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Full Length Research Paper

Geochemistry in surface sediments of the Kwar Katib lagoon, Red sea, Yemen

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The aim of this work is to gather information on the distribution of some metals in the surface sediments of the Kwar Katib lagoon, northern side of Hodeidah city, Yemen, Red Sea. Twenty samples were collected from this lagoon. Heavy metals such as (Fe, Al, Mn, Cu, Ni, Zn, Pb, Cr, Ti, La, Sr, Ba, Co and As) have been analyzed in the samples.

The concentration of organic matter is related by fine sediments and biological activities. The enrichment factors (EF), contamination factor (CF) geoaccumulation index (Geo-I) have been calculated as a criterion to assess if their concentrations represent contamination levels or can be considered Unpolluted and unpolluted - moderately polluted. Analytical results have been elaborated by using a Geographical Information System (GIS) software to show metals accumulation areas. Statistical analysis results have showed metals distribution in the Kwar Katib lagoon is principally influenced by Hodeidah port activities in the southern lagoon.

Keywords: heavy metals, Sediment, contamination lagoon, Kwar Katib, GIS, Red Sea

INTRODUCTION

Coastal environments receive sediment inputs from many different sources, including allochthonous terrestrial materials transported from land by rivers and groundwater, allochthonous marine materials brought in through tidal action from the open sea (Gon˜et al. 2003). Physical processes, such as currents, waves, tides, surges, etc., are usually very effective in coastal sedimentary environments.

Heavy metals are among the most common environmental pollutants and their occurrence in coastal sediment indicated the presence of both natural and anthropogenic sources. Heavy metals are natural components of the earth's crust, and that are transported via river discharge, marine dumping and aeolian processes (Conroy et al., 1996; Prange and Dennison, 2000; Radenac et al., 2001, Ruilian et al., 2008). Human activities such as industrial and municipal effluents, landfill leaching, non-point source runoff and atmospheric deposition have increased the flux of heavy metals in coastal environments. When these metals discharged into the aquatic environment, the metal is partitioned between sediment and water column phases (Füller et al., 1990 and Moore 2009).

Heavy metals deposited in coastal systems can become incorporated into different components of the sediment (particles, water, organisms), and are controlled by physical, chemical or biologic processes (Prange and Dennison, 2000; Locatelli and Torsi, 2000; Kalvins et al., 2000). Metals are least soluble in water get adsorbed and accumulated in sediments. Heavy metals may be recycled via chemical and biological processes, within the sedimentary compartment (Förstner, 1984; Tessier and Campbell, 1987). The accumulation of heavy metal contaminants in sediments can pose serious environmental problems to the surrounding areas such as water quality and bioassimilation.

The distribution and accumulation of heavy metals in coastal environments sediments are influenced by sediment texture, mineralogical composition, reduction/oxidation state, adsorption and desorption processes and physical transport (Manahan, 2000, Buccolieri et al., 2006). Moreover, metals can be absorbed from the water column onto fine particles surfaces and move thereafter towards surface sediments; metals participate in various biogeochemical mechanisms, have significant mobility, can affect the ecosystems through bio-accumulation and bio-magnification processes and are potentially toxic for environment and for human life.

