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METAL POLLUTION ASSESSMENT IN SEDIMENTS OF KARACHI COAST, PAKISTAN

*A. MASHIATULLAH, M.Z. CHAUDHARY, N. AHMAD[1], R. M. QURESHI[2], T. JAVED, A. GHAFFAR and M. S. KHAN

Isotope Application Division, PINSTECH, Islamabad, Pakistan

[1]Institute of Geology, University of the Punjab, Lahore, Pakistan

[2]Directorate of Coordination, PINSTECH, Islamabad, Pakistan

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Concentrations of eight metals (Fe, Mn, Cr, Mo, Ni , Pb , Sr and Zn) in surface sediments of Karachi Coast- Pakistan were determined to evaluate their distribution and pollution assessment. Measured metals in the sediments were found to be in the range of: Fe: 0.84 – 6.96 %, Mn: 300- 1300 µg/g, Cr: 12.0 – 319 µg/g, Mo: 0.49-2.03 µg/g, Ni: 1.53-58.9 µg/g, Pb: 9.0-49.5 µg/g, Sr:192-1185 µg/g, Zn: 15.6-666 µg/g. There is no significant correlations among most of these metals, indicating different anthropogenic and natural sources. To assess ecotoxic potential of marine sediments, Numerical Sediment Quality Guidelines (SQGs) were also applied. The concentrations of Pb in all the sediments were lower than the threshold effect concentration (TECs) showing that there is no harmful effect to marine life from Pb. On the other hand, the concentrations of Cr, Ni and Zn exceeded TEC in three station, indicating their potential risk. The degree of pollution in sediments for metals was assessed by calculating enrichment factor (EF) and pollution load index (PLI). The results indicated that sediments of Layari River Mouth Area, Fish Harbour and KPT Boat Building Area are highly enriched with Cr and Zn (EF > 5). Sediments of Layari River Outfall Zone were moderately enriched with Ni and Pb (EF > 2). The pollution load index was found in the range of 0.98 to 1.34. Lower values of PLI (≤ 1) at most of sampling locations imply no appreciable input from anthropogenic sources. However, relatively higher PLI values (>1) at Layari River Mouth Area, Fish Harbour and KPT Boat Building Area is attributed to increased human activity in the area.

Keywords: Karachi, Sea coast, Sediments, Metal, Pollution, Enrichment, Contamination

1. Introduction

Metals are natural constituents [1] and their deposition in aquatic environment can cause toxicity to its biota [2]. Metals are regarded as serious pollutants of aquatic ecosystems because of their environmental persistence, toxicity and ability to be incorporated into food chains. In marine waters metals are present in both dissolved as well as solid forms and play a role in many biogeochemical cycles. These metals are rapidly and efficiently removed to the sediments via adsorption onto surface particles, precipitation and incorporation into biogenic material [3]. Since ultimate sink of most of pollutants including metals are sediments, they are regarded as preferable monitoring tools for risk assessment studies [4].

In recent years, much attention has been paid to the chemical composition of marine sediments in coastal regions near large industrial and urban areas as it is linked to the deterioration of oceanic ecosystems [4,5]. In fact, during the last few decades, industrial and urban activities have contributed in increase of metals contamination into marine environment and have directly influenced the coastal ecosystems [6-8]. Pollution problems in such areas can increase heavy metal concentrations (e.g. Zn, Pb, Cd, and Cu) five to ten times higher than that of 50 to 100 years ago [9-11].

Sediment chemistry of Karachi coastal area has received wide attentions in recent years to understand elemental composition of these sediments and influence of anthropogenic activities. However investigations on geochemistry of sediment is necessary in order to assess the ecotoxic potential of metals. The aim of this study

* Corresponding author : azhar@pinstech.org.pk

was to examine the occurrence and distribution of metals, to explore the natural and anthropogenic input of metals, to assess the pollution status of metals on the area and to highlight relationships among metals.

