

METAL POLLUTION RECORDS IN CORE SEDIMENTS OF SOME RED SEA COASTAL AREAS, KINGDOM OF SAUDIA ARABIA

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ABSTRACT

In the last three decades, the industrial and human activities in the coastal area of Saudia Arabia have increased dramatically and resulted in the continuous invasion of different types of pollutants including trace metals. Seven sediment cores were collected during the period from three major industrialized areas; Jeddah, Rabigh and Yanbu, along the coast of Saudia Arabia to determine the spatial and temporal distribution of metals to assess the magnitude of pollution and their potential biological effects. Sediments were analysed for texture, CaCO₃, organic matter and trace metals (Al, Fe, Mn, Cd, Cr, Cu, Ni, Pb and Zn). Some metals like, Mn, Cr, Ni and Zn, were enriched in the upper 15 cm of core samples (recent deposition of sediments). Cadmium concentrations showed high fluctuations with depth and reverse pattern to that for Al, Fe and Mn which indicated land based sources of this element to the studied areas. Elevated concentrations of lead were recorded in the bottom layers of cores in Jeddah that indicated the most dramatic increase in usage of gasoline in early 1970s. The calculated CF's were found in the following sequences: Cd>Pb>Ni>Cu>Zn>Cr>Mn for all studied areas. Results of Pollution Load Index (PLI) revealed that Jeddah is the most polluted area, followed by Rabigh while Yanbu is the least contaminated area. Except for Ni, the concentrations of most metals in the majority of sediment samples were believed to be safe for living organisms. As no data were available on the concentration of metals in core sediments in the coastal area of Saudia Arabia, the results of this study would serve as a baseline against which future anthropogenic effects can be assessed.

1. INTRODUCTION

Human Activities have brought numerous potentially hazardous trace elements to the environment particularly in the industrial area (Nriago, 1996). These anthropogenically derived elements can be transported through the atmosphere to locations remote from emission sources. Bottom sediments provide an archive of environmental change both within the marine ecosystem and region and, therefore, have been used across the world in order to study natural environmental change

or human impact. The collection of geochemical information not only provides a close sight on the present environmental quality of the system but also serves as a baseline for future investigations. It could provide valuable information on the enrichment of sediments with different contaminants.

The study of the sediments cores can provide historical record of various influences in the aquatic system by indicating both natural background level and the man induced accumulation of elements over an

extended period of time (Winkels *et al.*, 1993; and Buckley *et al.*, 1995). It has also been postulated that an intact column of the sediment will remain for the sediments undisturbed by human activities, providing a record to indicate the levels of pollutants over a long period of time (Lo and Fung, 1992).

In the past three decades, Saudia Arabia has undergone a rapid transformation from a state of under devilmnt with severe constraints to development and public welfare to a modern industrial country. By 1987 about 8% of the Red Sea coast had been subjected to extensive development (Chiffing, 1989). Much of this development involved land filling and dredging which in turn affecting substantial areas of the inter-tidal and near-shore sub-tidal habitats. According to Lintner *et al.*, (1995) and others, much of the pressure from the 25,000 to 30,000 ships transiting through the Red Sea are associated with Saudia Arabia oil production and petrochemical industries on both coasts.

Most of the previous studies, dealing with the levels of heavy metal pollution in the coastal area of the Red Sea of Saudia Arabia, focused on the central and northern parts of the coastal waters of Jeddah city. Fahmy and Saad (1996) studied the concentrations of Mn, Zn, Cu and Cd in the water body of the area of Sharm Obhur, a creek situated just to the north of the area of Jeddah. Their data revealed a warning from the increase in concentrations of metals due to human impact. Rifaat and Al-Washmi (2001) characterized the sediments type in the area of Jeddah. They recorded that sediments of this area are composed of biogenic carbonate and aragonite, high and low-magnesium calcite in varying proportions.

With regards to the continuous invasion of different types of pollutants to the coastal area of Saudia Arabia during the past 20 years, it deemed necessary in the present survey to follow up the subsequent alterations in the geochemical composition of coastal sediments, especially metals concentrations, in response to these changes. The objective of

this work is to study the concentrations of nine metals, Aluminum (Al), Iron (Fe), Manganese (Mn), Chromium (Cr), Copper (Cu), Zinc (Zn), Cadmium (Cd), Nickel (Ni) and Lead (Pb) in seven sediment cores collected from three major industrialized areas along the coast of Saudia Arabia to investigate their distribution pattern along the cores and the processes that regulate them. Changes in sediment properties (grain size, % calcium carbonate and % organic matter) were also determined. To quantify the magnitude of pollution by different metals, three approaches were employed: Regression analysis with Al, Contamination factor (Cf) and Pollution Load Index (PLI).

2. STUDY AREA

The coastline of the Kingdom of Saudia Arabia is about 1,840 km in length, accounting for 79% of the eastern seaboard of the Red Sea (MEPA/IUCN, 1987). The present study focused on the coastal area of Saudia Arabia extending from 23° 57' to 21°21'N, and from 38°16' to 39°07'E (Fig. 1), to evaluate different contamination sources that affecting this area. Three distinctive areas, namely Jeddah, Rabigh and Yanbu, which have commercial and industrial facilities, were included in this study.

Most of the previous work was confined to the area of Jeddah which considered as the most industrialized area in the country during the last two decades. This city contains electrical power generation plants, huge municipal discharge, several desalination plants, petromine refinery plant, Armco refinery plant and commercial harbour. Yanbu, another relatively large industrial coastal city on the eastern coast of the Red Sea contains the industrial harbour, the largest oil transport harbour, oil refineries, petrochemical factories, cement factories, desalination plants and power generation plants. The ecological importance of Rabigh area is confined in Rabigh refinery, sewage discharge, cement factory, petromina, coast

guards marina and electrical power generation plant.

As human population multiplies and industrialization increases in the study area, the pollution problem of the environment (including trace metals) becomes more critical especially for the common type of coastal Saudi Arabia habitat along the Red Sea, i.e. saline mud flat (Sabkha), mangroves swamps, palm groves, coral reefs and sea grass beds (Al-Shawafi, 2000). Trace metals are transported as either dissolved species in

water or as part of suspended sediments and stored in the bottom sediments where they modified the natural physico-chemical characteristics of the sediments. Since biotic activities are very intense in such ecosystem, bioaccumulation processes of trace metals can turn out to be hazardous for the local population living along the area under investigation and possible using this area for fishing and recreation activities (El-Rayis *et al.*, 1997).

