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Heavy metals pollution in sediment cores from the Gulf of Aqaba, Red Sea

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ABSTRACT

The distribution of metals (Cd, Cr, Pb, Cu, Ni and Zn) was determined in sediment cores collected from five major areas representing different anthropogenic activities along the Jordanian coast during 27 February-11 March 2008. Metal concentrations in these sediments were relatively low compared to reported values from polluted areas. At some of the sites metal concentrations showed fluctuations with depth in the core suggesting changes in metal loading with time. The calculated contamination factors (CFs) for the suite of metals decreased in the following order Cd > Pb > Cr > Ni > Zn > Cu. The Pollution Loading Index (PLI) calculated for the different areas were highest at Phosphate Loading Berth (0.008, 0.2607, 0.0161, 0.007, 47.9375 and 0.0296 for Cu, Pb, Ni, Zn, Cd and Cr, respectively) and lowest at Hotel Area (0.0001, 0.0075, 0.0008, 0.0006, 1.0483 and 0.0005 for Cu, Pb, Ni, Zn, Cd and Cr, respectively) with others sites between these extremes. Result of this study could be used to assess the magnitude of pollution at each site and guide rational management decisions. Moreover, the data constitutes a baseline against which future anthropogenic effects can be assessed.

Keywords: Metals; Core sediments; Pollution Loading Index; Contamination Factor; Gulf of Aqaba; Red Sea

1. INTRODUCTION

Within rapid industrialization and economic development in coastal areas around the world heavy metals are introduced to the coastal environment [1,2]. Studies have been curried to evaluate heavy metal distribution in surface sediments to assess the degree of pollution in the marine environment [3,4]. Heavy metals are transported as either dissolve species in water or in association with suspended sediments and are subsequently deposited and stored in bottom sediments. After burial some the distribution of some redox sensitive metal could be modified by natural processes in the sediment. The bioaccumulation of heavy metals in coastal sediments can be hazardous to the local population which uses the coast area for fishing and recreation activities [5,6]. Metal abundance in sediments cores can provide a historical record of changes in metal contamination over time and their relation to historical changes in land use and anthropogenic activity [7,8]. Specifically, if the sediment core is intact and sediments remain undisturbed by human activities or extensive bioturbation then a continuous record over time could be obtained [6,9]. Most of the previous studies, dealing with levels of heavy metal pollution in the coastal areas along the Jordanian coast focused on relating heavy metals in surface sediments to those seen in living organisms such as algae and seagrass [10], sea urchin [11] and sea cucumber [12]. The objective of this work is to study the concentration of six metals nickel (Ni), copper (Cu), lead (Pb), zinc (Zn), cadmium (Cd) and chromium (Cr) in sediment cores collected at 3 water depths (5, 15 and 35 m) at five sites characterized by various industrial and tourism activities along the Jordanian coast of the Gulf of Aqaba. These data will provide a historical record of spatial and temporal changes in metal pollution. To quantify the magnitude of pollution two measures were employed: Contamination Factor (CF) and Pollution Load Index (PLI).

2. METHODS

2.1. Study Area

The Gulf of Aqaba is the north eastern segment of the Red Sea. It is located between 28˚ - 29˚30'N and 34˚30' -

35˚E [13] (**Figure 1**). The Gulf is deep (max. depth 1800 m) and narrow (180 km long, 14 - 26 km wide) and is surrounded by desert mountains with negligible inputs of fresh water or run-off. This area has a hot and dry climate with average temperature of 23˚C. The sea surface temperature ranges between 21˚C during winter and 27˚C during summer with temperatures of 21˚C even in deep waters. The net evaporation in this area is 0.5 - 1 cm·day^{-1} [13]. The study area lies within the Jordanian portion of the Gulf of Aqaba, located at the most northern and northeastern side of the Gulf and extended about 27 km [14]. The coastal areas on the Gulf are important environmental, economical, and recreational areas in Jordan.

