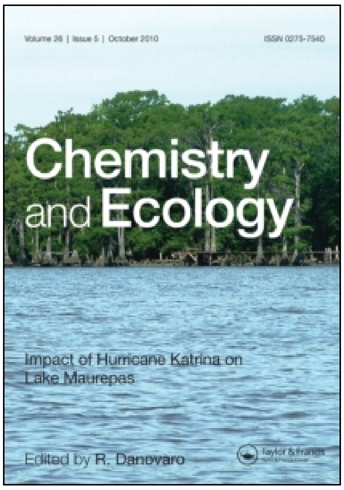
This article was downloaded by:
On: *15 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Chemistry and Ecology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455114

Geochemical forms of trace metals in mangrove sediments—Red Sea (Egypt)

M. A. Okbah[a]; M. A. Shata[a]; M. A. Shridah[a]
[a] National Institute of Oceanography & Fisheries, Alexandria, Egypt

To cite this Article Okbah, M. A. , Shata, M. A. and Shridah, M. A.(2005) 'Geochemical forms of trace metals in mangrove sediments—Red Sea (Egypt)', Chemistry and Ecology, 21: 1, 23 — 36
To link to this Article: DOI: 10.1080/02757540512331323953
URL: http://dx.doi.org/10.1080/02757540512331323953

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Chemistry and Ecology
Vol. 21, No. 1, February 2005, 23–36

Taylor & Francis
Taylor & Francis Group

Geochemical forms of trace metals in mangrove sediments – Red Sea (Egypt)

M. A. OKBAH*, M. A. SHATA and M. A. SHRIDAH

National Institute of Oceanography & Fisheries, Kayet Bay, Alexandria, Egypt

(Received 13 March 2004; in final form 5 October 2004)

Seven sediment samples from mangrove sediments of the Red Sea were taken in order to evaluate the possible contamination of the sediments by trace metals (iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), lead (Pb) and cadmium (Cd)). Sequential extraction techniques were performed to study the different geochemical forms of these metals. X-ray diffraction analysis has been performed to correlate the mineralogical composition with the geochemical forms of the studied elements. The results of Fe and Mn contents indicate that they are in large part from lithogenous origin. The elevated concentrations are associated with the residual form ranged from 70 to 93% for Fe and 46 to 70% for Mn. The percentage of Zn, Cu, Cd and Pb in the non-residual form was much greater than that of the residual fractions. This reflects the high mobility and bioavailability of these metals in mangrove sediments of the Red Sea. X-ray diffraction analysis revealed the presence of silicate components including quartz, feldspars and clay minerals in some locality. Non-silicate components recorded in the study area as calcite as well as, Mg-calcite. Quantitatively both components i.e. silicate and carbonate varied according to their source material.

Keywords: Mangrove sediments; Trace metals; Red Sea

1. Introduction

Mangrove communities are widely acknowledged to be important elements in coastal ecosystems in the tropics [1–5]. Also they stabilize mobile sediments and act as a buffer against coastal erosion [6–8]. Sediments are a matrix of materials, which are comprised of organic and inorganic detrital particles. It is relatively heterogeneous in terms of its physical, chemical and biological characteristics [9].

Trace metals in the sediments are found in various chemical forms and exhibit different physical and chemical behaviour in terms of chemical interactions, mobility, bioavailability and potential toxicity. Chemical fractionation schemes have been used extensively to partition trace elements in sediments [10–16]. The identification of geochemical forms of trace metals are used to understand the conditions in which contaminants may be released to the surrounding environment and the capacity of mobilization of the metals [17].

---

*Corresponding author. Email: mohamed_okbah@yahoo.com

Chemistry and Ecology
ISSN 0275-7540 print/ISSN 1029-0370 online © 2005 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02757540512331323953

The Red Sea hills predominantly consist of sedimentary or granitic rocks, which are susceptible to weathering and are easily eroded. Moufaddal [18] studied the assessment impacts of human activities on the coastal ecosystem of the Red Sea area. The results revealed several factors which caused changes in the environmental conditions along the Egyptian coast of the Red Sea. Examples are land infilling, dredging along the coast, improper diving practices, discharge of raw sewage and other wastes, and the use of destructive tools in fishing and oil pollution.

The authors reported that, the total urban area from north Hurgada to north Safaga was devolved for tourist facilities and the coastal strip for this area has been blocked by tourist constructions and has now become a 'forest of concrete'.

The aim of the present work is to determine the total concentrations of some trace metals (iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), cadmium (Cd), lead (Pb)) among the various geochemical forms in mangrove sediments collected from the Red Sea of Egypt, to evaluate bioavailability of the metals.

2. Materials and methods

2.1 *Study area*

The Red Sea is a semi-enclosed, narrow water body with no river inputs. It extends for approximately 1936 km and it's surface area is approximately 43970 km^2. It attains a depth of about 1800 m. The climate is hot; it lies in a very arid zone and its rainfall is scarce. The water is exceptionally clear and the eutrophic zone extends to a depth of about 80–90 m [19]. The sediments of the investigated area represent the tidal zone; mostly sand fraction, carbonate, shell fragments and reefal debris. The northern stations (I, II, III) which lie near the entrance of the Gulf of Aqaba (figure 1), receive sediments by out-flowing currents coming from the Gulf. The source of the sediments along the area from Safaga (station IV) to Hamata (station VII) is largely autochthonous, mainly biogenic or chemical precipitation of different mud facies.

2.2 *Sampling and analyses*

Duplicate sediment samples were collected from seven mangrove sites in the Red Sea region (figure 1). The sampling has been carried out by means of plastic tube (PVC), digging gently into the uppermost layer of the sediment. 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 [20]. The percentage of organic matter was calculated by multiplying total organic carbon percentage by 1.8. The carbonate content was determined using the calcimeter technique [21]. The total concentrations of trace metals were determined according to Oregioni and Aston [22]. Nought point five grammes of dried sample were 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 a 25 ml volumetric