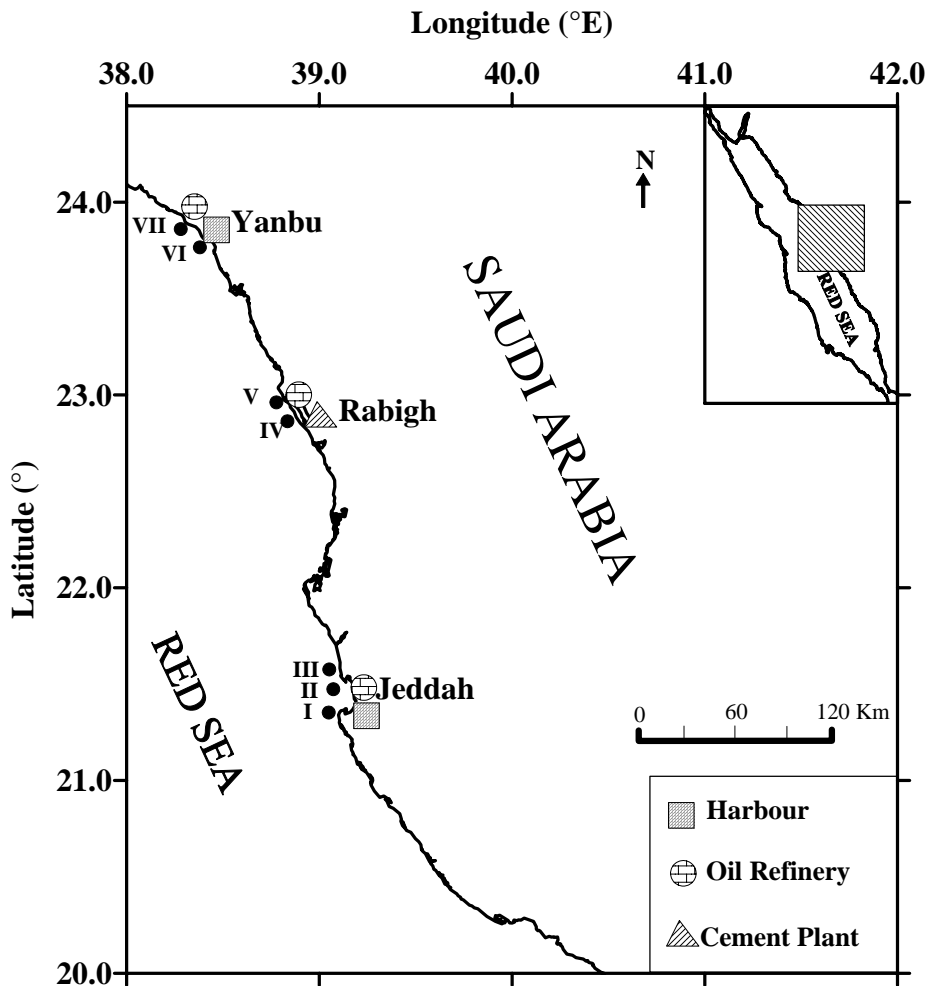


Fig. (1): Location of sampling sites.

3. MATERIALS AND METHODS

During February 2005, seven sediment cores were collected from the coastal area of the Red Sea of Saudia Arabia by scuba divers using PVC tubes 100 cm long and 5 cm in diameter. Three sites were chosen to cover areas which are known to be affected by land-based activities, Jeddah (core I north of a dry dockyard, core II in front of Petromine Refinery and core III from 2000 m away from the coastline), Rabigh (cores IV and V affected by Rabigh refinery, coast guard marina and Steam Power Generation Plant) and Yanbu area (cores VI and VII collected close to Yanbu industrial harbour, oil refineries and petrochemical factories).

In the lab, sediment cores were sliced at 5 cm interval, freeze dried and stored for further analysis. The total organic matter was determined in each slice according to the method of loss in weight by ignition described by Byers *et al.* (1987), while carbonate was determined by titration technique (Black, 1965). A representative portion of the sample (About 20 g) was used for grain size analysis using the standard dry sieving and sedimentation techniques (Krumbein and Pettijohn, 1938).

For trace elements analysis, a portion of each sediment layer was homogeneously mixed and dried at 105°C. Dried samples (0.2 g) were digested according to the method of Wade *et al.* (1993). The resulting solutions were analyzed by flame atomic absorption spectrophotometer AAS (Perkin Elmer, Model 2380 A Spectrophotometer).

For quality control (QC) and quality assurance (QA), replicates (about 20 % of the total number of samples) were analyzed under the same procedures mentioned above. A standard reference material (BCSS-1) was also digested and analyzed similarly to ensure the quality control and accuracy of the analysis. Table (1) shows the certified values and analysis results of the reference material as well as the recovery percentages of each metal.

Statistical tests including Pearson product-moment correlation and the performance of correspondence analysis were carried out to illustrate the most physical/chemical and sedimentological factors controlling the distribution of trace metals in core sediments. All statistical aspects were calculated on Excel XP and MINITAB, version 13.1.

Table (1): Comparison of BCSS-1 certified values with the present study.

Element	BCSS-1	Present study	Recovery (%)
Al ₂ O ₃	11.83±0.41	11.63	98
Fe ₂ O ₃	4.7 ± 1.4	4.48	95
Mn	229 ± 15	212	93
Cr	1.23 ± 1.4	1.28	104
Ni	55.3 ± 3.6	58.4	105
Cu	18.5 ± 2.7	17.2	93
Zn	119 ± 12	123.7	104
Cd	0.25 ± 0.04	0.27	108
Pb	22.7 ± 3.4	21.9	96

Values in µg/g dry weight except for Al₂O₃ and Fe₂O₃ in %

4. RESULTS AND DISCUSSION

4.1. Sediment types

At the area of Jeddah, results of grain size analysis revealed that cores I and II were characterized by silty sand texture, in which calm conditions in these sheltered areas allow the deposition of fine grains. On the other hand, the domination of sand texture in core III (>95%), collected from the breaker zone, indicated that wave action allows coarser grains to get deposited. The uniform grain size distribution, obtained along cores IV and V collected from the area of Rabigh, indicated stable depositional environment for a long period. The presence of nearly 96% of sand in core IV indicates the rough activity at the open water and the action of Longshore currents allowing the washout of finer particles (Gheith and Abou Ouf, 1996). Cores collected from Yanbu showed the minimum grain size of all cores. Core VI was dominated by silty sand texture, while core VII showed irregular distribution (silty sand, sand and muddy sand). This finding indicated long periods of different depositional conditions.

4.2. Calcium carbonate and total organic matter

The results of carbonate contents in core sediments showed minimum variations, with a very narrow range (37.00-58.75%). High carbonate content observed in sediments of near shore stations in the area of Jeddah (cores I and II), was attributed to the activities carried out along the cornich (dredging of shore sediments as well as ports expansion occurs at this area). According to Rifaat and Al-Washmi (2001), the sediments off Jeddah City were characterized by high carbonate contents due to their biogenic origin containing coral debris, molluscan shells, coralline algae, bryozoans and foraminifera. At the area of Rabigh, the

contribution of atmospheric deposition of cement dust to the marine environment may be the reason for high carbonate content, especially in core IV. According to Al-Washmi (1999), the sediments at the area of Rabigh are mainly consists of carbonate faces with coarse grained texture. The carbonate contents in cores VI and VII collected from Yanbu, showed almost similar vertical profiles of uniform distribution along the cores. According to Gheith and Abou Ouf (1996), the seafloor of the nearshore zone in coastal zone off Saudia Arabia is generally flat and is covered by a thin layer of unconsolidated sediments overlying the consolidated reefal limestone.