2. The Study Area

Karachi is located on the northern boundary of the Arabian Sea. It is the largest city of Pakistan and a hub of industrial activity. The coastal zone of Karachi is extended upto 135 km that is exposed to heavy pollution load of both domestic and industrial origin [12]. The domestic waste generated by a population of ~15 million and industrial waste generated by more than 1000 large industrial units is drained into Karachi sea mainly via Layari River which flows through the Karachi East and falls into the sea at Manora Channel. With increase in urbanization, discharges of sewage and industrial effluent into marine ecosystems is also on the rise. The pollution load of sewage depletes oxygen levels in water and indirectly reduces the diversity of animal and plant life.

Manora Channel is a semi enclosed navigational channel. It connects the Karachi Port with the Arabian Sea in the south. It spreads over an area of 7.17 km^2 (Fig. 1). About 3.4 million cubic meter water enters and leaves the channel during a tidal cycle. High levels of toxic heavy metals such as mercury have been documented, especially in the coastal waters and sea near Karachi [13]. These are likely to have both acute and chronic toxic impacts on human beings, marine biodiversity and fish-eating birds. The impacts of these pollutants on commercial fin-fish and shrimp fisheries are unknown, but are likely to be significant [14].

3. Material and Methods

Sediments samples were taken in January/Feburary, 2009 from sixteen locations. eleven samples were from Manora Channel and five were from open sea near coastal area as shown in Fig. 1. Latitude and Longitude for each site sample are illustrated in Table 1.

The surface sediment samples from each location were collected with the help of a grab sampler. A plastic spoon was used to minimize contamination. No contact with the edge of grab happened during the sub sampling procedure. Immediately after collection, the sediment samples were placed in a polyethylene bag and preserved at low temperature in ice box. In laboratory sediment samples were oven dried at 70°C until constant weight, sieved mechanically using a 0.5 mm sieve, homogenized and ground to fine powder. 2 gm of sample was digested with 20 mL aqua regia (HCl/HNO_3 3:1) in a beaker (open-beaker digestion) on a thermostatically controlled hot plate. The digested samples were heated to near dryness and cooled to ambient temperature. Then 5.0 mL of hydrogen peroxide was added in parts to complete the digestion and the resulting mixture was heated again to near dryness. The beaker walls were washed with 10 mL of de-ionised water and then 5 mL HCl was added, mixed and heated again. The resulting digest was allowed to cool and transferred into a 50 mL standard flask and made upto the mark with de-ionized water. Metal analysis was performed on Inductively Coupled Plasma Optical Emission Spectrograph (ICP-OES Model 3580). For quality control, standard reference materials (SL- 1 Marine sediments, National Research Council, Canada) were prepared, with each batch of samples analyzed.

3.1 Assessment of sediment contamination

3.1.1 Enrichment factor (EF):

As proposed by Simex and Helz (1981) [15], EF was employed to assess the degree of contamination and to understand the distribution of the elements of anthropogenic origin from sites. Fe was chosen as the normalizing element while determining EF-values, since in wetlands it is mainly supplied from sediments and is one of the widely used reference elements [16].

Enrichment factor was calculated as:

$$\text{Enrichment Factor} = \frac{(Cn/Fe)\,\text{sample}}{(Cn/Fe)\,\text{background}}$$

where, Cn is the concentration of element “n”. The background value is that of average shale [17].

3.1.2. Pollution load index (PLI):

Pollution load index for each site was evaluated as indicated by Tomilson et al. (1980) [18] and Jumbe and Nandini (2009) [19].

$$\text{Pollution load index} = (CF1 * CF2 * \ldots * CFn)^{1/n}$$

Where n is the number of metals (eight in the present study) and CF is the contamination factor.

Table 1. Geological locations of sampling points.

