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Distribution of trace metals in inter-tidal sediment along Karachi coast, Pakistan

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ABSTRACT: *Marine sediments are endpoints for trace metals emitted from anthropogenic sources and provide an archive for studying trace metal pollution. Contaminated sediments is a significant environmental problem affecting marine environments throughout the country. Most assessments of water quality have focused on water-soluble compounds, with relatively little attention paid to sediment, a repository for sorbed contaminants. The primary goal of this study was to determine the concentrations and spatial distribution of metals in marine sediments along Karachi coast. In the present study sediments samples from inter tidal along Karachi coast were analyzed on the ICP-EOS for trace metal concentration analysis using sediment standards namely SL-1, SL-3 and SL-5. Sediment samples were collected from pollution receipt zone namely: (i) Layari River out fall zone, (ii) Karachi Harbour Area (iii) Manora Channel Mains and open sea zone namely: (i) Manora Channel Exit (ii) North-West Coast of Karachi (iii) South East Coast of Karachi. In general, concentrations of toxic metal in sediment pertaining to Layari River mouth area and the Karachi Harbour area (which are pollution recipient areas) were higher as compared to toxic metal contents in sediments from other areas facing open sea (North-West Coast and South East Coast) and entrance to Manora Channel. In open sea zone, concentration of Cr, Cu, Ni, Pb, V and Zn were higher in sediments of Manora Channel exit as compare to South East Coast and North West Coast. Marine sediments belonging to the South-East coast off Karachi have relatively high concentrations of these toxic elements except (Pb, Sr, U) as compared to the North-West coast. Metal concentrations in surficial sediment shows that Karachi Harbour area is polluted area. Elevated concentrations of Cr (320 ppm), Ni (56 ppm), Sr (449 ppm), Zn (666 ppm), Pb (49 ppm) and U (1.66 ppm) occur in this area. Sewage and industrial wastes are the main sources of heavy metal pollution in Karachi Harbour. However, contamination in Karachi coast is not critical but heading towards it. Studies suggest incorporation of quick remedial measures to combat pollution in shallow marine environments off Karachi Coast.*

INTRODUCTION

Karachi is located on the northern boundary of the Arabian Sea. It is the largest city in Pakistan with coastline extending up to about 30km. The domestic waste generated by a population of ~10 million and industrial waste generated by more than 1000 large industrial units (chemical industry, textile industry, leather tanning industry, fish processing industry, cement industry, steel mills, thermal power plants, oil refineries etc.) is drained into Karachi sea mainly via Layari River, Malir River and Korangi Creek (Fig. 1). Maximum waste is discharged into the sea by Layari River via Manora Channel/Karachi Harbour (Ali & Jilani,

1995). This waste input to sea is further supplemented with oil spills from cargo ships and oil tankers in Manora Channel which includes Karachi Harbour, Naval Dockyard, Keamari Boat Basin, Keamari Fish Harbour and the backwaters area. The waste input in Manora channel is further supplemented with oil spills from cargo ships and oil tankers in Karachi Harbour. Manora Channel area is now considered to be the most heavily polluted marine site in Pakistan. Some sporadic and small scale pollution surveys involving classical hydro-geochemical and/or biological techniques have been made in the past to estimate the pollution status along the coast of Karachi (IAEA, 1987; Ali & Jilani, 1995; Khan & Salem, 1988: Ahmed, 1977). It has been documented that the discharge of sewage and industrial pollutants in the Karachi harbour/ Manora Channel has not only caused depletion of the Oyster beds in and around Karachi harbour area but the shrimps and fishes which were abundant in the Manora Channel, Manora Seaside and Hoxbay area have migrated to the deeper waters (Quraishee, 1985; Khan, 1995). Nevertheless, in spite of very high pollution levels in the Karachi Harbour area, it is still being used for bathing by tourists and the local population. The fish habitat and the mangroves in the Manora Channel/Karachi harbour and backwater areas are now under considerable stress due to contamination.

Surficial sediment are a feeding source for biological life, a transporting agent for pollutants and an ultimate sink for settling organic and inorganic matter (Algan et al., 1999). Their composition constitutes an important criterion for the assessment of long-term water quality. The metal content of sediment has natural and anthropogenic components. In heavily polluted sediment, the athropogenically introduced components by far exceed the natural component, and because of their bio-availability constitute a hazard to the marine ecosystem. Interactions between solid sedimentary matter and dissolved metals play an important role in the regulation of dissolved metal concentrations (which are the most bioavailable) in the water.

MATERIALS AND METHOD

Sampling and analysis

Sediments samples were collected from pollution receiving bodies namely: (i) Layari River out fall area, (ii) Karachi Harbour Area (iii) Manora Channel Mains and open sea side namely (i) Manora Channel Exit (ii) North-West Coast (iii) South East Coast (Fig. 1). Samples were collected during the low tide period using conventional mechanized tourist. The location of sampling points was determined with the help of a Garmin GPS-100 Personal Navigator™ (M/S Garmin, 11206 Thompson Avenue, Lenexa, KS 66219). Sediment samples were collected with the help of conventional Peterson Grab and contained in high quality polythene bags. Petersen grab samplers consist of a pair of weighted, semi-cylindrical jaws that are held open by a catch bar. The impact with the sediment loosens the tension on the catch bar allowing the jaws to close. As there is no access through the top of the sampler, only bulk samples can be taken. Petersen samplers are suitable for collection of hard bottom material. These samplers are restricted to low current conditions and may produce a bow/shock wave that disturbs fine grained sediments. From each site more than one samples were collected depending upon the area. Detail of sampling point in each area is given in Table 1.