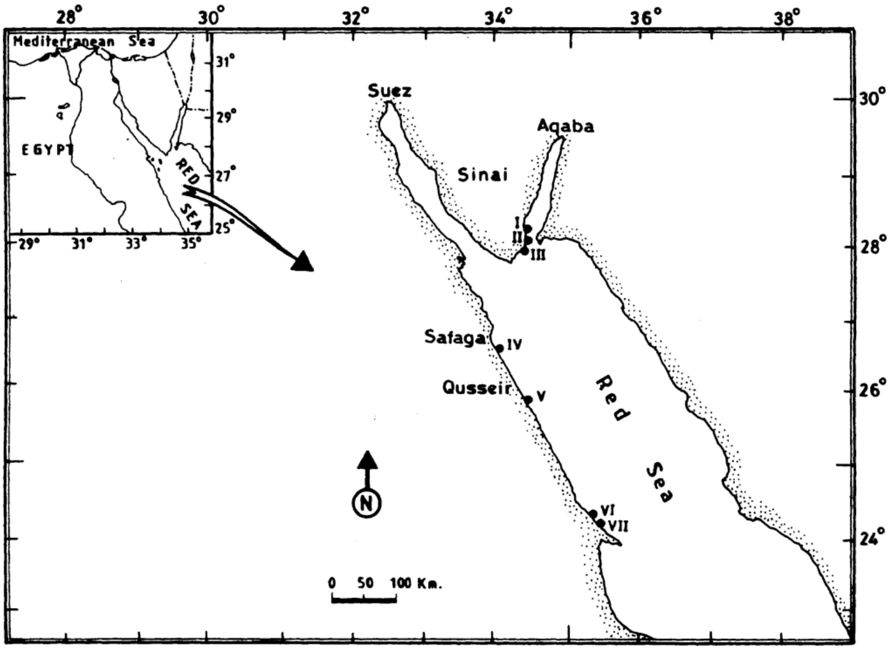


Figure 1. Map of sampling sites (Red Sea).

flask with 0.1 M HCl. The total concentrations of the measured trace elements and their fractions were measured using A.A.S (Perkin Elmer model 373).

The sequential extraction scheme of Tessier, Campbell and Bison [11] was performed (table 1). 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 [23].

Table 1. Extraction procedures for different fractions of trace metals [11].

Fraction	Solution	Conditions
1-Exchangeable	8 ml of 1 M sodium acetate	pH 8.2, shake at room temperature for 1 hour with continuous agitation
2-Bound to Carbonate	Residue from (1) + 8 ml of 1 M sodium acetate (adjusted with acetic acid)	pH 5.0, shake at room temperature for 1 hour with continuous agitation
3-Bound to Fe–Mn oxides	Residue from (2), 20 ml of 0.05 M hydroxylamine hydrochloride in 25% (v/v) Acetic acid	pH 2.0, performed at 70 °C, agitation for 6 hours
4-Bound to organic matter	Residue from 3 + 3 ml of 0.02 M nitric acid + 5 ml of 30% H_2O_2 extracted with 5 ml of 3.2 M ammonium acetate in 20% (v/v) nitric acid	pH 2, shaking for 2 hours at 85 °C
5-Residual	Digested with acid mixture (HNO_3/$HClO_4$/HF; 3:2:1)	evaporated to near dryness at 80 °C, complete with 0.1 M HCl to 25 ml volumetric flask.

Table 2. The concentrations for different metals (mg kg^{-1}) in the reference materials (HISS-1, National research of Council of Canada).

Metal	Found	Certified
Fe	0.240 ± 0.09	0.236 ± 0.017
Mn	60.85 ± 4.2	61.24 ± 2.30
Zn	4.74 ± 0.79	4.60 ± 1.21
Cu	2.19 ± 0.37	2.08 ± 0.08
Pb	3.03 ± 0.40	2.83 ± 0.74
Cd	0.024 ± 0.09	0.022 ± 0.028

2.3 *Method validation and quality control studies*

Method validation and quality control samples were done using a reference material (HISS-1, National Research of Council of Canada) and applying the computerized 4.3 quality system program provided by DANIDA from VKI. 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 2 illustrates the concentrations for different metals in the reference materials. The variation coefficients were 5.7% for Fe; 8.5% for Mn; 4.2% for Cu; 7.4% for Zn; 6.5% for Pb and 8.7% for Cd. Recovery of metal spikes added to the sediments studied were 102% for Fe; 97% for Mn; 95% for Cu; 103% for Zn 96% for Pb and 101% for Cd.

2.4 *Mineralogical analysis*

For the mineralogical analysis, the samples were ground in a mortar to pass through a 44 μ-mesh sieve, then sprinkled on to Vaseline on a glass slide to ensure random orientation. An X-ray diffractometer (Model 1060/80), with a copper target tube and nickel filter, was used. Diffraction was made at 30 kV, 30 mA. Chart speed was 2°/min in the range 4–60°.

3. Results and discussion

3.1 *Grain size, carbonate and organic matter studies*

The results of grain size analysis of the studied sediments, carbonates and organic matter contents are listed in table 3.

The sediments were composed mainly of sand and silt, except for site VII which was covered mainly by sandy silt (70% silt). The organic matter varied from 2.01% at site II to 3.75% at site VII. The carbonate content revealed its maximum value (89.4%) at site I. A significant value (57%) was recorded at site VI. In the other sites, the carbonate content revealed lower values ranging from 8.2 to 29.3%. The variation in the carbonate content was owed to the variability of the mineralogical components.

3.2 *Mineralogical characteristics*

X-ray diffraction was made to determine the different mineral associations and their variability throughout the whole investigated area. X-ray diffraction patterns (figure 2) showed

Table 3. Properties of mangrove sediments – Red Sea.

		Grain size analysis (%)				
Sample	Location	Sand	Silt	Clay	Organic matter (%)	$CaCO_3$
I	28° 10′ 59″ 34° 26′32″	79.81	16.37	3.82	3.72	89.4
II	28° 08′ 50″ 34° 26′39″	85.18	10.52	4.30	2.01	8.2
III	28° 07′ 15″ 34° 26′31″	76.34	18.5	5.16	3.36	26.9
IV	26° 37′ 02″ 348° 00′39″	76.65	17.9	5.45	3.03	29.3
V	25° 52′ 01″ 34° 24′49″	71.45	21.3	7.25	3.65	17.8
VI	24° 22′ 52″ 35° 15′41″	87.9	6.83	5.27	3.32	57.0
VII	24° 18′ 44″ 35° 21′37″	23.4	70.2	6.41	3.75	28.8