The results of total organic matter showed normal coastal sediments content in most cores, ranging from 0.20% in core I to 4.86% in core V, as a minimum and maximum percentage values, respectively. Although core III was collected from about 2000 m distance from the shore, an enrichment of TOM was recorded with an average percentage value of 3.04 ± 0.79 . A shallow depth (3 m) at this area may allow the accumulation of TOM before significant oxidation. Further, the higher content at 5-10 cm depth in core III indicates adsorption and incorporation of organic materials from the overlying water column with accumulation of fine-grained terrigenous inorganic material (Janaki-Raman *et al.*, 2007). Moreover, the current regime that explained by Rifaat, *et al.*, (2001) indicated high accumulation of contaminant at this area. The higher average percentage value of TOM in core V (2.60 ± 1.28) from Rabigh area, with a noticeable irregular vertical distribution, was attributed to the direct sewage discharge in a semi-enclosed coast guard marina (Fig. 1). The activities existing in Yanbu Commercial Harbour are the reason for the highest TOM contents of core VI sediments (2.93-4.17%). Following up the TOM% in the coastal sediments in the area of Jeddah detected by Rifaat, *et al.* (2001) with a range of 0.28 to

0.35%, it appeared clearly that TOM contents are, in general, recently enriched where the magnitude of enrichment was differed between regions.

4.3. Trends of element concentrations in the sediment cores

The trace metals concentration profiles obtained from the collected cores are shown in Figs. (2 and 3). As the sites presented in this work are not in one area, due to the difference in waste discharges and geochemistry, different elements exhibited different trends in their vertical distribution among the collected cores.

4.3.1. Major elements

4.3.1.1 Aluminum (Al)

The main aim of performing total aluminum analysis in the collected sediments is to be used in trace metals normalization process. Elevated concentrations of total aluminum are generally recorded in core samples of the study area (Figs. 2 & 3). In the area of Jeddah, similar vertical distribution was noticed from the surface till the depth of 15 cm among the three collected cores. This indicated the stability in depositional environment in recent years. However, different distribution was noticed in the deeper parts of the cores. These variations were rather irregular probably reflecting the diverse in influence of terrigenous and authogenic materials. Higher aluminum concentration was detected in the area of Rabigh, (core V with average of $2015.31 \pm 576.64 \mu\text{g/g}$), which also contains the maximum fluctuation among all other cores. This indicated alternative stages of massive and minor terrigenous materials supply to the coastal area, which may be

explained by carrying out the eroded particles at this region via wadi system.

The similarity in the intermediate maxima at the depth of 30-40 cm in cores IV and V revealed similar depositional environment. At the area of Yanbu, almost regular distribution was noticed along the two cores with minor fluctuation in core VI.

4.3.1.2 Iron (Fe)

Iron represented the maximum abundance of the studied metals during the present work. This enrichment may be related to the distribution of ferromagnesium minerals supplied by the terrigenous materials (Sagheer, 2004). El-Sabrouti (1990) pointed out that the enrichment of Fe results either from its precipitation from overlying water or the upward migration of the pore water rich in solubilized Fe ions.

The vertical profiles of Fe (Figs. 2 & 3), followed exactly the same pattern of Al. The vertical variation in the iron concentrations is controlled by a variety of processes occurring in the investigated areas. In Jeddah and Rabigh, the features of depth profiles showed, in general, irregular vertical distributions. This observation suggests diagenetic enrichment during which Fe oxy-hydroxides dissolve in the partly reduced sediment layer producing Fe II species (Shaw *et al.*, 1990), which migrate upward in the sediment column and get precipitated near the oxic-suboxic interface. The above inference is well supported by high values of Fe in the depth 0-10 cm in the area of Jeddah (cores II and III), and low values at greater depth. The lower values in the bottom part may be due to the increase of sulfate reduction while iron content has decreased because of FeS formation (Goldhaber and Kaplan, 1974).

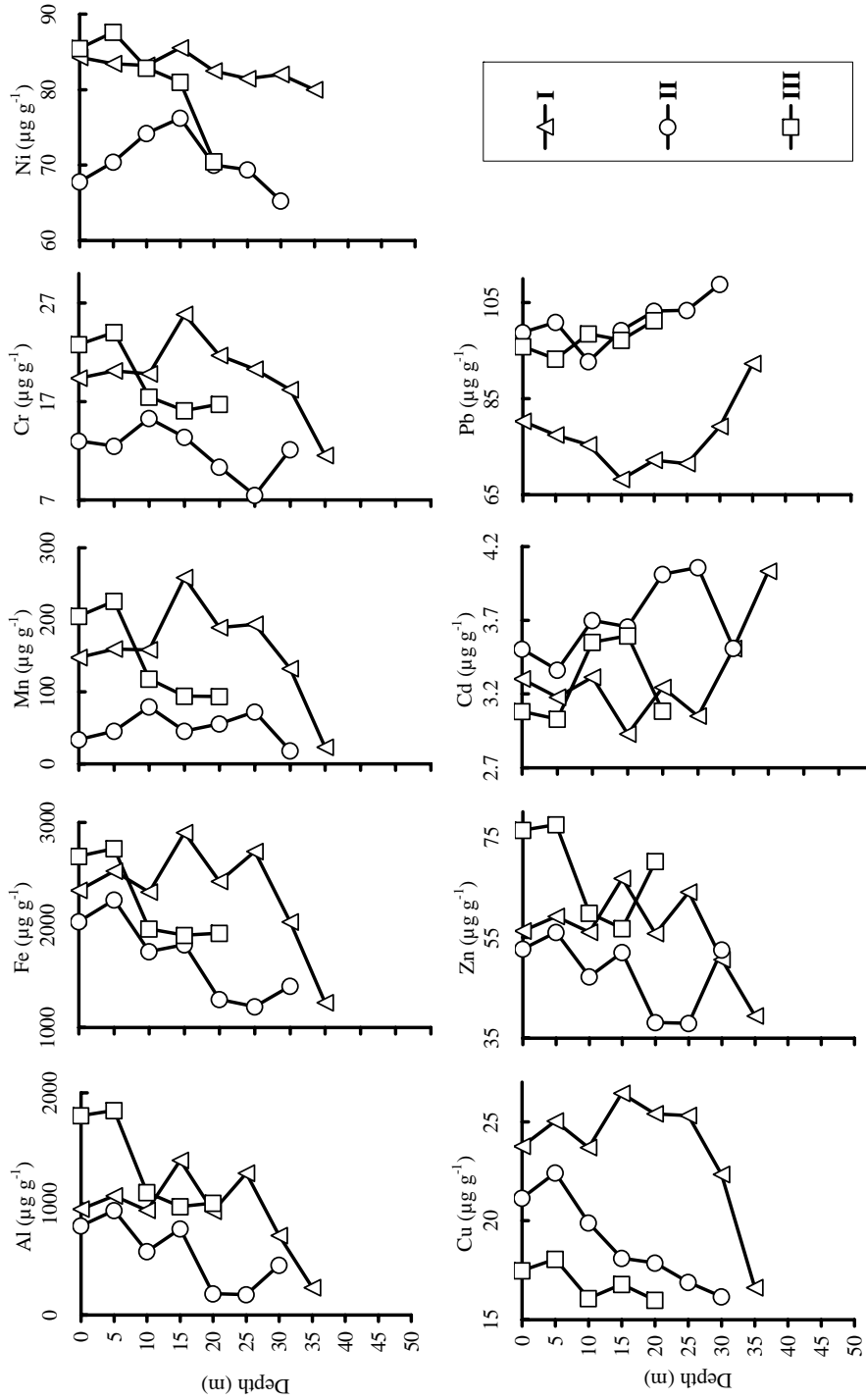


Fig. (2): Depth profile of metals in cores (I,II & III) collected from the area of Jeddah, coast of Saudia Arabia