2.2. Sample Collection and Treatment

Sediments were collected by scuba diving at five coastal locations along the Jordanian coast (Hotels Area (HA), Phosphate Loading Berth (PLB), Marine Science Station (MSS), Tala Bay (TB) and Industrial Area (IA)) (**Figure 1**). Cores were all obtained within a short time interval between the 27th of February and 11th of March 2008. The selected locations represent the different types and extend of anthropogenic activities occurring along the Jordanian coast. Specifically the Hotels Area lies on the beach of city of Aqaba and is impacted by a high density of visitors; the Phosphate Loading Berth (PLB) is situated about 3 km south of Aqaba city and it is the port used for loading and export of phosphate from Jordan; the Marine Science Station (MSS) is located 10 km south of Aqaba city close to the passengers port where ferry traffic arrives from Egypt, the MSS sites is known for its wide variety benthic habitants and excellent back reef lagoon; Tala Bay Marina (TB) lies about 14 km south of the city of Aqaba, it is an integrated residential and tourist resort; the Industrial Area (IA) site is located 15 km south of the main port of Aqaba, at this location several plants for fertilizer and phosphate ore production and handling as well as storage and loading facilities. Sediment cores were collected at three different water column depths (5 m, 15 m and 35 m) at each location using a sharp stainless steel core of 8 cm in diameter. Each core was about 15 cm long and was sectioned in the laboratory into three sections (0 - 5 cm, 5 - 10 cm and 10 - 15 cm). Sediment samples were dried until a constant weight was obtained, after that samples were homogenized and kept in Naylon bags. A subsample (100 g) was used for grain size analysis using standard dry sieving and sedimentation techniques [15].

2.3. Heavy Metal Analysis

For heavy metal analysis 0.2 g of the homogenized sediment was dried at 105˚C, placed in pre-cleaned 100 ml glass beakers, and 8 ml of 69.5% ultra-pure nitric acid was added to each beaker. Samples were left to react at room temperature for 4 hrs. Beakers were then put on a hot plate at 100˚C for 6 hrs, allowed to cool to room temperature and heated again to near dryness in order to remove the nitric acid. The residue was dissolved in 8ml of 1% nitric acid and kept on a hot plate for about 1 hr to

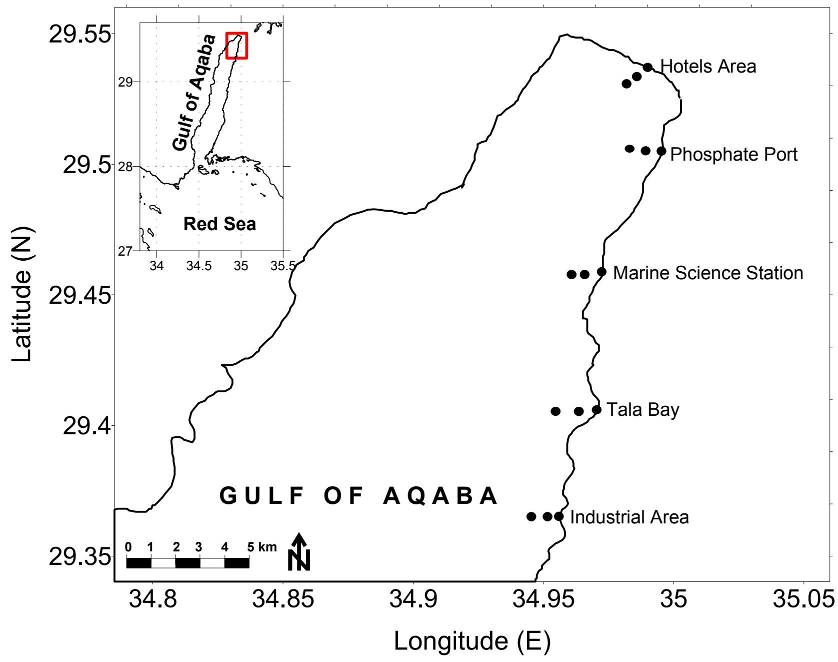


Figure 1. Sampling sites at the northern Gulf of Aqaba, Red Sea.

enhance dissolution. The samples were allowed to cool to room temperature and then filtered on a Whatman filter paper number 43. Samples were finally diluted to 25 ml with 1% nitric acid. Concentrations of Cd, Cr, Ni, Pb, Cu and Zn were measured on a Jena AA 400 atomic absorption spectrophotometer by direct aspiration into air-acetylene flame. The instrument was programmed to report the mean value and standard deviations of three repeat analyses of each sample. The precision of the whole procedure was assessed by 10 replicates for a sample and the results agreed to within 3%. Duplicate blanks were prepared and analyzed with each batch of digested samples. The mean value of the blank was subtracted from the readings of the sample to give the final reading. Three standard solutions that expected range of the element concentrations in the samples were also prepared and analyzed along with the samples. The standard calibration curves were linear. The final element concentrations are reported in $\mu g \cdot g^{-1}$ unit.