Location	Latitude	Longitude
Layari River Mouth Area	24°51'45"	66°57'43.61"
Kakapir	24°50'05"	66°55'35"
Shamspir	24°50'34"	66°55'39"
Fish Harbour	24°50'59"	66°58'39"
Karachi Port Trust (KPT) Boat Building Area	24°50'21"	66°58'03"
KPT Shipyard	24°49'59"	66°58'02"
Baba Island	24°49'27"	66°57'53"
Bhit Island	24°49'00"	66°58'03
Manora Light House	24°47'33"	66°58'54"
Oil Jetty	24°48'12"	66°59'22"
Keamari Oil Terminal	24°48'08"	66°59'13"
Opposite NIO	24°48'20"	66°59'33"
Gizri Area	24°45'23"	67°03'39"
Sandspit	24°49'15"	66°55'23"
Buleji	24°49'04"	66°50'41"
Paradise Point	24°50'12"	66°47'56"

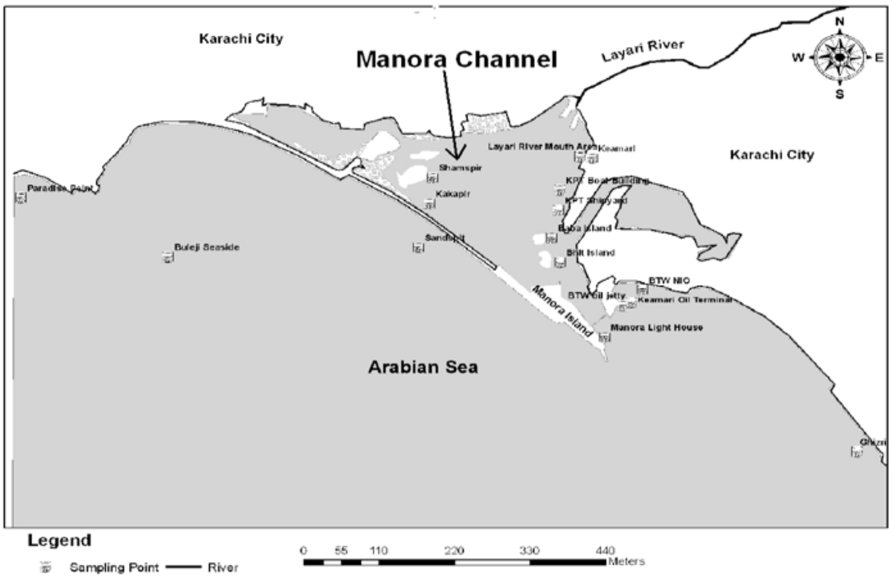

Figure 1. Map of sampling locations.

The contamination can be calculated from; Contamination factor (CF) = metal conc. in sediments/Background values of the metal.

3.1.3 Correlation analysis

Pearson correlation's analysis was adopted to analyse and establish inter-metal relationship.

4. Results and Discussions

4.1. Metal Distribution in Sediments

Metal concentrations in sediments of the area are shown in Table 2. The elements are in the range of : Fe: 0.84 – 6.96 %, Mn: 300- 1300 µg/g, Cr: 12.0 – 319 µg/g, Mo: 0.49-2.03 µg/g, Ni: 1.53-58.9 µg/g, Pb:9.0-49.5 µg/g, Sr:192-1185 µg/g and

Zn: 15.6-666 µg/g. Mean contents of the metal studied are: Fe: 3.07 %, Mn: 500 µg/g, Cr: 96.8 µg/g, Mo: 1.34 µg/g, Ni: 31.4 µg/g, Pb:23.24 µg/g, Sr:374 µg/g and Zn: 204 µg/g. Aarrangement of the metals from higher to lower mean content in this area is as: Fe > Mn > Sr> Zn > Cr> Pb> Ni> Mo. Highest concentration of Cr (319 µg/g), Mo (2.03 µg/g) and Zn (666 µg/g) was recorded in the sediments of KPT Boat Building Area, followed by sediment of Layari River Mouth Area. Fe (6.96%) and Ni (58.9 µg/g) were higher in the sediment taken in between Oil Jetty and Oyster Rock. Highest concentration of Pb (49.5 µg/g) was recorded at Layari River outfall zone. Sr (1185 µg/g) and Mn (1300 µg/g) were higher at paradise point.

Zn concentration in Layari River out fall Zone, KPT Boat Building Area, Fish Harbour and Oil terminal is quite high. Zn can enter the aquatic environment from a number of sources including sewage effluent and runoff. Input of organic wastes into the estuary, which comes from sewage, contributes to the Zn increase in sediments [5].