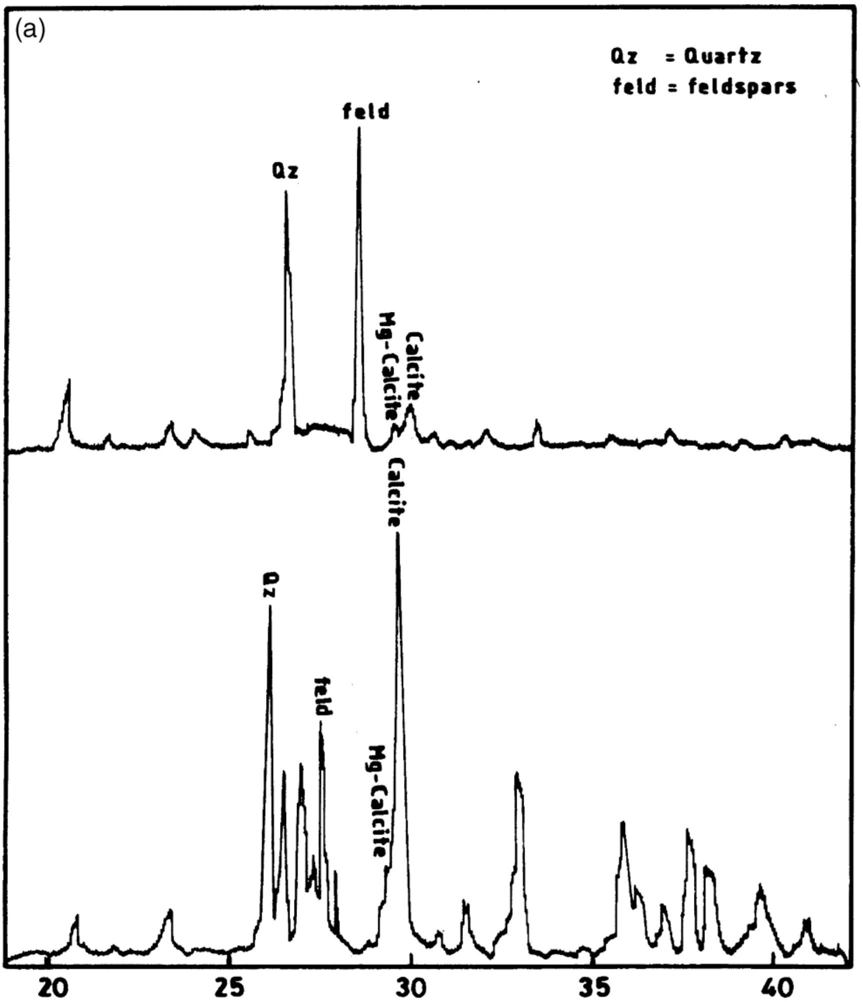


Figure 2. X-ray diffraction patterns of the sediments in the southern part of the study area.

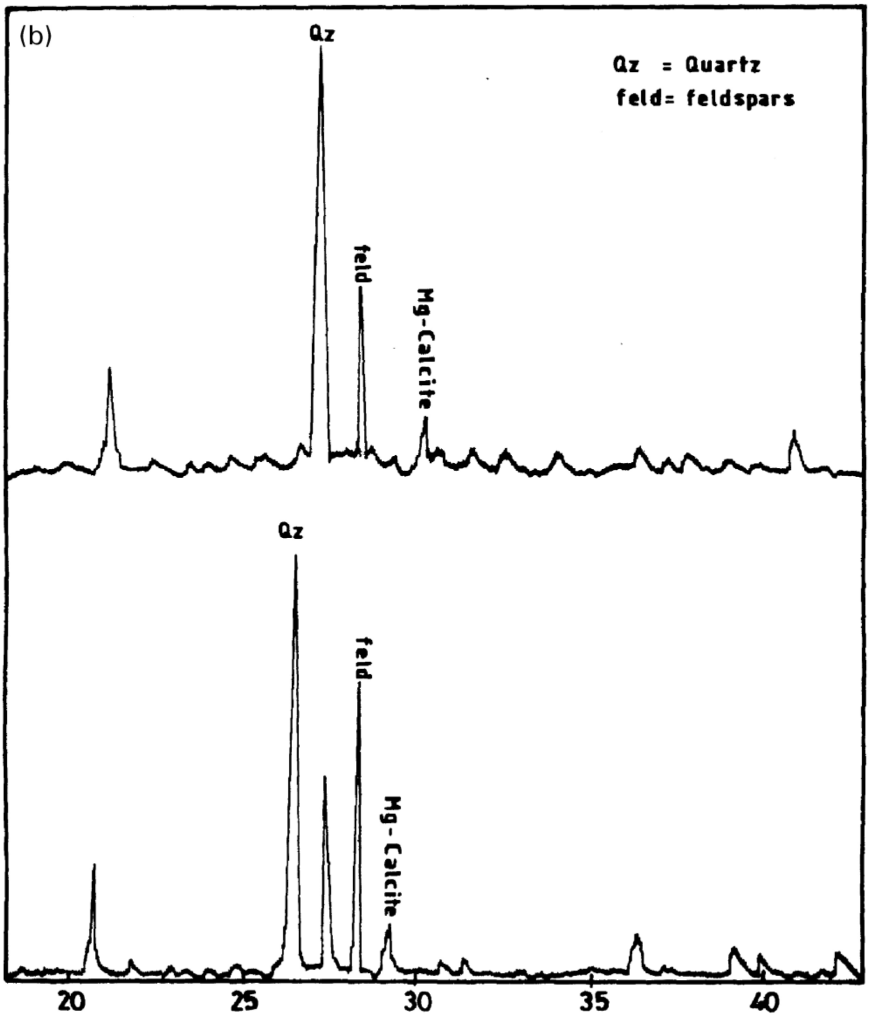


Figure 2. (*Continued*)

well-crystallized mineral matrices in all analyzed samples. At site I, carbonate minerals dominated the mineralogical composition ($CaCO_3$; 89.4%; table 4). They were represented by calcite and Mg-calcite which were formed either through diagenetic processes and/or ecological conditions that prevailed in the area of study. Based on Graf [24] and Goldsmith, Graf and Heard [25], it was found that the existing Mg-calcite with $d(104)$ of 2.98 was in an 80–20 proportion. The silicates included quartz and feldspars. Marked deficiencies in carbonate constituents were observed at site II ($CaCO_3\% = 8.2$). Moreover, the transformation of calcite into Mg-calcite became more intensive. Kaolinit was also detected at the same site. The dominance of silicate and the marked deficiency of the carbonates may suggest either fluviomarine or detritus-origin of the sediments at this site.