3. RESULTS AND DISCUSSION

3.1. Sediment Type

The texture and chemical properties of the sediment at the different sites were quite different. Sediments from the northernmost locations were fine, black and oxygen deficient, whereas sediments from the southern locations were white, better oxygenated, and slightly coarser [16]. **Table 1** shows the sediment type at the various sampling locations. The sediment texture is sandy at MSS, TB and IA indicating of the high energetic regime of alongshore currents allowing the washout the finer particles [6,17]; the hotel area has sandy silt sediments and the sediments are PLB are dominated by clays. The fine sediments at PBL are a result of substantial amounts of phosphate powder deposited at the site from dust ore blowing during the process of shipment. This site also has a higher sedimentation rate compared to the other sites along the Jordan coast [16].

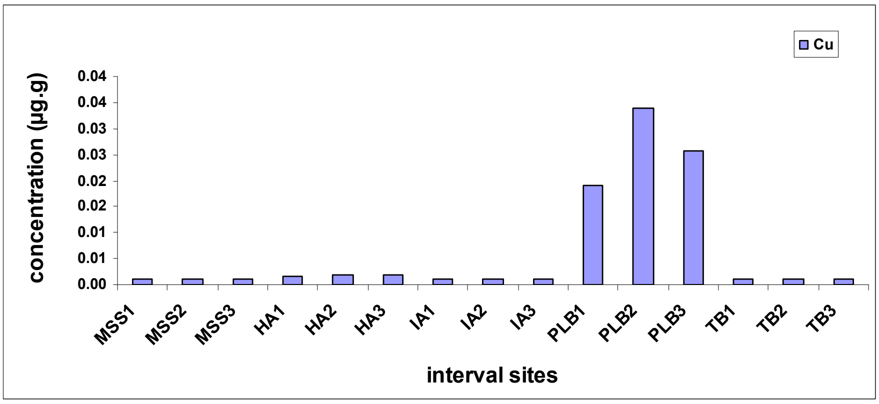
3.2. Trends in Element Concentrations in the Sediment Cores

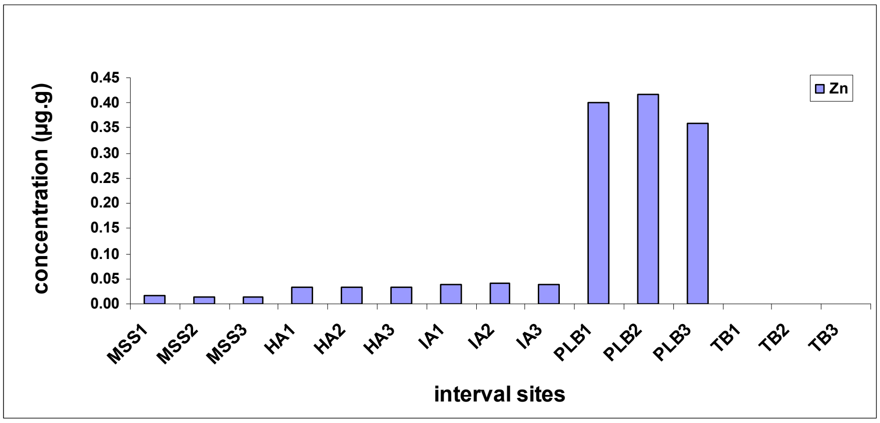
The heavy metals concentration profiles obtained from the collected cores are shown in **Figure 2**. Different elements exhibited different trends in their vertical distribution at the different sites.