Coastal lagoons are fragile ecosystems widely distributed

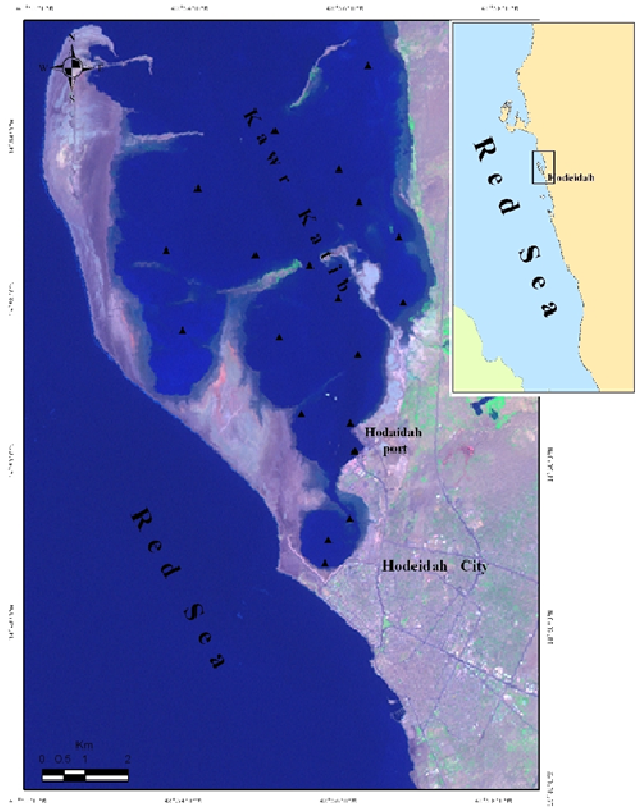

Figure 1: study area and sampling sites of Kawr Katib lagoon

distributed along the coastal areas worldwide and now subjected to an increasing anthropogenic pressure. Most of them have a high biological diversity, rich and complex food chains and may constitute important fishery and nursery grounds (Ruiz et al., 2006).

The analysis results of the sediment samples from Yemen coastal region of the Red Sea showed that mainly natural with some anthropogenic inputs are the sources of trace metals to region. This is indicated by the low concentrations of all metals except for Cd, Co and Pb in seawater and sediments, which designate possible anthropogenic sources (Al-Shiwafi et al., 2005). Sagheer (2008) discussed the minerals composition of sediments in the Kwar Katib lagoon, and recorded the main composition minerals of lagoon sediments are quartz, feldspars, hornblende, pyroxene and biotite and aluminosilicates minerals.

Kwar Katib is the important lagoon in Yemen Red Sea, is geographically located between 42°52 41 and 42° 57 09 E (longitude), and 14° 48 46 and 14°55 35 N (latitude), north the Hodeidah city. This lagoon is elongated in a north–south direction and extends about 9 Km. It is shallow (generally 1–10 m average depth) and discontinuous. It has an area of 54.7 km^2, with range in wide from 35 to 6970 meters (Figure. 1).

The Kwar Katib lagoon is enclosed in the irregular embayed Hodeidah shoreline and Kwar Katib. It is generally protected from open sea circulations by Ras Katib spit. Sediments in the lagoon are derived from terrigenous inputs at Wadi Siham mouths as well as carbonate inputs from coral debris. The bottom sediments of the lagoon vary from mud, sand and gravels to local skeletal fragments and coral debris. It is rich in mangroves, seagrasses and small patch of coral reef. The slope of the bottom surface is generally less than 5◦. The aim of this paper is to gather information on the distribution of heavy metals (Fe, Al, Mn, Ba, Cu, Ni, Zn, Pb, Cr, Ti, La, Sr, Co and As), to provide preliminary data on the environmental conditions in the surface sediments of Kawr Katib lagoon.

MATERIAL AND METHOD

The Superficial sediment samples were collected from the selected sites by hand, while the bottom of lagoon sediment samples were collected using a grab sampler, from 20 sites in the Kawr Katib lagoon (figure. 1). The position of each site was determined using a global positioning system (GPS) receiver. The samples were washed and dried in a steamer between 35 and 40 C.

The grain size analysis was carried out using the method described by Folk (1980).The sand and gravel fractions were sieved at diameters, and the mud fractions were determined by the pipette method. The sediment texture classes proposed by Blair and McPherson (1999)