3.3 *Geochemical forms of trace metals*

3.3.1 Iron (Fe) and manganese (Mn). Iron (Fe) was mostly concentrated in the residual fraction, although it was found in other fractions. The greater percentage of Fe in the residual

Table 4. Fe concentrations (mg kg^{-1}) in each fraction of mangrove sediments – Red Sea.

Station	Exchangeable fraction	Carbonate fraction	Fe–Mn oxides fraction	Organic fraction	Sum of all fractions	Total conc.	Residual fraction
I	8.5	374	156.4	2482	3020.9	10,944	7923.1
II	27.2	105.4	85	646	863.6	3719	2855.4
III	6.8	343.4	156.4	1292	1798.6	11,475	9676.4
IV	13.6	210.8	125.8	850	1200.2	10,625	9424.8
V	8.5	295.8	153	1020	1477.3	16,043	14,565.7
VI	10.2	336.6	210.8	2754	3311.6	11,263	7951.4
VII	18.7	207.4	71.4	275.4	572.9	9031	3302
Mean	13.36	267.63	136.97	1331.34	1749.30	10,442.86	7956.97
Std. dev.	7.31	96.42	47.59	936.56	1049.13	3664.87	4010.03

fraction ranged between 70.6% at station VI and 93.66% at station VII. This reflects the greater tendency of Fe to be in the lattice structure of the sediment. Several authors have observed that the majority of Fe content was found in the residual fraction [26]. The sum of all fractions content, except residual, was 1749.3 ± 1049.13 mg kg^{-1} and represented 16.8% of the total. Among the non-residual fractions, the organic fraction constitutes the greatest amount of Fe throughout the whole study. Its mean content reached to 1331.34 ± 936.6 mg kg^{-1}. Organic matter plays an important role in trapping through the direct adsorption, complexation processes and the formation of insoluble sulphides. Clark *et al.* [27] showed that mangrove forest sediments can provide a sink for trace metals, because the mangroves create a baffle that promotes the accumulation of fine grained organic matter-rich sediment, which is usually sulphidic due to the presence of sulphate-reducing bacteria. The amount of Fe present in the other fractions was as follows; 13.36 ± 7.31 mg kg^{-1} for exchangeable, 267.63 ± 96.42 mg kg^{-1} for carbonate fraction and 136.97 ± 47.59 mg kg^{-1} for Fe–Mn oxide fraction. The concentration of Fe–Mn oxides fraction was relatively low compared with those found in the organic fraction (table 4). The relative percentage of exchangeable represented less than 1% of the total iron content; the carbonate form ranged from 1.84 to 3.42%; Fe–Mn oxides ranged from 0.79 to 2.29% and organic fraction ranged between 3.05 and 24.45% (figure 3).

The relative percentage of Mn bounded to the exchangeable and water soluble fraction was in the order: site VI (0.29%) < site I & III (0.35%) < V (0.45%) < site II (0.49%) < IV (1.02) and < VII (1.28%). The levels of Mn concentration in the carbonate fraction ranged

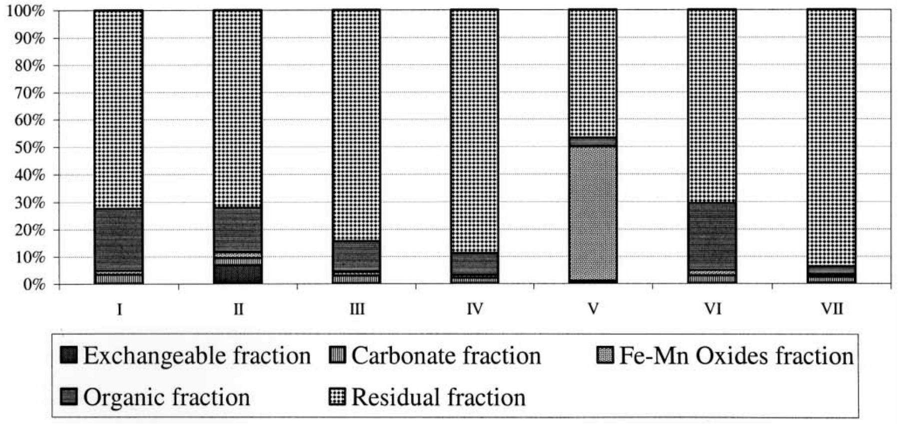


Figure 3. Percentage of Fe in each fraction, to the total content of mangrove sediments – Red Sea.

Table 5. Mn concentrations (mg kg^{-1}) in each fraction of mangrove sediments – Red Sea.

Station	Exchangeable fraction	Carbonate fraction	Fe–Mn oxides fraction	Organic fraction	Sum of all fractions	Total conc.	Residual fraction
I	0.96	33.6	7.2	39.6	81.36	271.4	190.04
II	3.36	15.6	9.6	8.4	36.96	68.6	31.64
III	0.96	110.4	25.2	10.8	147.36	273.5	126.14
IV	1.98	26.4	9.6	25.2	63.18	193.7	130.52
V	1.44	78	61.3	18	158.74	321.8	163.06
VI	0.96	62.4	31.2	32.4	126.96	333.2	206.24
VII	2.4	32.4	10.8	8.4	54	187.7	133.7
Mean	1.72	51.26	22.13	20.40	95.51	235.70	140.19
Std. dev.	0.92	33.90	19.54	12.39	48.43	92.75	56.99

from 15.6 mg kg^{-1} at site II, to 110.4 mg kg^{-1} at site III (table 5), representing 50% of the non-residual fraction. The concentration of Mn associated with organic fraction ranged between 8.4 and 39.6 mg kg^{-1} with a mean value of 20.4 ± 12.39 mg kg^{-1} (table 5).

The relative percentage of Mn bounded to residual fraction ranged from 46.1 % (sites II, III) to 71.23% (site VII) of the total concentration (figure 4). The high concentrations of Mn and Fe in the residual form may be due to the mineralogical composition variation within the study area. The results of Mn geochemical association forms revealed that more Mn was associated with the non-residual fraction, which increased potential Mn mobility and bioavailability.