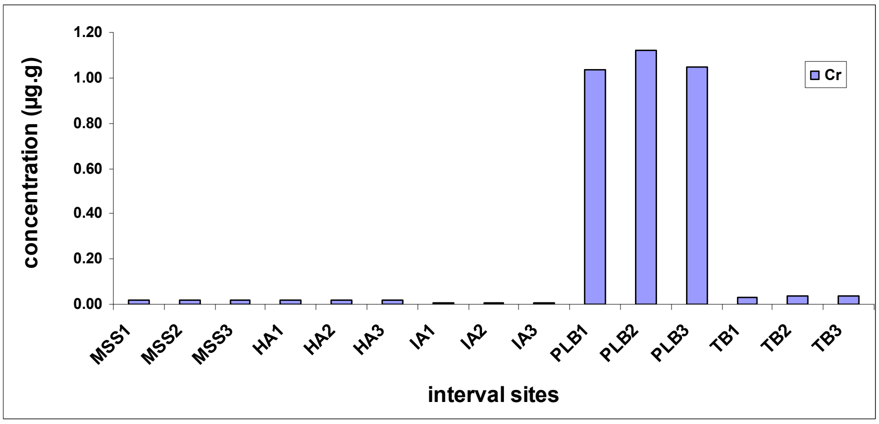
For *Chromium* (Cr), at most sites the highest detected concentrations were recorded in the interval between 10 - 15 cm. However, PLB Cr profiles showed an additional peak at 5 - 10 cm. Analytical results obtained by [18,19] indicated that Cr as (Cr^{6+}) is relatively mobile and migrate to the reduced zone which is typically present at the deeper levels in our cores. Indeed this may explain the presence of a Cr peak at the deepest interval where oxygen is most depleted and the presence of a peak at shallower depth at PLB where sedimentation rates are highest and thus oxygen penetration is retarded. *Nickel* (Ni), which is quite abundant in the Earth's crust, enters surface waters from the dissolution of rocks and soil, from biological sources, atmospheric fallout, and especially

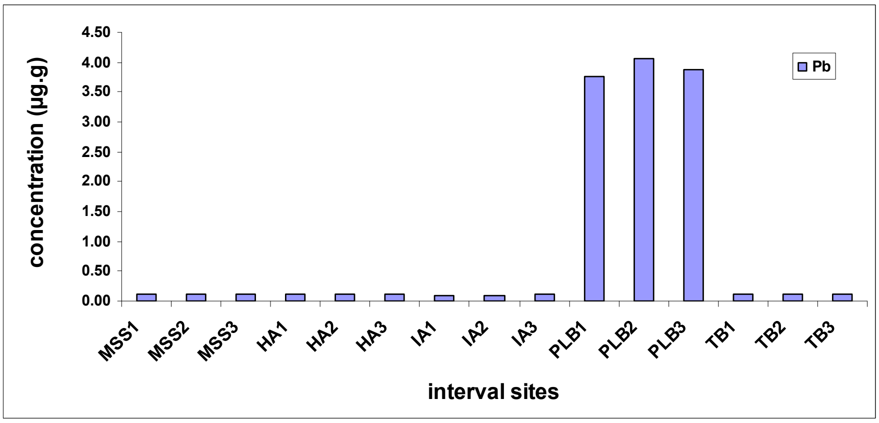
Table 1. Depth, date, location color, type and organic matter content in sediments at each of the sampling sites.

Site	Depth (m)	Date	Latitude	Longitude	Color	Type
MS	5	7 Mar 2008	29˚27'555"N	34˚58'435"E	Brown to Gray	Sandy
MS	15	4 Mar 2008	29˚27'555"N	34˚58'435"E	Brown to Gray	Sandy
MS	35	7 Mar 2008	29˚27'555"N	34˚58'435"E	Brown to Gray	Sandy
HA	5	27 Feb 2008	29˚27'986"N	34˚59'532"E	Black	Sandy Silt
HA	15	4 Mar 2008	29˚27'986"N	34˚59'532"E	Black	Sandy Silt
HA	35	4 Mar 2008	29˚27'986"N	34˚59'532"E	Black	Sandy Silt
IA	5	12 Mar 2008	29˚22'705"N	34˚57'602"E	White	Sandy
IA	15	12 Mar 2008	29˚22'705"N	34˚57'602"E	White	Sandy
IA	35	12 Mar 2008	29˚22'705"N	34˚57'602"E	White	Sandy
PL	5	10 Mar 2008	29˚30'191"N	34˚59'465"E	Gray to Black	Clay
PL	15	10 Mar 2008	29˚30'191"N	34˚59'465"E	Gray to Black	Clay
PL	35	10 Mar 2008	29˚30'191"N	34˚59'465"E	Gray to Black	Clay
TB	5	11 Mar 2008	29˚26'386"N	34˚58'148"E	Brown to Gray	Sandy
TB	15	11 Mar 2008	29˚26'386"N	34˚58'148"E	Brown to Gray	Sandy
TB	35	11 Mar 2008	29˚26'386"N	34˚58'148"E	Brown to Gray	Sandy