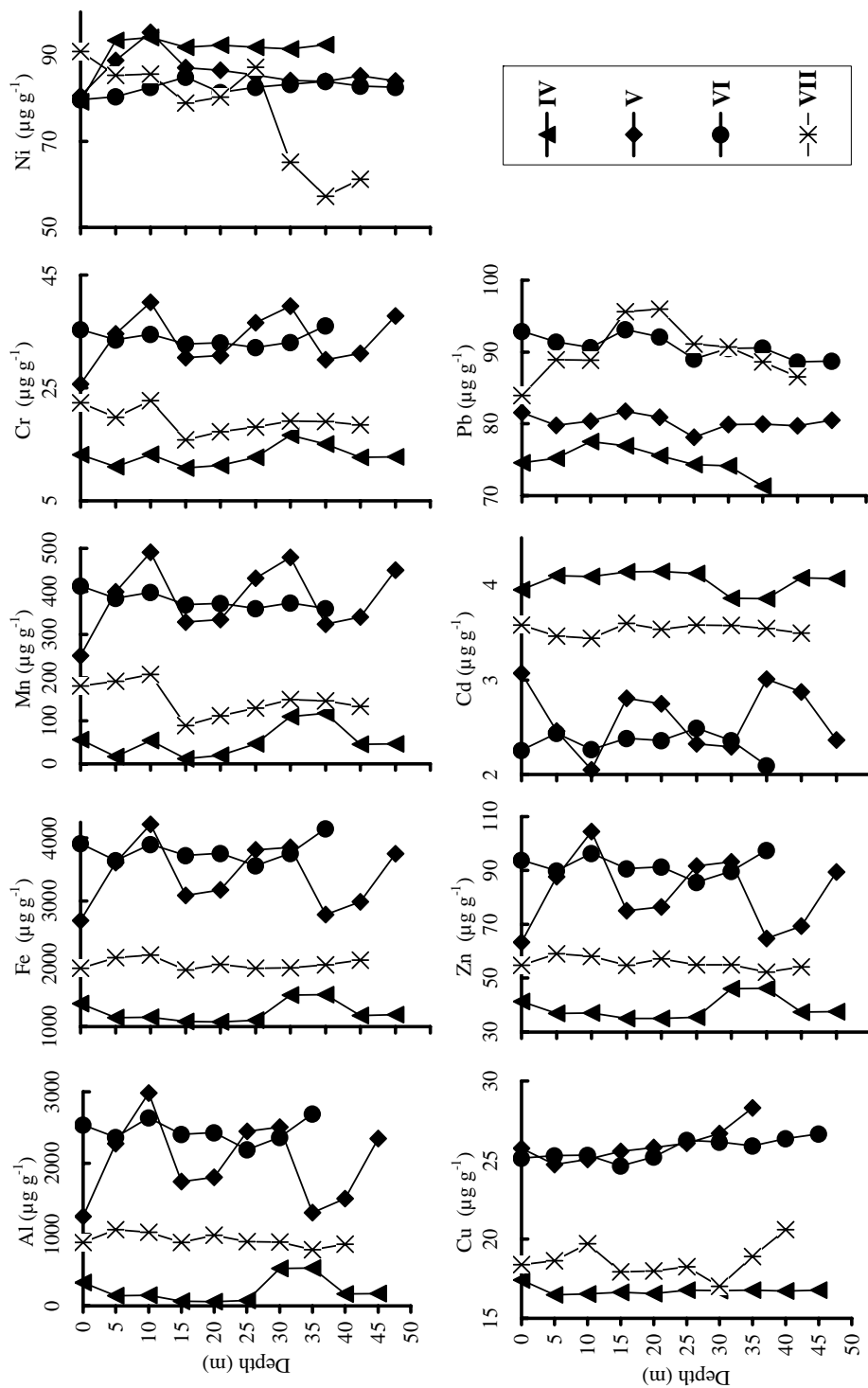


Fig. (3): Depth profile of metals of sediments in cores (IV & V) in the area of Rabigh and cores (VI & VII) in the area of Yanbu, coast of Saudia Arabia

4.3.1.3 Manganese (Mn)

Mn is an element of low toxicity having considerable biological significance. It is one of the more biogeochemical and active transition metals in aquatic environment (Evans *et al.*, 1977). During the present study, vertical distribution of Mn shows variation with depth and characterized by the presence of subsurface peaks at 10-15 cm, except in core III found at 5-10 cm (Figs. 2 & 3). Reduced concentrations of Mn at the surface of sediments indicate that dissolved Mn ions with greater mobility are easily removed from the pore water of surface sediments to the upper water column through active diffusion and advection processes (Janaki-Raman *et al.*, 2007). Moreover the change in the redox state as a result of organic matter oxidation, causing the manganese to be soluble and relatively remain in solution. Organic matter digenesis and sediment re-suspension lead to the regeneration of Fe and Mn oxides in sediments, which may alter redox-sensitive heavy metal compositions in the sediment deposits (Breckela, *et al.*, 2005). The obtained positive significant correlation between Mn and TOM in some cores, III, IV and V ($r = 0.95$, $p < 0.05$) may support this conclusion.

Manganese subsurface maxima and decreasing values down the cores were found to be in a good agreement with the findings of Pattan (1993), who attributed this observation to the supply of dissolved Mn^{2+} via pore waters from the reducing zone at subsurface depth and get oxidized to Mn^{4+} at the surface. This is in accordance with the usual redox geochemistry of this element (Janaki-Raman *et al.*, 2007).

4.3.2. Trace elements

4.3.2.1. Chromium (Cr):

Vertical distribution of Cr in the core samples of the present work indicates a

pattern similar to Fe and Mn (Figs. 2&3). In most cores, the highest detected concentration of Cr was recorded in the interval between 10-15 cm, except for cores I and III, where the maximum concentration of 25.84 and 24.03 $\mu\text{g/g}$ were detected at interval between 15-20 cm and 0-5 cm, respectively. However, in Rabigh area, Cr profiles reported another peak in the bottom layers between 30-35 cm (Fig. 3). Diagenetic modifications, however, play a major role in the vertical distribution of Cr indicating a peak at subsurface and greater depth in most core samples (Janaki-Raman *et al.*, 2007). Analytical results obtained by (Gaillard *et al.*, 1989) indicated that Cr (as Cr (VI)) is relatively mobile and migrate to the reduced zone at deeper levels.

Likewise the results obtained by several authors (Pattan *et al.*, 1995; Orlic and Tang, 1999), very similar profiles were obtained for Cr and Mn in all core samples (except in core II). This is supported by strong significant positive correlation between Cr and Mn ($r = 0.99$, $p < 0.05$) in most cores. Pattan, *et al.*, (1995) found that Cr, as one of the redox sensitive metals, was suggested to be co-precipitated with authigenic Mn-oxyhydroxide.

4.3.2.2. Nickel (Ni):

Nickel, which is quite abundant in the Earth's crust, enters surface waters from the dissolution of rocks and soils, from biological cycles, from atmospheric fallout, and especially from industrial processes and waste disposal (Prego *et al.*, 1999). About 84 % of the obtained data of total nickel during the present work was found ranging from 75 to 95 $\mu\text{g/g}$, which represent a narrow range and indicate the homogeneity along the studied cores.