3.3.2 Zinc (Zn) and copper (Cu). The relative percentage of Zn in the non-residual from was much greater than that of the residual fractions (figure 5). The concentration of Zn associated with the non-residual fractions on the investigated area ranged from 29.32 to 53.35 mg kg^{-1} (table 6) with a mean value of 39.46 ± 7.61 mg kg^{-1}. The significant higher Zn content in the non-residual form indicates that the mobility and potential bioavailability of Zn in the sediments are significant. The remaining residual form was relatively high at site VI (27.28 mg kg^{-1}, 38.59%) and decreased to the lowest level (1.48 mg kg^{-1}, 4.81%) at site IV. Also the Zn content remaining as the residual form at site V (15.25 mg kg^{-1}, 22.23%) was more or less comparable (table 6) to the content at site III (15.9 mg kg^{-1}, 31.55%). The major content of Zn was bound with the organic and carbonate fractions, which represented

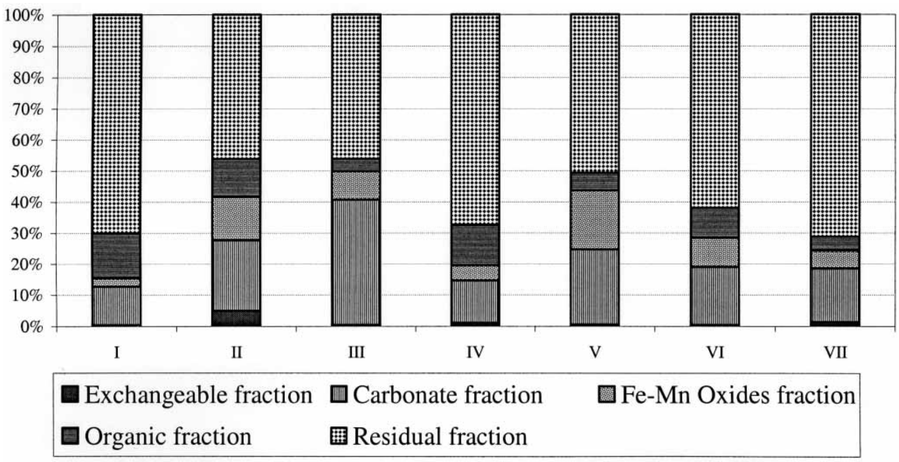


Figure 4. Percentage of Manganese in each fraction to the total content of mangrove sediments – Red Sea.

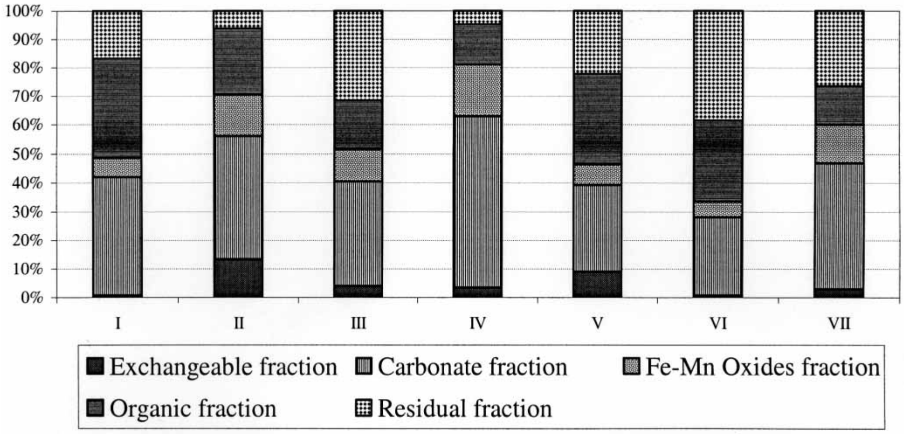


Figure 5. Percentage of Zn in each fraction to the total content of mangrove sediments – Red Sea.

more than 50% of the total concentration (figure 5). The concentration of Zn bound to an exchangeable fraction revealed the highest percentage at sites II and V (13.39 and 8.97%, respectively) and decreased considerably at sites I (0.31 mg kg^{-1}, 0.67%), II (0.42 mg kg^{-1}, 0.59%), IV (1.22 mg kg^{-1}, 3.96), VII (1.41 mg kg^{-1}, 2.84%) and III (2.00 mg kg^{-1}, 3.97%).

The distribution of Zn content in various chemical forms was the opposite to the extent of Zn contamination in mangrove Red Sea sediments. This was clear from the highest potential Zn mobility and bioavailability in these sediments. The highest levels of Zn in the non-residual fraction were recorded as a comparison to those found in the residual form. Li *et al.* [17] showed that calcium carbonate is a strong absorbent for forming complexes with Zn as double salts ($CaCO_3$ $ZnCO_3$) in the sediments. Förstner and Wittmann [28] observed that the co-precipitation of Zn with carbonates is an important chemical form when organic matter and iron oxide are low in concentration within the sediment.

The results of sequential chemical extraction of Cu in mangrove Red Sea sediments are found in table 7. The concentration of total Cu in the sediments ranged from 17.5 to 22.5 mg kg^{-1} with an average of 21.43 ± 2.44 mg kg^{-1}. The mean values of different Cu fractions were: 1.31 ± 0.2 mg kg^{-1} for exchangeable, 12.04 ± 3.03 mg kg^{-1} for carbonate, 1.94 ± 0.43 mg kg^{-1} for Fe–Mn oxides, 2.97 ± 0.60 mg kg^{-1} for organic matter and 3.16 ± 2.33 mg kg^{-1} for residual fractions. The exchangeable fraction was contributor for Cu concentration; its relative percentage ranged between 4.8 and 8%. Except for sites II and IV (1.6 mg kg^{-1}), all sites had Cu contents of 1.2 mg kg^{-1}. Cu in the sediments was dominant in the carbonate fraction, as it ranged from 32 to 67.56% (figure 6). This indicates that

Table 6. Zn concentrations (mg kg^{-1}) in each fraction of mangrove sediments – Red Sea.

Station	Exchangeable fraction	Carbonate fraction	Fe–Mn oxides fraction	Organic fraction	Sum of all fractions	Total conc.	Residual fraction
I	0.31	19.1	3.1	15.9	38.41	46.2	7.79
II	5.81	18.5	6.3	10.1	40.71	43.4	2.69
III	2	18.4	5.6	8.5	34.5	50.4	15.9
IV	1.22	18.2	5.6	4.3	29.32	30.8	1.48
V	6.15	20.8	4.9	21.5	53.35	68.6	15.25
VI	0.42	19.5	3.8	19.7	43.42	70.7	27.28
VII	1.41	21.9	6.5	6.7	36.51	49.7	13.19
Mean	2.47	19.49	5.11	12.39	39.46	51.40	11.94
Std. dev.	2.47	1.38	1.27	6.67	7.61	14.07	8.90

Table 7. Cu concentrations (mg kg^{-1}) in each fraction of mangrove sediments – Red Sea.