▫ Cu
concentration (µg.g)
0.04
0.04
0.03
0.03
0.02
0.02
0.01
0.01
0.00
MSS1
MSS2
MSS3
HA1
HA2
HA3
IA1
IA2
IA3
PLB1
PLB2
PLB3
TB1
TB2
TB3
interval sites


▫ Zn
concentration (µg.g)
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
MSS1
MSS2
MSS3
HA1
HA2
HA3
IA1
IA2
IA3
PLB1
PLB2
PLB3
TB1
TB2
TB3
interval sites


▫ Cr
concentration (µg.g)
1.20
1.00
0.80
0.60
0.40
0.20
0.00
MSS1
MSS2
MSS3
HA1
HA2
HA3
IA1
IA2
IA3
PLB1
PLB2
PLB3
TB1
TB2
TB3
interval sites


▫ Pb
concentration (µg.g)
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
MSS1
MSS2
MSS3
HA1
HA2
HA3
IA1
IA2
IA3
PLB1
PLB2
PLB3
TB1
TB2
TB3
interval sites

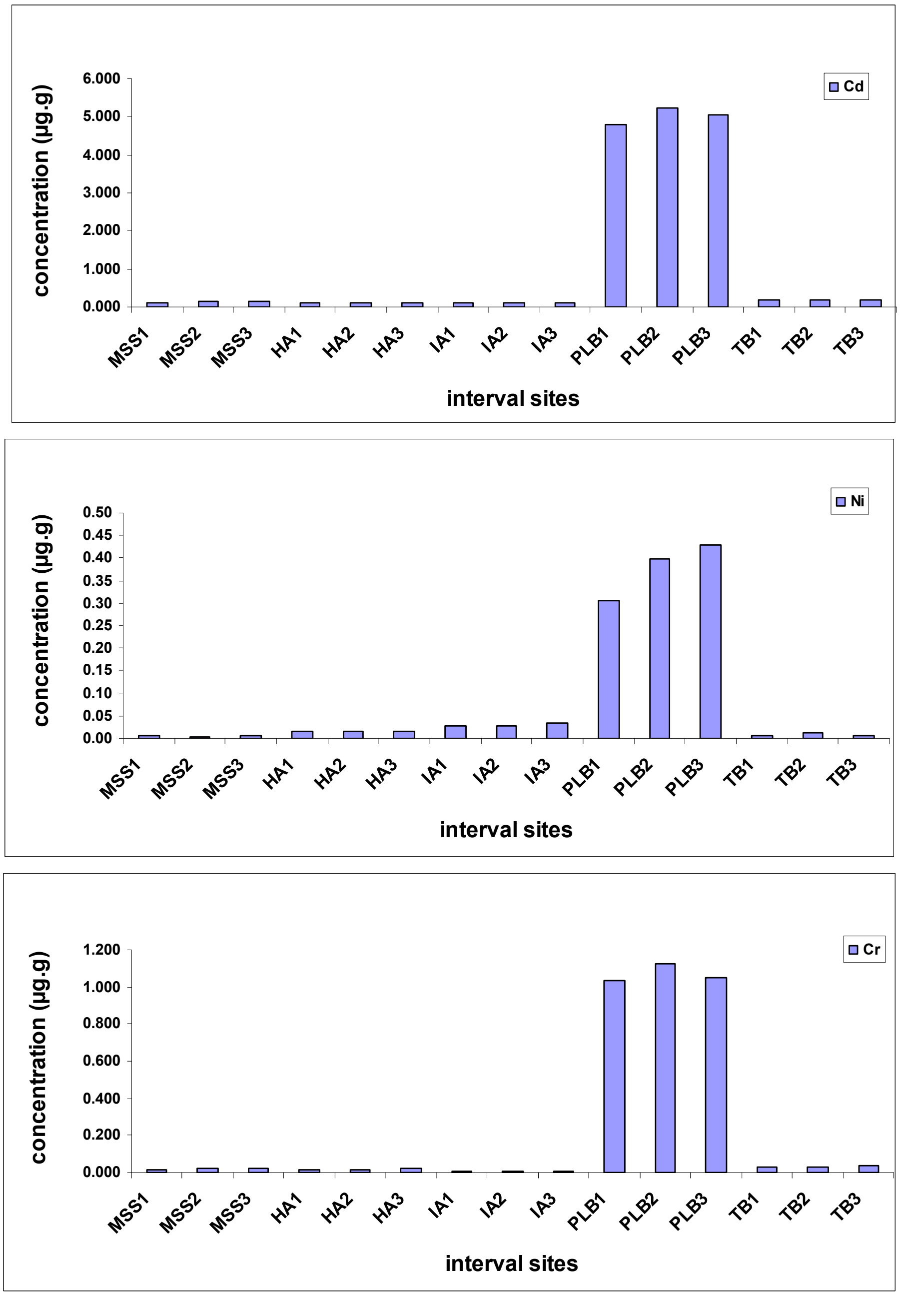


Figure 2. Mean metal concentration (µg·g^{-1}) at all sampling site.

from industrial processes and waste disposal [20]. The vertical distribution of Ni exhibited a distinct increase in concentrations in the 10 - 15 cm section at both PLB and IA and similar profiles with somewhat lower concentrations at other sites. According to [21], the increase of Ni content at subsurface layers is due to Ni sorption onto manganese oxyhydroxides. It is well known that Ni is insoluble at the pH values of marine environment (>6.7) and exist predominantly as Ni hydroxides [22] which is turn are quickly incorporated into particles. *Copper* (Cu), is one of the most common contaminants associated with urban runoff. Important anthropogenic inputs of Cu in estuarine and coastal waters include sewage sludge dump sites, municipal waste discharge, and antifouling paints [23]. In relatively clean sediments, Cu concentrations are about 50 µg·g^{-1} while sediments with concentration of >60 µg·g^{-1} are classified by the EPA as contaminated [24]. According to the calculated overall average concentration of Cu (0.03 µg·g^{-1}) in the five studied sites the sediments studied are uncontaminated with respect to Cu. The vertical profiles of Cu in the studied cores showed similar patterns of distribution at all sites. At PLB slightly higher concentration at 5 - 15 cm (0.034 $\mu g \cdot g^{-1}$) was recorded but the difference between this concentration and those recorded at other sites is not statistically significant. *Zinc* (Zn) is a naturally abundant element present as a common contaminant in agricultural food wastes, manufacturing of pesticides as well as in antifouling paints. The vertical distribution pattern of Zn was similar to that of Cr. Down