4.2 Ecotoicological Sense of Heavy Metal Contamination

The accumulation of heavy metals in sediments can be a secondary source of water pollution, once environmental condition is changed. Therefore, an assessment of metal contamination in sediments is an indispensable tool to assess the risk of an aquatic environment. To assess metal risk in sediments, Numerical Sediment Quality Guidelines (SQGs) was applied [1]. SQGs include a threshold effect concentration (TEC) (Table 2). If the metals in sediments are below the TEC, harmful effects are unlikely to be observed. If the metals are above the PEC, harmful effects are likely to be observed. MacDonald et al. (2000) [20] noted in his studies that most of the TECs provide an accurate basis for predicting the absence of sediment toxicity.

In present study, the concentrations of Pb in all the sediment samples are lower than the TECs indicated that there are no harmful effects from this metal. Cr and Zn at KPT Boat Building and Zn at Kaemari oil terminal exceed respective TEC indicating that these stations are at potential risk (Table 2).

Some researchers use numerical sediment quality guidelines as predictors of contaminants in aquatic sediments [21]. The chemical contamination in the sediments was evaluated by comparison with the sediment quality guideline proposed by USEPA [22]. These criteria are shown in Table 3. Comparing the results from Table 2 with Table 3, it is noted that Cr in ten and Mn in three station are heavily polluted while Mn in all other station is modernly polluted, Cr in two stations is non polluted while four sampling locations are moderately polluted with Cr. All the sampling station are either unpolluted to modernly polluted with respect to Pb and Ni.

4.3. Correlation Coefficient

Inter elemental association has also been evaluated by pearson correlation coefficient (r) and the results are presented in Table 4. It is obvious from the results that elemental pairs Fe/Mo (r = 0.6 P<0.01), Fe/Ni (r=0.79, P<0.01), Cr/Mo (r= 0.71, P<0.01), Cr/Ni (r= 0.61, P<0.01), Cr/Pb (r= 0.87, P<0.01), Cr/Zn 9 r =0.77, P<0.01), Mo/Ni (r= 0.84, P<0.01), Mo/Pb (r= 0.76, P<0.01), Ni/Pb (r= 0.70, P<0.01), Pb/Zn, (r = 0.75, P < 0.01) are significantly correlated with each other, whereas the rest of elemental pairs show no significant correlation with each other. Elemental association may signify that each paired elements has identical source or common sink in the marine sediments [23, 24]. In many cases, however, there is no significant correlations among the metals, suggesting that these metals are not associated with each other and they might have different anthropogenic as well as natural sources. Possible anthropogenic sources are untreated effluents such as automobile batteries, electroplating, car painting dying, and glass industries via Malir and Layari river into the sea.

4.4 Metal Pollution Assessment

Metal pollution can be assessed with respect to world surface rock averages [25] or the widely used average shale [26] with reference to the degree of contamination. The source of pollution is, therefore, determined through the normalization of geo-accumulation values to the reference element. The degree of pollution in sediments can be assessed by determining the enrichment factor and pollution load index.

Table 2. Metal concentration in surface sediments of Karachi coast.