Station	Exchangeable fraction	Carbonate fraction	Fe–Mn oxides fraction	Organic fraction	Sum of all fractions	Total conc.	Residual fraction
I	1.2	13.6	1.6	3.2	19.6	25	5.4
II	1.6	6.4	2.4	2.4	12.8	20	7.2
III	1.2	15.2	2.4	3.2	22	22.5	0.5
IV	1.6	12	1.6	2.4	17.6	20	2.4
V	1.2	9.86	1.6	3.2	15.86	17.5	1.64
VI	1.2	12.8	1.6	4	19.6	22.5	2.9
VII	1.2	14.4	2.4	2.4	20.4	22.5	2.1
Mean	1.31	12.04	1.94	2.97	18.27	21.43	3.16
Std. dev.	0.20	3.03	0.43	0.60	3.11	2.44	2.33

carbonate may be the major carrier of Cu in the sediments. Han *et al.* [29] reported that Cu concentration in the carbonate fraction might be dominant as the available form of Cu within marine bivalves under natural physicochemical conditions. Organic matter also plays an important role in the chelating and complex formation of Cu, due to the high formation constants of organic Cu compounds (Stumm and Morgan [30]). The relative percentage of Cu content in the organic fraction was relatively high (figure 6) and ranged from 10.67% (2.4 mg kg^{-1} at site VII) to 18.29% 3.2 mg kg^{-1} at Site V. In highly polluted areas of Vill-franche Bay, 80% of Cu was mostly bound to the organic matter/sulfide fraction [31]. In the present study, the organic matter content was relatively low ranging from 2.01 to 3.72% (table 3). The distribution of the relative percentage of Cu in the Fe–Mn oxides similar to that found in the organic fraction, ranged from 6.4% at Site I to 12% at Site II. Li *et al.* [17] reported that Fe–Mn oxides became more significant for binding Cu when the content of organic matter was low. The high level of Cu content in the carbonate fraction, as well as the other forms in the present study, indicated that Cu was considered to be more bioavailable in these sediments. The results shown in table 6 revealed no significant differences in the total Cu concentration and chemical fractions between the samples of mangrove Red Sea sediments.

3.3.3 Lead and cadmium. The results of Pb content in the different fractions are shown in table 8. The average concentrations were 7.00 ± 1.00 mg kg^{-1} for exchangeable fraction, 30.86 ± 5.64 mg kg^{-1} for the carbonate fraction, 17.14 ± 4.60 mg kg^{-1} for Fe–Mn oxides;

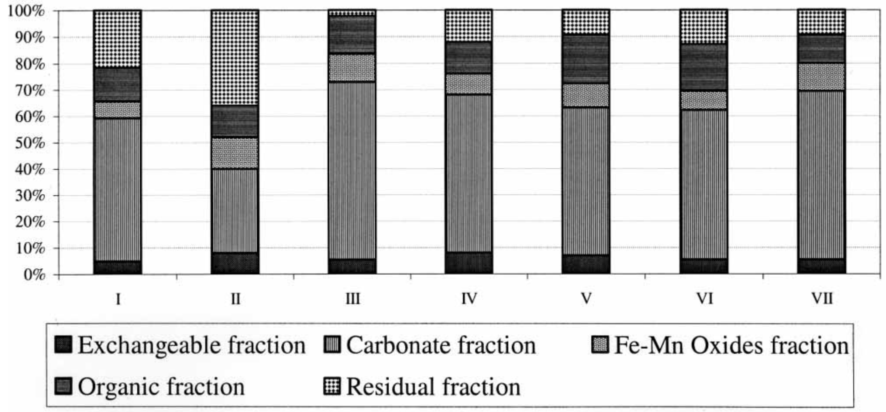


Figure 6. Percentage of Cu in each fraction, to the total content of mangrove sediments – Red Sea.

Table 8. Pb concentrations (mg kg^{-1}) in each fraction of mangrove sediments – Red Sea.

Station	Exchangeable fraction	Carbonate fraction	Fe–Mn oxides fraction	Organic fraction	Sum of all fractions	Total conc.	Residual fraction
I	6	34	14	18	72	86.8	14.8
II	8	22	26	24	80	168.8	88.8
III	8	32	14	24	78	83.8	5.8
IV	6	28	18	18	70	75	5
V	7	28	14	18	67	75	8
VI	6	40	14	24	84	93.8	9.8
VII	8	32	20	24	84	112.5	28.5
Mean	7.00	30.86	17.14	21.43	76.43	99.39	22.96
Std. dev.	1.00	5.64	4.60	3.21	6.83	33.20	30.13

21.43 ± 3.21 mg kg^{-1} for the organic fraction and 22.96 ± 30.13 mg kg^{-1} for the residual form. The residual form represents the lithogenous portion of metal in the sediments, while the sum of other forms, *i.e.*, exchangeable, carbonate, Fe–Mn oxides and organic fractions represent the portion of metal of non-lithogenous origin, *i.e.* anthropogenic [32]. The results in figure 7 show a markedly high content of Pb in the mangrove sediments. This is demonstrated by the high relative percentage of Pb in the non-residual form, ranging from 47.39% to 93.33%. Significant amounts of Pb were presented within carbonate and organic fractions. Beltagy [33] showed that Pb and Zn were both present in relatively high concentrations in the carbonate phase, and the sediments from the African side of the Red Sea had higher Pb content than sediments from the Arabian side.

The average total concentration of Cd in mangrove sediments was 6.75 ± 2.48 mg kg^{-1} (table 9). Site V had higher total Cd concentration (11.7 mg kg^{-1}) than other sites. Most of the Cd found in the non-residual fraction, ranged from 76 to 98%. Figure 8 shows more than 50% of the total Cd contents associated with the carbonate and Fe–Mn oxides fractions. The relatively high content of Cd bound to Fe–Mn oxides was in agreement with previous works [34]. The different forms of Cd were in the order: carbonate (2.33 ± 0.77 mg kg^{-1}) > Fe–Mn oxides (1.84 ± 0.58 mg kg^{-1}) > exchangeable (0.95 ± 0.37 mg kg^{-1}) > organic (0.83 ± 0.30 mg kg^{-1}) > residual (0.80 ± 0.92 mg kg^{-1}). The bioavailability of Cd in the exchangeable fraction ranged from 8.61 to 22.86% of the total concentration. The concentration of Cd associated with organic fraction was similar to the exchangeable fraction at all sites