core profiles of Zn suggest no changes in Zn pollution over time in this region as also recognized by [25]. However, at PLB a maximum in Zn was found in the 5 - 10 cm interval (0.42 $\mu g \cdot g^{-1}$) with lower values above and below. This finding might be attributed to the upward migration of Zn during organic matter degradation [25] or possibly to a period with higher Zn pollution at this site. Cadmium (Cd) which is a transition element behaves in the environment as a cumulative toxin [24]. It is listed by EPA as one of 129 priority pollutants and among the 25 most hazardous substances. Moreover, there is an international agreement forbidding discharge of any Cd into the sea [26]. It has been suggested that natural sources of Cd contribute 10% - 30% through windblown transport of soil particles and volcanic emissions [23]. The main source of Cd to the marine environment is mainly anthropogenic through atmospheric loading of refining and use of Cd [23]. The vertical distribution pattern of Cd in our cores showed an increase of its content with increasing depth in the core. Higher Cd contents in the PLB core (4.79 - 5.23 $\mu g \cdot g^{-1}$) compared to the concentrations at other sites of this study (0.098 - 0.187 $\mu g \cdot g^{-1}$) is consistent with the higher metal contamination at this site. It is well recognized that Cd is sensitive to redox changes; it is soluble in oxygenated conditions and precipitates immediately where reducing conditions are encountered [27]. Lead (Pb) compounds are also potentially harmful, especially tetraethyl lead [28]. It is listed by EPA as a carcinogen material. Concentrations of Pb in the studied sediments like Cd and Zn show low concentrations (0.1 - 0.123 $\mu g \cdot g^{-1}$) with slightly higher values of Pb in PLB core, The maximum value of (4.07 $\mu g \cdot g^{-1}$) was obtained in the 5 - 10 cm, interval and the minimum value was in the 0 - 5 cm section. High Pb concentrations are attributed to several sources such as boat exhausted systems, spillage of oil and other petroleum compounds form mechanized boats employed for fishing [29,30], all of these sources are present in the study area. In addition to these sources, atmospheric input of Pb generated from automobile exhaust emission can contribute a significant amount of Pb at PLB area which is located at the main port area where intensive traffic activities exists.