Sediment Sample	Fe %	Mn (µg/g)	Cr (µg/g)	Mo (µg/g)	Ni (µg/g)	Pb (µg/g)	Sr (µg/g)	Zn (µg/g)
Layari River Mouth Area	2.99	300	293	1.75	48.8	49.5	192	537
Kakapir - Layari Channel side	2.54	400	89	1.33	36.9	21.9	339	85.0
Shamspir - Layari Channel side	2.86	400	106	1.56	32.4	22.4	297	111
Fish Harbour Channel	3.60	400	102	1.31	25.6	29.4	313	581
KPT Boat Building Area Channel	3.45	400	319	2.03	56.5	33.8	307	666
KPT Shipyard Channel	1.79	300	92.0	1.07	1.53	18.9	449	83.9
Baba Island Channel	2.60	400	80.0	1.19	27.5	20.6	393	95.0
Bhit Island Channel	3.13	500	70.0	1.42	30.6	21.7	348	96.0
Keamari Oil Terminal Channel	4.00	600	82.0	1.31	39.1	23.7	262	524
Manora Light House Channel	0.84	300	14.0	0.49	7.04	9.00	581	15.6
BTW Oil Jetty & Oyster Rocks	6.96	900	85.0	1.64	58.9	27.03	193	161
BTW NIO/ Manora Lighthouse	4.84	500	70.0	1.48	43.7	22.92	216	119
Gizri Area Seaside	1.88	400	12.0	1.29	18.8	16.94	217	41.4
Sandspit Seaside	2.14	400	33.0	1.17	23.9	15.42	325	49.8
Buleji Seaside	3.44	600	80.0	1.74	38.1	25.10	375	80.4
Paradise Point	1.99	1300	20.0	0.63	12.8	13.64	1185	27.8
Mean	*3.07*	*500*	*96.8*	*1.34*	*31.4*	*23.2*	*374*	*204*
Max	*6.96*	*1300*	*319*	*2.03*	*58.9*	*49.5*	*1185*	*666*
Min	*0.84*	*300*	*12.0*	*0.49*	*1.53*	*9.00*	*192*	*15.6*
TEC	--	--	43.4	--	22.7	35.8	--	121

Table 3. Comparison of heavy metal in present study with USEPA guideline.

Metals	Non Polluted (µg/g)	Moderately Polluted (µg/g)	Heavily Polluted (µg/g)	Present Study (µg/g)
Cr	< 25	-75	> 75	12- 293
Mn	< 300	300- 500	> 500	400-1300
Ni	< 20	20-50	> 50	1.53 – 48.78
Pb	< 40	40-60	> 60	9.0 – 49.46

Table 4 Pearson correlation among metals in Karachi sea sediments.

	Fe	Mn	Cr	Mo	Ni	Pb	Sr	Zn
Fe	1.00	0.32	0.21	0.60**	0.79**	0.43	-0.45	0.31
Mn		1.00	-0.28	-0.21	0.07	-0.22	0.62	-0.22
Cr			1.00	0.71**	0.61**	0.87**	-0.34	0.77**
Mo				1.00	0.84**	0.76**	-0.69	0.52
Ni					1.00	0.70**	-0.55	0.52
Pb						1.00	-0.49	0.75
Sr							1.00	-0.34
Zn								1.00

** Correlation is significant at the 0.01 level (1-tailed).

4.4.1 Enrichment Factor (EF)

An element qualifies as a reference one if it is of low occurrence variability and is present in the environment in trace amounts [27]. Naturally driven elements have an EF value of nearly unity, while elements of anthropogenic origin have EF values of several orders of magnitude.

Six categories of metal enrichment are recognized: < 1 background concentration, 1- 2 depletion to minimal enrichment, 2 – 5 moderate enrichment, 5 – 20 significant enrichment, 20 – 40 very high enrichment and > 40 extremely high enrichment [28].

Enrichment Factor values for metals are shown in Table 5. Sediments of Layari River Mouth Area are highly enriched with Cr and Zn (EF >5). Sediments from Fish harbour and KPT Boat Building Area are highly enriched with Cr and Zn (EF > 5), and moderately enriched with Ni (EF > 2). Sediments of Layari River outfall zone, which receives domestic/industrial waster into sea are moderately enriched with Ni and Pb (EF > 2) and highly enriched with Zn (EF > 5). The average metal EF in sediments follows the order as Zn > Cr > Sr > Ni > Pb>Mn>Mo. Sediments of sandspit area, which belong to claen sea environment, do not show enrichment of metals. Similarly no enrichment was observed at sampling locations at Baba and Bhit Island. Although these location are situated in Manora Channel where large amount of Layari river water enters, this is attributed to continues dragging of sediments from this area [12]. Mn and Mo is in background level or minimal enriched (EF<1) in all the sediments of the area as value close to 1 (mean 1.08 and 1.05), which could indicate some crustal origin for these metal.