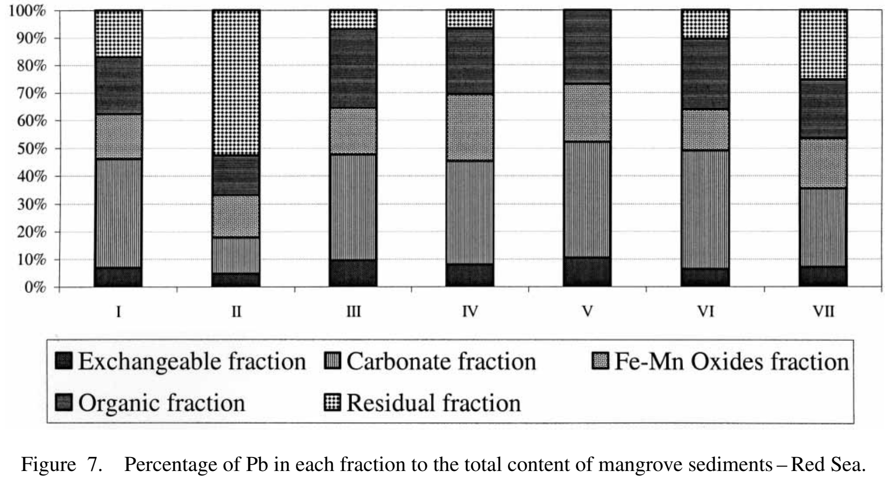


Figure 7. Percentage of Pb in each fraction to the total content of mangrove sediments – Red Sea.

Table 9. Cd concentrations (mg kg^{-1}) in each fraction of mangrove sediments – Red Sea.

Station	Exchangeable fraction	Carbonate fraction	Fe–Mn oxides fraction	Organic fraction	Sum of all fractions	Total conc.	Residual fraction
I	1.04	1.6	1.04	0.62	4.3	4.55	0.25
II	1.56	3.4	2.7	1.25	8.91	11.7	2.79
III	0.73	1.7	1.66	0.62	4.71	5.6	0.89
IV	0.62	3.37	1.87	0.62	6.48	7.2	0.72
V	0.52	2.12	1.46	0.62	4.72	5.2	0.48
VI	0.94	1.7	1.66	0.83	5.13	5.2	0.07
VII	1.25	2.4	2.49	1.25	7.39	7.8	0.41
Mean	0.95	2.33	1.84	0.83	5.95	6.75	0.80
Std. dev.	0.37	0.77	0.58	0.30	1.71	2.48	0.92

except site IV. Bruland [35] showed that the biogeochemistry of Cd is strongly dominated by the organic matter cycle. In the marine environment, Cd is fixed by phytoplankton in the surface water and transported toward the floor with the remains of these organisms, when organic detritus as decomposed Cd is liberated with other mineralization products.

Pb like other trace metals is controlled by the presence of fine-grained sediments which absorb more metals than sandy sediments, as well as the presence of Fe and Mn oxides, carbonate minerals and organic matter. Previous studies revealed a low proportion of reactive metals in mangrove sediments, which was mainly attributable to the formation of metal sulfide and metal organic matter complexes [27, 36–38].

The results by Kehrig *et al.* [39] reported that 87% of trace metal concentration (Pb, Cd, Cu, Fe) were not bioavailable due to the elevated organic carbon (16–21%) and sulphide content in the sediments.

Recent coral and reef building organisms with carbonate skeletons may be contributed by an increase of trace metals in the sediments during diagenetic sedimentation processes [32].

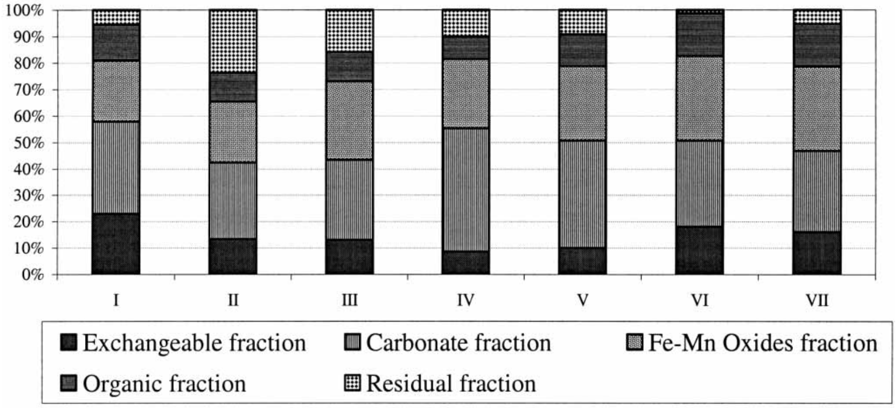


Figure 8. Percentage of Cd in each fraction to the total content of mangrove sediments – Red Sea.

4. Conclusions

One environmental aspect that has not been previously studied in this area of investigation, is the occurrence of trace metals in the mangrove sediments associated with the different geochemical forms. Trace metals present in the mangrove sediments showed a difference in the pattern of partitioning among different chemical forms of the sediments. Partitioning patterns also varied among the sampling sites except for Cu and Pb in the exchangeable fraction. Mn, Zn, Cu and Pb showed strong affinity for carbonate fraction in all sampling sites. Significant amounts of Cu and Pb were present in the loosely bound fraction *i.e.* exchangeable form. Some metals such as Pb tend to be concentrated in carbonate and organic fractions.