As shown in Figs. (2&3), the vertical distribution of Ni exhibited distinct increase in concentration in the 10-20 cm section followed by decreasing in concentrations with depth. Moreover, no similarity with the

profiles of other metals was noticed. According to Zwolsman *et al.*, (1996), the increase of Ni content at subsurface layers is due to Ni sorption onto manganese oxyhydroxides. The redox status of the sediments determines the extent to which mobilization of Mn and associated Ni will occur. A positive significant correlation between Ni and Mn especially in Rabigh area ($r = 0.970$, $p < 0.05$) was recorded. In addition, it is well known that Ni at the pH values of the marine environment (> 6.7) is insoluble and exists predominantly as insoluble Ni hydroxides (Sunderman and Oskarsson, 1991) which in turn quickly incorporated in sediments.

4.3.2.3. Copper (Cu):

Copper is one of the most common contaminants associated with urban runoff. Important anthropogenic inputs of copper in estuarine and coastal waters include sewage sludge dumpsites, municipal waste discharge, and antifouling paint (Kennish, 1996). In relatively clean sediments, copper concentration was found to attain $50 \mu\text{g/g}$ (ATSDR, 1990), while sediments having higher concentration than $60 \mu\text{g/g}$ is classified by the EPA as contaminated sediments (Ingersoll and Nelson, 1989). According to the calculated overall average concentration of copper ($21.32 \mu\text{g/g}$) during the present work, the sediments of the three studied areas can be considered uncontaminated with this element. Moreover, the detected maximum concentration of $28.32 \mu\text{g/g}$ is far below the background concentration.

The Vertical profiles of Cu in the studied cores showed neither regular pattern nor similar pattern to other metals. In the area of Jeddah (Fig. 2), relative excess at 5-10 cm ($25.03 \mu\text{g/g}$) and 20-25 cm ($26.43 \mu\text{g/g}$) in core I and at 5-10 cm in cores II ($22.43 \mu\text{g/g}$) and III ($18.05 \mu\text{g/g}$) were recorded. These findings indicate the presence of recent anthropogenic input to this area. On the other hand, vertical distribution of Cu showed no strong variations in the other two areas which

indicate the addition of Cu to the marine sediments from limited sources as antifouling paint from ships.

4.3.2.4. Zinc (Zn):

Zinc is a naturally abundant element present as a common contaminant in agricultural, food wastes, manufacturing of pesticides as well as antifouling paint. The vertical distribution pattern of Zn was found following the same distribution pattern of Al and Fe (Figs. 2&3). This observation can be supported by the results of correlation analysis where Zn was found highly correlated with Al ($r = 0.996$, $p < 0.05$) and Fe ($r = 0.991$, $p < 0.05$).

Down core profiles of Zn indicate fluctuations in most cores of the area under investigation. The same observation was recognized by Rubio *et al.*, 2001 in sub-tidal sediments, NW Spain. They attributed this finding to the upward migration of zinc during organic matter degradation. Another factor that causes zinc to be co-precipitated with Mn- oxyhydroxides is the redox potential of sediments. This can be supported by the significant positive correlation that obtained with Mn in most cores ($r = 0.900$, $p < 0.005$). Pattan, *et al.* (1995) found that Cu, Ni and Zn follow a similar trend of Mn in all sediment types including the coarse-grained ones. Moreover, Rubio *et al.*, 2001 suggested that Zn is fixed mainly to the oxyhydroxides during deposition.

4.3.2.5. Cadmium (Cd):

Cadmium as a transition element behaves in the environment as a cumulative poison (Roy, 1997). It is listed by EPA as one of 129 priority pollutants and listed among the 25 hazardous substances. Moreover, there is an international agreement about cadmium not to be dumped into the sea, since it is included in the black list (Clark *et al.*, 1997). The natural sources of cadmium contribute 10-30% through windblown transport of soil particles and volcanic emissions. The main

source of Cd to the marine environment is mainly anthropogenic through refining and use of cadmium, copper and nickel smelting, and atmospheric loading (Kennish, 1996) in which most of them are deposited in bottom sediments (Clark *et al.*, 1997).

The detected Cd value in the collected core sediments represented high concentrations. This indicates an anthropogenic source of the metal into sediments which may include discharge of refining wastes and untreated sewage effluents (Ismail and Awad, 1984).

The vertical distribution pattern of Cd along the collected cores showed fluctuations especially in cores I, II, III and V with a reverse pattern to that noticed for Al, Fe and Mn (Figs. 2&3). This is suggesting that an anthropogenic signal of Cd was relatively high in these cores. Moreover, it is well recognized that cadmium is sensitive to redox changes, where it is known to be soluble in oxygenated conditions and to precipitate immediately where post-oxic conditions are encountered (Thomson *et al.*, 2001).

4.3.2.6. Lead (Pb):

All lead compounds are potentially harmful or toxic, especially tetraethyl lead (Jenkins, 1981). It is listed by EPA as a carcinogen material. Concentrations of lead in the studied sediments showed high values in all cores, in the range of 68.23 µg/g at 15-20 cm in core I to 108.86 µg/g at 30-35 cm in core III as a minimum and a maximum value, respectively. AbuHilal (1987) and Laxen (1983) attributed high Pb concentrations to several sources such as boat exhaust systems, spillage of oil, and other petroleum from mechanized boats employed for fishing, and the discharge of sewage effluents into water, in which all of these sources exist in the study areas. In addition to these sources, atmospheric input of Pb that generated from the automobile exhaust emission can be attributed as the most significant source to the studied area that situated close to the high way and the cities roads. Frignani, *et al.*

(1997) considered that Cd, Pb and Zn are mostly introduced to the marine environment through atmospheric input.

Except for the slightly higher concentrations of total lead in bottom layers of cores in Jeddah area, no significant variations were noticed for Pb vertical distribution in core sediments (Figs. 2&3). Moreover, it didn't follow the vertical distribution of any of the controlling factors considered for metals accumulation in sediments (e.g. Al, Fe, Mn, clay% or TOM). This is indicating the increased land-based activities as well as using leaded gasoline in the last four decades.

5. STATISTICAL ANALYSIS

In order to study the inter-elemental associations, the correlation coefficients of the elements analyzed were computed for the collected cores separately. In addition, the correspondence factor analysis was used in an attempt to extract the similarities and dissimilarities between cores. It permits the projection of a large set of points (stations and variables) into a much reduced space. Reciprocally, each factor axis contributes to defining the position of a given point with respect to the center of the cloud of all projected points. The correlation and the correspondence factor analysis were performed from a data matrix comprising 57 observations (sliced sections of cores) and 13 variables (% CaCO₃, % TOM, % WC, % Clay, Al, Fe, Mn, Pb, Cu, Ni, Cr, Cd, and Zn).

Iron plays a vital role in trace metals scavenging and their incorporation into sediments. According to Duchart *et al.*, (1973), trace metals are first sorbed or precipitated on to the Fe oxides forming films or layers near the sediment surface. The widespread occurrence of dispersed oxides at the surface of recent sediments and the well documented ability of these oxides to scavenge trace elements from solution make this process a very possible reason for the

high concentrations of the studied metals in the collected core sediments.