4.4.2 Pollution Load Index (PLI)

This index is used to determine the mutual contamination effect of the studied metal species and has been derived as the Pollution Load Index (PLI) as the nth root of the contamination factor (CF) of studied metals in an aquatic ecosystem. The value for contamination factor of the metal is obtained by the dividing the concentration of the individual metal species to its respective background value [20].

The pollution load index does not show much fluctuation (0.98 to 1.34) as shown in Table 5. Lower values of PLI (≤ 1) imply no appreciable input from anthropogenic sources. In general, a decrease in PLI values indicates dilution and dispersion of metal content with increasing distance from source areas. However, relatively higher PLI (>1) values at Layari River Mouth Area, Fish Harbour and KPT Boat Building Area is due to increased human activity. PLI shows the magnitude and extent of the heavy metals deposition in the sediment of the study area over a long period of time. In this case, the results suggest that the sediment bed in Layari River Outfall, Fish harbour and KPT Boat Building Area, in particular, are deposited with more heavy metal accumulation than those in the other locations.

Table 5. Enrichment factor and pollution load Index of metals in sediments of area.

Sampling Locations	Mn	Cr	Mo	Ni	Pb	Sr	Zn	PLI
Layari River Mouth Area	0.55	8.65	1.29	2.71	3.01	0.63	10.68	1.34
Kakapir	0.83	3.09	1.16	2.42	1.57	1.31	1.99	1.09
Shamspir	0.75	3.27	1.21	1.88	1.42	1.02	2.31	1.11
Fish Harbour	0.46	2.50	0.80	1.18	1.48	0.85	9.59	1.33
KPT Boat Building Area	0.65	8.18	1.30	2.72	1.78	0.87	11.47	1.36
KPT Shipyard	1.08	4.54	1.32	0.14	1.92	2.45	2.79	1.14
Baba Island	0.89	2.72	1.01	1.76	1.44	1.48	2.18	1.10
Bhit Island	0.89	1.97	1.00	1.62	1.26	1.09	1.83	1.08
Keamari Oil Terminal	0.87	1.81	0.72	1.62	1.08	0.64	7.78	1.29
Manora Light House	1.91	1.47	1.28	1.39	1.95	6.76	1.10	1.01
Oil Jetty	0.79	1.08	0.52	1.40	0.71	0.27	1.37	1.04
Opposite NIO	0.57	1.28	0.68	1.50	0.86	0.44	1.47	1.05
Gizri Area	1.13	0.56	1.51	1.66	1.64	1.13	1.31	1.03
Sandspit	1.15	1.36	1.20	1.86	1.31	1.48	1.38	1.04
Buleji	0.96	2.05	1.12	1.84	1.33	1.07	1.39	1.04
Paradise Point	3.83	0.89	0.70	1.07	1.25	2.82	0.83	0.98
Average	*1.08*	*2.84*	*1.05*	*1.67*	*1.50*	*1.71*	*3.72*	

Conclusion

The present study reveals that

- Concentrations of eight heavy metals (Fe, Mn , Cr , Mo , Ni , Pb , Sr and Zn) in surface sediment from Karachi coast indicates that there are no significant correlations among most of these metals, indicating they have different anthropogenic and natural sources.
- The concentrations of Pb in all the sediment samples are lower than the threshold effect concentration (TECs) showing no harmful effects from these metals on marine environment. On the other hand, the concentrations of Cr, Ni and Zn exceeded TEC in three station, indicating that these stations were in potential risk.
- Layari River Mouth Area, Fish Harbour and KPT Boat Building area sediments are highly enriched with Cr and Zn (EF > 5), and moderately enriched with Ni and Pb (EF > 2). Mn and Mo had a EF value close to 1 (mean 1.08 and 1.05) , which could indicate some crustal origin for these metal
- The pollution load index (PLI) does not show much fluctuation (0.98 to 1.34) However, relatively higher PLI (>1) values at Layari River Mouth Area, Fish Harbour and KPT Boat Building Area is due to increased human activity.
- Natural processes such as weathering and erosion of bedrocks are main supply sources of heavy metals in sediments.

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