References

[1] B.G. Hatcher, R.E. Johannes, A.I.C. Robertson. Review of research relevant to the conservation of shallow tropical marine ecosystems. *Oceanogr. Mar. Biol.*, **27**, 337 (1989).
[2] A.I. Robertson. Plant animal interactions. Environment and the structure and function of mangrove forest ecosystems. *Aust. J. Ecol.*, **16**, 433 (1991).
[3] E.A. Gihad. Camel's impacts on Mangrove plants. Symp. on conservation of mangrove ecosystems. UAE University, 15–17 December (1996).
[4] M.A. Shridah. Heavy metals in mangrove sediments of the United Arab Emirates Shoreline (Arabian Gulf). *Water Air Soil Pollut.*, **116**, 523 (1999).
[5] M.A. Shridah. Chemistry of the mangrove waters and sediments along the Arabian Gulf Shoreline of the United Arab Emirates. *Indian J. Mar. Sci.*, **29**, 224 (2000).
[6] G. Rodriguez. Structure and production in Neotropical Mangroves. *Trends Ecol. Evolut.*, **2**, 264 (1987).
[7] G. Cintron-Molero, Y. Schaeffer-Vovelli. The use of mangroves as indicators of sea-level change. Symp. on conservation of mangrove ecosystems. UAE University, 15–17 December (1996).
[8] Y.A. Al-Nabulsi. Mangrove habitats effects on coastal erosion and organic sedimentation. Symp. on conservation of mangrove ecosystems. UAE University, 15–17 December (1996).
[9] L. Hakanson. Sediment variability. In *Sediment Toxicity Assessment*, G.A. Burton (Ed.), pp. 19–36, Lewis publishers, Boca Raton, FL (1992).
[10] S.K. Gupta, K.Y. Chen. Partitioning of trace metals in selective chemical fractions of near sediments. *Environ. Lett.*, **10**, 129 (1975).
[11] A. Tessier, P. Campbell, M. Bison. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.*, **51**, 844 (1979).
[12] R.M. Harrison, D.P.H. Laxe, S.J. Willson. Chemical association of lead, cadmium, copper and zinc in street dusts and roadside soils. *Environ. Sci. Technol.*, **15**, 1378 (1981).
[13] L.M. Shuman. Fractionation method for soil microelements. *Soil Sci.*, **140**, 11 (1985).
[14] W.P. Miller, D.C. Martens, L.W. Zelazny. Effects of sequence in extraction of trace metals from soils. *Soil Sci. Soc.*, **50**, 594 (1986).
[15] C. Kheboian, C.E. Bauer. Accuracy of selective extraction procedure for metal speciation in model aquatic sediments. *Anal. Chem.*, **59**, 1417.
[16] N.D. Kim, J.E. Fergusson. Effectiveness of a commonly used sequential extraction technique in determining the speciation of cadmium in soils. *Sci. Total Environ.*, **105**, 191 (1991).
[17] X. Li, Z. Shen, O.W.H. Wai, Y. Li. Chemical partitioning of heavy metal contaminants in sediments of the pearl River Estuary. *Chem. Speciation Bioavailability*, **12**, 17 (2000).
[18] W.M. Moufaddal. Assessment of anthropogenic and natural changes along the Red Sea coastal zone between Ras Gemsha and Safaga, Egypt, using multidata satellite data. PhD Thesis, Saint Petersburg State University (2002).
[19] M.A. Shriadah, M.A. Okbah, M.S. El-Deek. Trace metals in the water columns of the Red Sea and the Gulf of Aqaba, Egypt. *Water Air Soil Pollut.*, **153**, 115 (2004).
[20] W.E. Dean. Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition comparison with other methods. *J. Sedimentry Petrology*, **44**, 242 (1974).
[21] C.A. Black. Methods of soil analysis. *Agron. Amer. Soc. Madison*, **9**, 1379 (1965).
[22] B. Oregioni, S.R. Aston. 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, (1984).
[23] M. Kersten, U. Förstner. Effect of sample pretreatment on the reliability of solid speciation data of heavy metals: implications for the study of early digenetic processes. *Mar. Chem.*, **22**, 299 (1987).
[24] D.L. Graf. Geochemistry of carbonate sediments and sedimentary carbonate rocks. *Div. III, Surveyb Circ.*, **297**, parts 1–5 (1960).
[25] J.R. Goldsmith, D.L. Graf, H.C. Heard. Lattice constants of the calcium–magnesium carbonates. *Am. Mineralogist.*, **43**, 84 (1961).

[26] M.A. Shata, M.S. El-Deek, M.A. Okbah. Fractionation of Mn, Fe, Zn and Cu in sediments of khor kalabsha, Lake Nasser, Egypt. *Chem. Ecol.*, **8**, 89 (1993).

[27] M.W. Clark, D.M. McConchie, D.E. Lewis, P. Saenger. Redox stratification and heavy metal partitioning in Avicennia dominated mangrove sediments a geochemical model. *Chem. Geol.*, **149**, 147 (1998).

[28] U. Förstner, G.T.W. Wittmann. *Metal Pollution in the Aquatic Environment*, 2nd edn. Springer Verlage, Berlin (1979).

[29] B.C. Han, W.L. Jeng, T.S. Hung, M.Y. Wen. Relationship between copper speciation in sediments and bioaccumulation by marine bivalves of Taiwan. *Environ. Pollut.*, **91**, 33 (1996).

[30] W. Stumm, J.J. Morgan. *Aquatic Chemistry*, 2nd edn, p. 780, Wiley Interscience, New York (1981).

[31] F. Rapin, G.P. Nembrini, U. Förstner, J.I. Garcia. Heavy metals in marine sediment determined by sequential chemical extraction and their interaction with interstitial water. *Environ. Technol. Lett.*, **4**, 387 (1983).

[32] I.H. El-Sokkary. Assessment and speciation of chromium, nickel, lead and cadmium in the sediments of the River Nile, Egypt. *Sci. Total Environment*, **97**/**98**, 455 (1990).

[33] A.I. Beltagy. Elemental geochemistry of some recent marine sediments from north Red Sea. *Bulletin Institute Oceanography & Fisheries. ARE*, **10**, 1 (1984).

[34] J.T. Szakova, I. Pavel, D. Balik, V. Vanek. The sequential analytical procedure as a tool for evaluation of As, Cd and Zn mobility in soil. *J. Anal. Chem.*, **363**, 594 (1999).

[35] K.W. Bruland. Oceanic distributions of cadmium, zinc, nickel and copper in the North Pacific. *Earth Planet Lett.*, **47**, 176 (1980).

[36] L.D. Lecerda, C.E. Rezende, G.T. Aragon, A.R. Ovalle. Iron and chromium transport and accumulation in a mangrove ecosystem. *Water Air Soil Pollut.*, **57**/**58**, 513 (1991).

[37] N.F.Y. Tam, Y.S. Wong. Spatial and temporal variations of heavy metal contamination in sediments of mangrove swamp in Hong Kong. *Mar. Pollut. Bull.*, **31**, 254 (1995).

[38] W. Machado, E.V. Silva-Filho, R.R. Oliveira, L.D. Lacerda. Trace metal retention in mangrove ecosystems in Guanabara Bay, SE Brazil. *Mar. Pollut. Bull.*, **44**, 1277 (2002).

[39] H.A. Kehrig, F.N. Pinto, I. Moreira, O. Malm. Heavy metals and methylmercury in tropical coastal estuary and a mangrove. *Braz. Org. Geochem.*, **34**, 661 (2003).