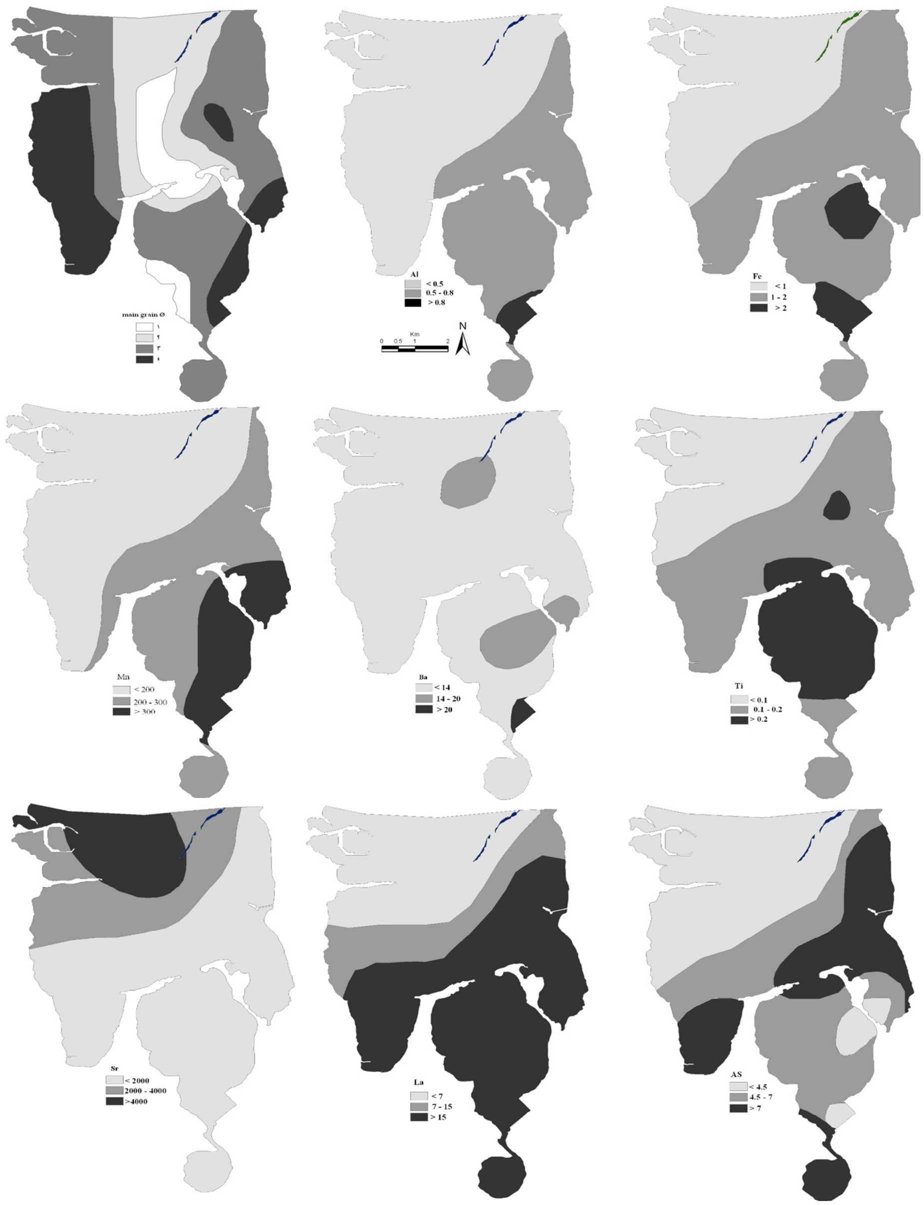

Figure 2: Spatial distribution of grain size and heavy metals (Al, Fe, Mn, Ba Ti, La and As) in the Kwar Katib lagoon

were applied for the study samples by using SEDSTAT program. The total concentrations of heavy metals (Fe, Al, Mn, Ba, Cu, Ni, Zn, Pb, Cr, Ti, La, Sr, Co and As) have been determined in politic fraction (minus 63 Am) of twenty surface sediments from the Kawr Katib lagoon. These metals were determined using Atomic Absorption Analyst/800 by ACME Analytical Laboratories LTD in Canada. Moreover, analytical results have been elaborated by using Geographic Information System (GIS) Arc-Info 10 software, to show distribution of the heavy metals accumulation. Multivariate statistical analysis has been used to evaluate the possibility todistinguish sampling sites, in relation to their geographical location.

RESULTS

Distribution Sediments

The grain size distribution and related textural classification of the surface sediments in the Kwar katib lagoon are summarized in figure (2). The surface sediments of the investigated area ware found to consist of a variety of textural classes, gravely sand, muddy sand and sandy mud. Fine grained sediments referred to as

Figure 3: Spatial distribution of heavy metals (Cr, Pb, Co, Cu, Ni and Zn),CF and I geo values in the Kwar Katib lagoon

silt, with average (0.8- 32.8%) where coarse grained sediments contain higher sand (99- 67.2%). Detailed microscopic investigations of the sand fractions of the sediments samples revealed present that both terrigenous and biogenic materials are present in varying abundance. Coral reef, gastropods, bivalves and foraminifers are the main biogenic constituents. Quartz, feldspars, mica, clay minerals represents the terrigenous constituents.

The highest concentration of organic carbon (OC) was found at Hodeidah Port (9.3%) while lowest concentration Was located at Katib spit (0.8%). The average concentration of OC is 2.3%.