By studying the results of Pearson correlation analysis, it was found that Cr exhibited the strongest significant positive correlation with Mn ($r = 0.99$, $p < 0.05$), which support the previously discussed notice according to the vertical distribution pattern. Also, Cr was found in inter-elemental positive significant correlation in most cores with Al, Fe and Zn, to some extent with TOM and negative significant correlation with Cd and Pb. Results of the correspondence analysis (Fig. 4), agreed with the same observations that noticed from the correlation analysis in which Cr was found categorized with other metals as well as TOM.

The correlation analysis of Ni and other studied parameters, showed a positive significant correlation with Mn, especially in Rabigh area ($r = 0.90$, $p < 0.05$) and to some extent with clay %. Based on results of corresponding analysis, except for core 5 where Ni was detected with Mn, it was found situated at different areas of the graphs.

No consistent significant correlation was obtained for Cu either with sediment quality parameters or with other metals. Similarly, the data represented in Fig. (4) that based on the correspondence analysis led to the same conclusion. This observation indicates that Cu behavior in the studied areas was different and its deposition is affected by different processes.

In addition to significant positive correlation that obtained between Zn and each of TOM ($r = 0.90$, $p < 0.05$), Al ($r = 0.99$, $p < 0.05$), Fe ($r = 0.98$, $p < 0.05$) and Mn ($r = 0.90$, $p < 0.05$), it was also found in positive significant correlation with the studied redox sensitive metals like Cr and in some cores with Ni and Cu, as noticed from correspondence factor analysis (Fig. 4).

A negative correlation was detected between Cd and all other redox sensitive metals except for Pb, which exhibited poor positive correlation. This could be attributed to the deposition of Cd, without change in oxidation state, except in the presence of H_2S ,

it is usually removed from solution as insoluble CdS (Gwenaelle, *et al.*, 2002). In the same aspect, the results of correspondence analysis supported the same finding where it was found in the opposite area to that of Al, Fe Mn and Zn (Fig. 4)

Similarly, the results of statistical analysis (correlation and correspondence analyses) indicated no consistent relation between Pb and any of other parameters (Fig. 4). These observations indicate the anthropogenic source of lead to the marine sediments of the study area.

6. ASSESSMENT OF METALS POLLUTION

Metals background concentrations in sediments are mainly driven by weathering, unpolluted natural atmospheric deposition and these from components of sediment matrices (Yang and Rose, 2005). Metal increases in sediments due to pollution can be separated from its natural background, and passive tracer element can be used to evaluate the pollution level (Norton and Kahl, 1991).

Windom *et al.* (1989), and Summers *et al.* (1996) presented a simple method of distinguished natural changes from those induced by anthropogenic activity. Metal concentrations were normalized to aluminum or iron to determine whether a sediment sample was enriched with metals when compared to the sample's natural conditions. Because Al is tightly associated with alumino-silicate fraction that is dominant metal-bearing phase of the sediment, Al was used as a normalization factor in predicting the enrichment or depletion of trace metals in sediment. Contaminated samples have been identified by plotting metal concentrations against Al concentrations (Windom *et al.*, 1989). On a scatter plot, the data pointed out that fall within 95% confidence levels of the data base was taken to be natural, and that was above the confidence limit was considered to be enriched and introduced to the bottom sediments via terrigenous sources.

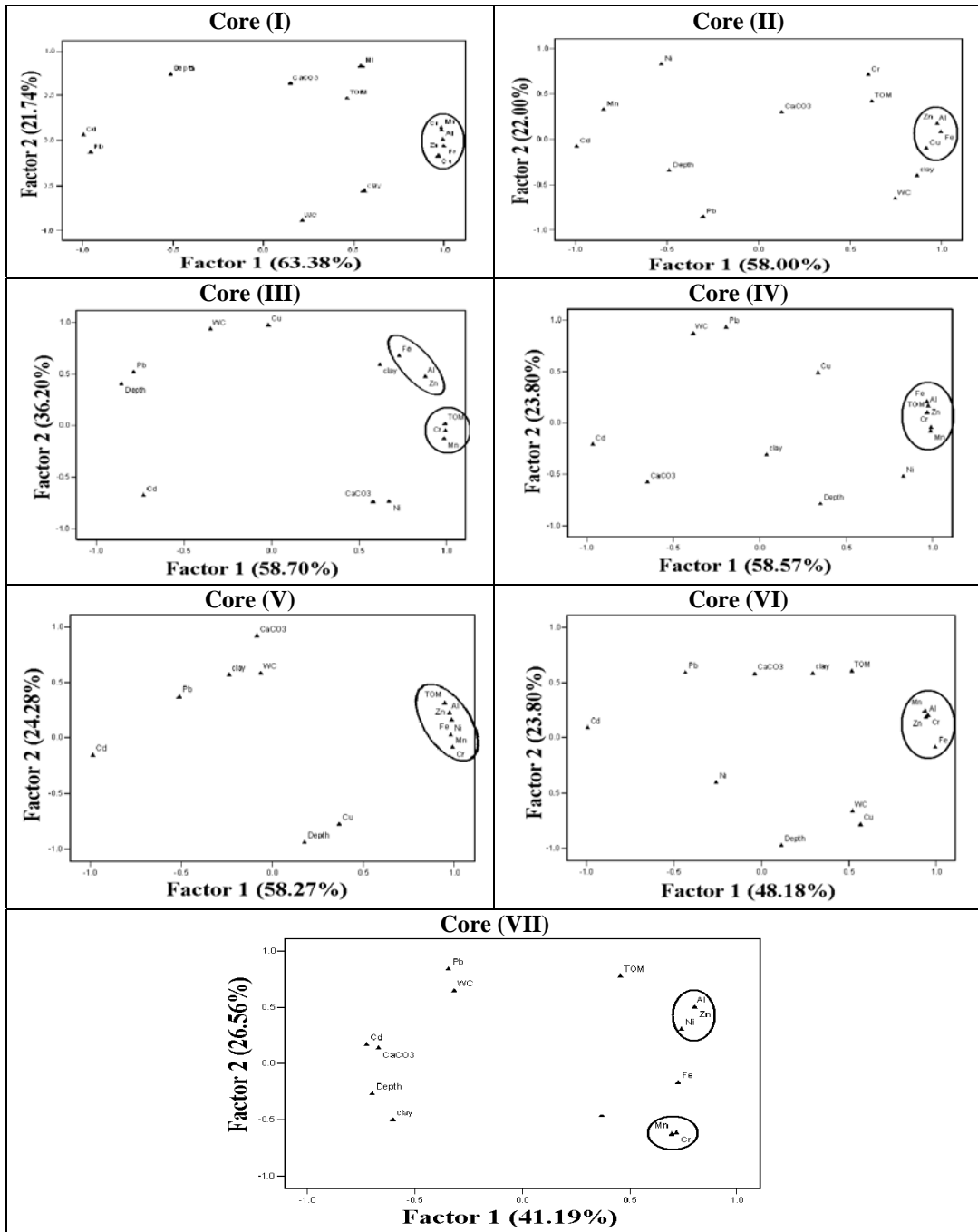


Fig. (4): Correspondence factor analysis of different variables in the different cores.

Based on results obtained in the present study, similar regression plots were noticed between Mn, Cr and Al with slight deviation at the areas of Jeddah and Rabigh. Since Cr is used as anticorrosive material, the slight elevation of this metal may be related to anthropogenic inputs.