3.3. Estimating Pollution Impacts

A number of methods have been put forward for quantifying the degree of metal enrichment in sediments. Various authors [2,6,31,32] have proposed pollution impact scales or ranges to convert the numerical concentration results into broad groups of pollution ranges (e.g. low to high intensity). A contamination factor [33] is defined as the metal concentration in sediment divided by some background base value for each element. The background value corresponds to the baseline concentrations reported by [34] and is based on element abundances in sedimentary rocks (shale) (**Table 2**). The ranges used to describe the contamination factor are: CF < 1 is considered as low contaminated; 1 < CF < 3 is moderate contamination; 3 < CF < 6 is considerable contamination and CF > 6 is high contaminations.

The CF values for the various metals are shown in **Table 3**. The metal CF levels at all sample sites are present in the following order Cd > Pb > Cr > Ni > Zn > Cu. Cadmium concentration are relatively high in the study area, the CF ranged between 1 - 1.8 suggesting low to moderate contamination in all stations except at PLB where the CF value indicates extreme contamination (CF = 48). Low contamination factor was observed for Pb, Cr, Ni, Zn and Cu at all stations.

We also computed the pollution loading index (PLI) for our samples according to [33] using the following equation:

$$PLI = \left(CF_1 \times CF_2 \times CF_3 \times \cdots \times CF_n\right)^{\left(\frac{1}{n}\right)}$$

where: *PLI* = pollution loading index; *CF* = contamination factor; *n* = number of metals investigated.

The *PLI* was calculated for the five areas under investigation using the six investigated metals (Cd, Pb, Ni, Cu, Zn and Cr). It was observed that the highest *PLI* was found at PLB (0.06), while the lowest was calculated for Tala Bay (0.001), the calculated *PLI* were found in the following sequences: PLB > HA > IA > MSS > TB. The PLI values computed in our study are much lower than those reported [6], for the Red Sea (7.5 - 5.6; **Table 4**) and may indicate that the specific region we studied is less polluted.

4. CONCLUSIONS

Our results represent the first study on metals in core sediments of Jordanian coastal areas of the Gulf of Aqaba, Red Sea. The data indicate that the sediments at most of our sampling sites are uncontaminated. The only site with significant contamination particularly for Cd was found at the PLB site likely due to the extensive industrial activity at this site. The calculated CFs were found in the following order Cd > Pb > Cr > Ni > Zn > Cu. The pollution Loading Index (PLI) calculated for different areas were found in the following sequences:

Table 2. Metal concentrations ($\mu g \cdot g^{-1}$) in average continental crust used for calculating *PLI* [34].

Elements	Average continental crust	Elements	Average continental crust
Cr	35	Pb	14.8
Cu	25	Zn	52
Ni	19	Cd	0.1

Table 3. Contamination Factors for surface sediments.

Area	Cu	Pb	Ni	Zn	Cd	Cr
MSS	0.0001	0.0077	0.0003	0.0003	1.2617	0.0005
HA	0.0001	0.0075	0.0008	0.0006	1.0483	0.0005
IA	0.0001	0.0070	0.0015	0.0008	0.9550	0.0002
PLB	0.0008	0.2607	0.0161	0.0077	47.9375	0.0296
TB	0.0001	0.0084	0.0003	0.0000	1.7600	0.0009

Table 4. Concentrations of metals ($\mu g \cdot g^{-1}$) in surface sediments worldwide compared to those in the present study.

Location	Cu	Pb	Ni	Zn	Cd	Cr	Reference
Gulf of Aqab	0.03	4.07	0.43	0.42	5.25	1.12	Present study
Red Sea, KSA	25.76	92.86	90.79	93.86	3.95	35.36	[6]
Red Sea, Egypt	21.43			51.4			[35]
Al-Hodeidah, Yemen	11.3	3.48	13.25	30	14.2	20.2	[36]
Aegean Sea	9.6	22.3	38.4	75	0.25	35.7	[37]
Gulf of Mannar	57	16	24	73	0.16	177	[28]
South East Coast-India	506.21	32.36	38.61	126.83	6.58	194.83	[2]
Gulf of Mannar	57	16	24	73	0.16	177	[38]

PLB > HA > IA > MSS > TB. The results of this study could be used as a baseline against which future anthropogenic effects can be assessed and for management decision to reduce pollution particularly at the PLB site.

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