Heavy Metals Distribution

Results of analysis for the studied heavy metals are shown in figures (2 and 3). The heavy metals concentration in surface sediments showed a wide range of values. Al and Fe contents vary respectively from 0.13 % to 1.33% and from 0.23% to 2.89 %. It is noticeable that there is a progressive increase in the contents of these two metals towards the south of the lagoon.

The Mn, Ti, Ba and La concentrations vary in general, from 41 to 5431ug/g for Mn; from 0.008 to 0.255 ug/g for Ti; from 8 to 26 ug/g for Ba, and from 1 to 21 ug/g for the La. The range concentrations (ug/g) was 99- 6978 for Sr; 2.6 – 9.9 for As; 2.1 – 33.2 for Ni and 0.8 – 12.1 for Co. the high concentration of Cr is 34 and the low concentration is 5 ug/g. The concentration of Cu varies between 2.2 and 113 ug/g while Pb between 1.5 and 13.8. also the high concentration of Cr is 115 and the low concentration is 5 ug/g.

DISCUSSION

The fine grains sediments in the Kwar Katib lagoon increase toward the south and decrease toward the north. The distribution of the grain size sediments within the lagoon is governed, mainly, by the marine dynamics and source sediments. The sediments in the north of the lagoon are composed terrigenous and biogenetic (reef fragments) sediments and effect by marine dynamics, while the south side is mainly terrigenous sediments and semi close lagoon.

The concentration of organic matter is related to fine sediments and biological activities. The relatively high concentration of OC at Hodeidah port may be attributed to the human activities in the port.

The concentration of the Fe and Mn are mainly related to the distribution of ferromagnesian minerals (hornblende, pyroxene and biotite) enrichment in oxide and/or oxhydroxide minerals. The Al is related to aluminosilicates and feldspar minerals. Sagheer (2008) studied the mineralogy in the sediments of the lagoon, he is recorded the ferromagnesian, aluminosilicates and feldspar minerals.

The concentration of the Sr is related to biogenic sediments in the north of the study area. The other heavy metals concentration are associated with the fine grains and source sediments (aluminosilicates and ferromagnesian minerals). According to Francolls (1988), most of the Pb derived from seawater is adsorbed by colloidal fraction of sediments probably the clay minerals. Caccia et al., (2003), revealed a positive correlation of Al with elements Co, Cr, Cu, Ni, Pb and Zn suggesting that these metals are strongly associated with the fine fraction of the sediments (aluminosilicates). Carman et al., (2007) found that the dispersal of heavy metals in sediments is related to the transport and deposition processes from sources to sinks in the coastal area. Taher and Arafa (2000) suggested that the sediments source is a major factor controlling the elemental spatial variations. Rodriguz et al (2010) showed relatively high organic carbon contents and high levels of Cr, Cu, Ni, Pb and Zn. In the Red Sea of Yemen the main natural sources of trace metals are from rock weathering, mineral dissolution in sediments and regional dust transport. Minor anthropogenic inputs are local wastes from coastal facilities and human and developmental activities in main coastal cities (Al-Shiwafi et al., 2005). Heavy metals distribution in the lagoon is related to grain size sediments, mineralogical composition and human activity in the Hodeida port.

The measured heavy metal concentration of the studied sediments are compared with average shale standard (Turekian and Wedepohl, 1961 and Al-Shiwafi et al., 2005), also with base line levels of metals in sediments of the Al-Luhayyah coastal area, situated about 40 km north of the Kwar Katib by Sagheer (2004). Average shale composition is a global reference basis and satisfies the basic requirement as a source of uncontaminated argillaceous sediment, when no local background values are available (Taher and Arafa, 2000).

To reduce the metal variability caused by variations in grain size and composition, and to identify anomalous metal contributions, geochemical normalization of the heavy metal data to conservative elements such as Al (Rule, 1986, chen and Kandasamy 2008) has been used in this study. Besides, anthropogenic input of Al is a very rare phenomenon (Selvaraj et al., 2004). Also Al has been commonly used as a reference element, not only in order to minimize grain size effects, but also to determine the primary source rocks and the accompanying soils and deposits in aquatic environments (Ergin et al., 1996 and Dong et al., 2012). Normalization can also be applied to determine enrichment factors (EFs) which provide a tool to evaluate sediment quality. EFs close to unity point to crustal origin and >10 are considered as non-crustal sources (Nolting et al. 1999). The enrichment factors (EFs) values were calculated as following equation:

$[metal/Al]_{Sample} / [metal / Al]_{background}$ *Rule (1986)*

Maanan et al. (2004) separated the sediment of Sidi Moussa lagoon into two

Groups: (i) non-enriched elements (EF > 1): Zn, Ni and Cr;

(ii) slightly impoverished elements (EF < 1): Fe and Cu

The metals have EFs >1 thereby suggest their enrichments in offshore sediments likely due to dumped iron and steel slag (chen and Kandasamy 2008). The interpretation of EFs values as suggested by Birth (2003) for the metals studied is outlined as following classification:

EF < 1: no enrichment,
EF = 1 – 3: minor enrichment,
EF = 3 – 5: moderate enrichment,
EF = 5 – 10: moderate to severe enrichment,
EF = 10 – 25: severe enrichment,
EF = 25 – 50: very severe enrichment and
EF > 50: extremely severe enrichment

Table (1) show the enrichment factor of the heavy metals in the Kwar Katib lagoon sediments.

Table 1: enrichment factor value of the heavy metal in the lagoon sediments

metal	Enrichment Factor	metal	Enrichment Factor
Fe	0. 86 - 1.85	Co	0.10 - 0. 21
Mn	0.13 – 0.31	Cr	0.10 - 0.91
As	0.10 -. 92	Cu	0.13 – 0.80
Ba	0.12 - 0.33	Ni	0.14 – 0.33
Ti	0.03 – 0.31	Pb	0.06 - 0. 27
Li	0.12 - 0.33	Zn	0.24 - 0.38

Table 2: Hökanson classification for the enrichment factor (Hökanson 1980)

Cf value	class	Quality of sediment
Cf < 1	1	Low Contamination Factor
1≤ Cf < 3	2	Moderate Contamination Factor
3≤ Cf < 6	3	Considerable Contamination Factor
Cf ≥ 6	4	Very high Contamination Factor

Table 3: Müller's classification for the I_{geo} (Müller, 1981)

I geo value	Class	Quality of sediment
≤ 0	0	Unpolluted
0-1	1	From unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	From moderately to strongly polluted
3-4	4	Strongly polluted
4-5	5	From strongly to extremely polluted
> 5	6	Extremely polluted

According to EF calculations and classification of Birth (2003), concentrations of heavy metals are no enrichment. The level of contamination expressed by the contamination factor (CF); (Hökanson 1980), it was calculated as the following:

$CF = [\text{metal content}]_{Sample} / [\text{metal content}]_{background}$

According to Hökanson (1980) the contamination factor was classified into four groups (table 2).

The high value of the CF in the sediments of the study area is located in the Hodeidah port 1.35, while the other sites in the lagoon is low than 1.0 (fig.3).

The environmental state of the lagoon was determined by the Geo-accumulation index "I_{geo}" according to Müller (1979), defined by the following equation:

$\text{Geo-I} = \text{Log } [\text{Metal content}]_{Sample} / [1.5 \text{ metal content}]_{background}$

According to Müller (1981) the scale of the intensity of pollution is classified into seven classes of I_{geo} (table 3).

The distribution of the I_{geo} of the lagoon sediments is classified into two class; unpolluted and from unpolluted to moderately polluted (Figure.3). The second class is located in the Hodeida port. According to EF and I_{geo} calculations, concentrations of Cu, Zn and Pb were not measurably affected by pollution from anthropogenic sources (Mahmood et al., 2011). The heavy metal content of the sediments of lagoon are widely controlled by lithogenic influences whilst the sediment of the port reflects the anthropogenic and lithogenic influences. The activity in the port and sewage outfall results in an increase of concentration of the heavy metal.

CONCLUSIONS

The enrichment of the fine silt sediments are enriched by heavy metal, while the Sr elements are related by coarser grain. The concentration of the Fe and Mn are mainly related to the distribution of ferromagnesian minerals, in oxide and/or oxhydroxide minerals. The Al is related to aluminosilicates and feldspar minerals. Most of the concentrations of these metals in the Kwar Katib lagoon are lower than in other Red Sea sediments.

According to contamination Factor, enrichment factor and geoaccumulation indexes, the samples are classified into the Unpolluted and Unpolluted to moderately polluted. The Unpolluted to moderately polluted is located in the center of Hodeidah Port. The coupling of GIS and statistical techniques appear as being a remarkable tool to identify contamination areas.

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