Ni normalization results showed linear and weak positive relationship with Al, with a wide area within the confidence limits. Several points belonging to the areas of Jeddah and Rabigh were found scattered outside the confidence intervals, which indicate the anthropogenic source of this metal. Because Ni is used as a catalyzing agent in the oil refining process, two cores (II and IV) located in the vicinity of Petromina and ARMCO outfalls recorded high concentrations of these elements.

A poor positive correlation between Al and Cu indicating the anthropogenic input of this element through antifouling paints from ships lift especially in cores I, V and VI (close to inlets of dry dockyard and coast guard marina). The results of Zn normalization with Al indicate the deposition of high Zn concentrations normally during Al deposition.

The regression plot between Al and Cd (strong negative correlation) indicates the enrichment of the sediments with anthropogenic source of Cd in the three studied areas with different degree of contamination (Jeddah > Rabigh > Yanbu). Also, the results obtained for Pb revealed that the area of Jeddah seems to be the most enriched area with lead.

The contamination factor (Tomlinson *et al.*, 1980) was calculated (CF = metal concentration in sediment/base value for that metal). The base value corresponds to baseline or background concentrations reported from elements abundance in sedimentary rock (shale) of the earth crust. The terminologies used to describe the contamination factor are: CF<1 low contaminated; 1<CF<3 moderate contamination; 3<CF<6 considerable

contamination and CF>6 high contamination. The calculated CF's were found in the following sequences:

Cd>Pb>Ni>Cu>Zn>Cr>Mn for all studied areas. It was noticed that Cd is the major pollutant to cause relatively high pollution load while Cr and Mn is the least metals to influence the pollution load.

Pollution load index (PLI) was computed according to Tomolinson *et al.*, (1980) from the following equation:

$$PLI = (cf_1 \times cf_2 \times \dots \times cf_n)^{\frac{1}{n}}$$

Where:

PLI = pollution load index.

CF = contamination factor

n = number of metals investigated

The Pollution Load Index (PLI) was calculated for the three areas of study, for the seven investigated metals (Cd, Pb, Ni, Cu, Zn, Cr and Mn) as well as for Cd and Pb. It was observed that PLI values for cores in case of Cd and Pb were much higher (i.e 5.24-8.36) than those calculated for all metals (0.80-1.95). This may be related to the high concentrations of both elements and great variations in concentrations of other metals.

From the calculated CF, it was found that Cd is the main pollutant that may cause relatively high pollution load in all cores, while Mn is the least metal to influence the pollution load. The highest PLI was computed for Jeddah (7.5); followed by Rabigh (6.4), and the lowest was found for Yanbu (5.6). It follows that Jeddah is the most polluted area, while Yanbu is the least compared to other areas.

Compared to the results of previous studies (Table 2), concentrations of metals reported in the present study showed that the levels of Cd, Ni and Pb recorded higher concentrations than most of the published data. However, the other metals; Cr and Mn, recorded lower levels compared to their concentrations in world wide sediments. In case of Zn, most of the compared results were

found lower or close to that obtained during the present work. However, higher concentrations were recorded in the Red Sea, Yemen and Gulf of Aden. The published data

of Cu ranged between higher and lower values than that in the present study. The closest value of total copper was recorded in the Egyptian Red Sea coastal sediments.

Table (2): Surface concentrations of metals ($\mu\text{g/g}$) in some selected sediments world wide compared to study areas.

Location			Fe	Mn	Cr	Ni	Cu	Zn	Cd	Pb	Reference
Red Sea	Jeddah	Av	2351.95	119.39	17.90	76.64	20.62	64.55	3.30	89.54	Present study
		STD	451.63	121.16	6.95	12.53	4.45	16.70	0.30	13.06	
	Rabigh	Av	2027.65	153.50	19.44	80.09	21.28	52.40	3.51	87.21	
		STD	935.04	137.90	8.85	0.57	5.44	15.61	0.62	7.99	
	Yanbu	Av	2919.16	296.81	28.87	85.00	22.07	74.32	2.92	79.27	
		STD	1404.26	164.18	9.19	8.20	5.22	27.63	0.93	6.62	
Red sea, Jeddah	Av	-	23.80	-	-	13.20	17.95	3.90	-	Rifaat, 1996	
	STD	-	21.35	-	-	16.83	17.89	2.97	-		
Gulf of Aden	Av	2454.59	398.55	125.47	32.12	59.55	142.67	-	76.43	Saleh, 2006	
	STD	445.02	368.15	153.39	22.56	72.77	170.87	-	87.16		
Red Sea, Egypt	Av	9881.00	117.85	-	10.72	25.70	-	-	-	Okbah et al., 2005	
	STD	8714.38	166.67	-	15.15	36.35	-	-	-		
Red sea, Yemen	Av	3657.00	42.85	20.20	12.00	32.05	113.30	-	6.91	Hassan & Nadia, 2000	
	STD	818.83	31.32	6.08	3.82	10.25	34.93	-	2.53		
Gulf of Mannar, India	Av	6500.00	295.50	171.50	23.57	-	72.53	-	15.99	Jonathan & Mohan 2003	
	STD	7495.33	7.78	33.23	1.32	-	2.16	-	0.02		
Gulf of Mexico	Av	-	230.70	51.50	38.78	11.26	39.82	-	10.21	Macias-Zanora et al., 1999	
	STD	-	308.58	68.59	53.91	10.52	56.26	-	14.13		
Florida Bay	Av	-	675.50	202.00	29.45	-	-	-	-	Caccia et al., 2003	
	STD	-	656.90	205.06	34.72	-	-	-	-		
Al-Hodeidah, Yemen	Av	-	-	13.23	6.88	6.52	21.50	7.40	2.34	Al-adrise, 2002	
	STD	-	-	9.86	9.02	6.53	12.02	9.62	1.61		
Arabian Gulf	Av	-	-	2363.00	-	-	-	-	-	Ahmed, 1996	
	STD	-	-	3317.60	-	-	-	-	-		
Abu Kir Bay, Egypt	Av	-	-	-	-	235.35	-	-	-	Badr, 1993	
	STD	-	-	-	-	174.16	-	-	-		
Jordan Gulf of Aqaba	Av	-	-	-	-	-	-	8.90	-	Abu-Hilal, 1987	
	STD	-	-	-	-	-	-	7.07	-		
Arabian Gulf	Av	-	-	-	-	-	-	1.65	-	Hashim et al., 1994	
	STD	-	-	-	-	-	-	1.06	-		
Gulf of Aden, Yemen	Av	-	-	-	-	-	-	1.25	-	Heba et al., 2000	
	STD	-	-	-	-	-	-	0.92	-		
El-Mex Bay, Egypt	Av	-	-	-	-	-	-	2.85	-	Khairy, 2004	
	STD	-	-	-	-	-	-	2.24	-		
South Africa	Av	-	-	-	-	-	-	2.80	-	Richardson et al., 1994	
	STD	-	-	-	-	-	-	2.12	-		
Lavaca Bay, Hong Kong	Av	-	-	-	-	-	-	0.23	-	Fung & Lo, 1997	
	STD	-	-	-	-	-	-	0.22	-		

7. ADVERSE BIOLOGICAL EFFECTS

Many trace metals are highly toxic and have chronic effects on living organisms. Elevated concentrations of trace metals in sediments could cause detrimental effects to benthic organisms as well as other aquatic organisms. In the present study, concentration of metals are compared to the Effects-Range Low (ERL) and Effects-Range Median (ERM) concentration guidelines derived from the database of Long *et al.* (1995) to understand the extent of contamination (Table 3). Concentrations below the ERL value are rarely associated with biological effects while, those equal/or above the ERL, but below the ERM, indicate a possible range in which effects would occasionally occur.

The concentrations equivalent to and above ERM values indicates that the effects would occur frequently.

As seen in Table (3), except for Ni, none of the metal concentrations in the sediments of study area were as high as above ERM values. In addition, Cr, Cu, Zn levels in the study area were below established limits (ERL) for biological effects. This suggests that the concentration range of these metals in coastal sediments of selected areas would rarely be associated with biological effects. Cadmium and lead levels at all sites were higher than ERL values but were lower than ERM values. All sediment samples had Ni concentrations above the ERM, indicating possible detrimental effects to benthic organisms (Table 3).

Table (3): Number of samples that had metal concentrations above the sediment effects data of ERL and ERM in collected cores.

Metal	ERL	ERM	Jeddah (3 samples)			Rabigh (2 samples)			Yanbu (2 samples)		
			Below ERL	Between ERL&ERM	Above ERM	Below ERL	Between ERL&ERM	Above ERM	Below ERL	Between ERL&ERM	Above ERM
Chromium	81.0	370.0	3	-	-	2	-	-	2	-	-
Nickel	20.9	51.6	-	-	3	-	-	2	-	-	2
Copper	34.0	270.0	3	-	-	2	-	-	3	-	-
Zinc	150.0	410.0	3	-	-	2	-	-	2	-	-
Cadmium	1.2	9.6	-	3	-	-	2	-	-	2	-
Lead	46.7	218.0	-	3	-	-	2	-	-	2	-

ERL: Effect Range Low

ERM: Effect Range Median

Data from Long *et al.*, 1995

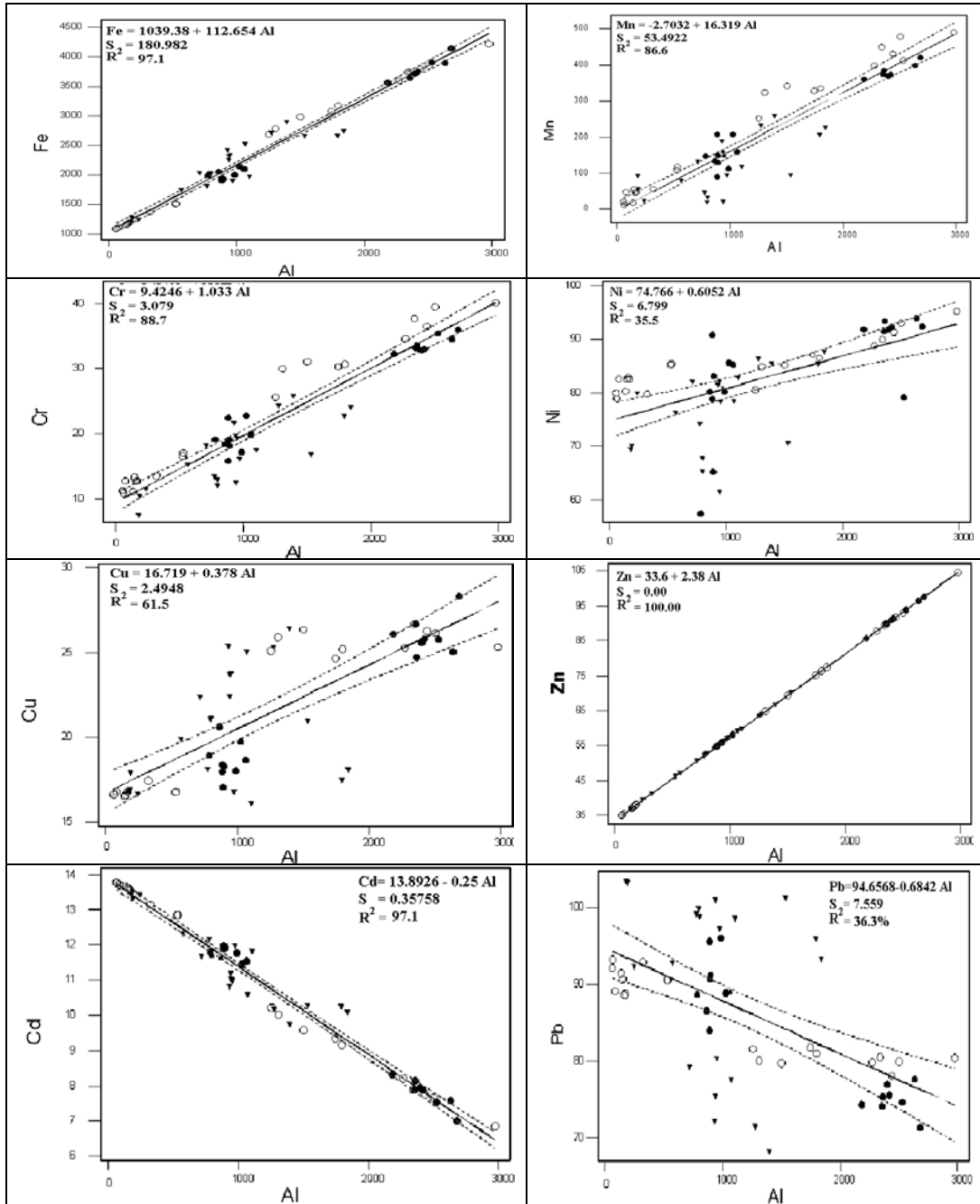


Fig. (5): Relationship of trace metal concentrations (µg/g, dry weight) with that of Al (µg/g, dry weight) in the sediments from different cores.

8. CONCLUSION

The preliminary database, on trace metals in core sediments of coastal area of Saudia Arabia, indicates the dominance of silty sand and sand textures in the collected cores. The increasing man made impact, by discharging uncontrolled industrial and sewage wastes, is reflected on the enrichment of Mn, Cr, Ni and Zn in upper 15 cm of core samples (recent deposition of sediments). The detected maximum concentration of Cu was far below the background concentration and its vertical distribution showed neither regular pattern nor similar to other metals. Cadmium concentrations showed high fluctuations with depth and reverse pattern to that for Al, Fe and Mn which indicated land based sources of this element to the studied areas. Elevated concentrations of lead were recorded in the bottom layers of cores in Jeddah. This indicated the most dramatic increase in usage of gasoline in early 1970s, which recently showed worldwide decrease, due to the implementation of environmental laws.

The calculated CF's were found in the following sequences:

Cd>Pb>Ni>Cu>Zn>Cr>Mn for all studied areas. The Pollution Load Index (PLI) calculated for different areas indicated that Jeddah is the most polluted area, followed by Rabigh while Yanbu proved to be the least contaminated area. Except for Ni, the concentrations of most metals in the majority of sediment samples were believed to be safe for living organisms. Cd and Pb levels in all areas were higher than ERL values but were much lower than ERM values

Factor analysis in this study acts as a powerful tool in grouping and identification of metals associations that can be interpreted in terms of mineralization, metalo-organic complexing and diagenetic conditions of the environment.

The results of this study could be used as a contribution to the knowledge and rational

management of these regions in the future and would serve as a baseline against which future anthropogenic effects can be assessed.

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