TABLE 1. NUMBER OF SAMPLING POINTS FROM VARIOUS AREAS

Sr. No	Sampling Area	Sampling point
1	Layari River out fall Area	3
2	Karachi Harbour Area	3
3	Manora Channel Mains	4
4	Manora Channel Exit	2
5	North-West Coast	5
6	South East Coast	5

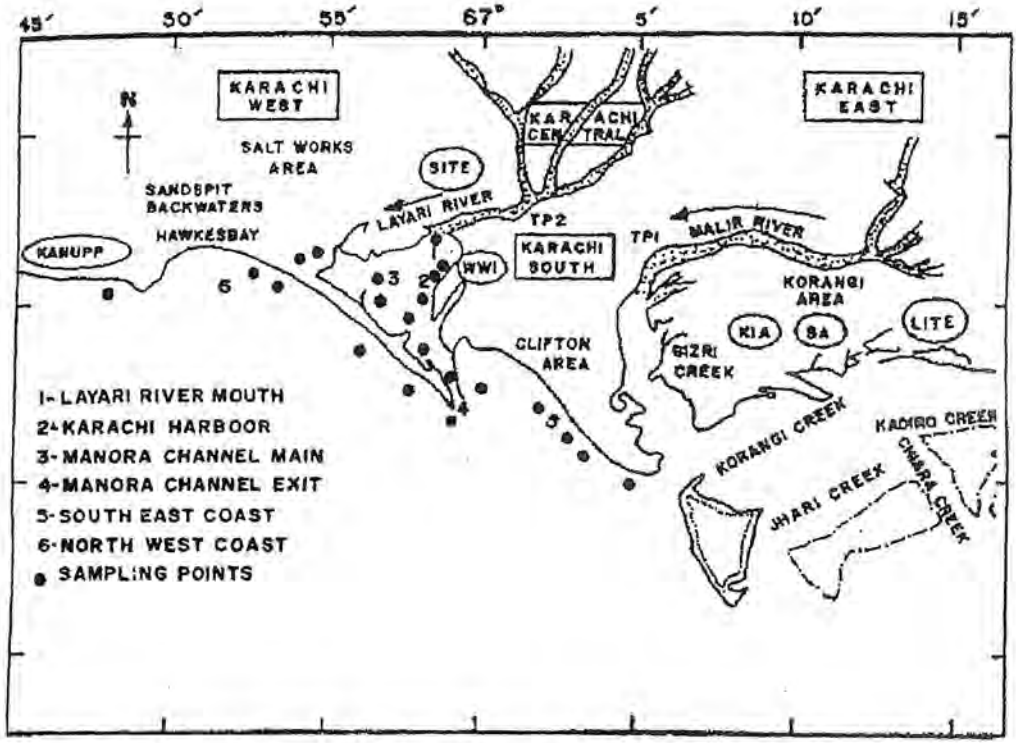

Fig. 1. Coastal map of Karachi showing location of industrial sites and drainage courses of polluted rivers into Karachi sea.

In the laboratory the samples were oven dried to constant weights. The dried samples were then milled into a fine powder using a mortar and pestle. A 500 ml of sediment samples was added to a Teflon beaker and treated with 20 ml of HF and 5 ml HNO_3. The mixture was heated at 120°C upto dryness. The residual was allowed to cool. It was treated with 10 ml each perchloric acid and nitric acid and digested at 200°C till alight brown solution is obtained. The solution was then transferred to a 100 ml calibrated volumetric flask and diluted to mark using a stock 4% (v/v) HNO_3. Selective toxic/trace element analyses (except uranium analysis) of dried/pulverized sediments (80 mesh size) were performed on a fully computerized Inductive couple plasma optical emission spectrometer (ICP-OES, Model 3580, Applied Research Laboratories, Switzerland) using standards namely SL-1, SL-3 and Soil-5 as well as with Flame Atomic Absorption Spectrophotometric (Perkin Elmer Model 3300, only for Cu, Cr, Ni, Pb, Zn) and concentration of uranium in sediments was measured with a 26-000 Jerrel Ash Fluorometer.

RESULTS AND DISCUSSION

Pollution receipt zone

Table 1 shows the minor and trace element concentrations in shallow sea bottom sediments in Layari River outfall Zone, Karachi harbour area and Manora Channel Main. Results are discussed in the following section:

Layari river outfall area: Layari River outfall area comprises of Layari River outfall (Karachi harbour), Layari River outfall

Shamspir Channel side and Layari River outfall Kakkapir Channel side. It may be noted that significantly high concentrations of Cr (293 ppm), Ni (48 ppm), Pb (49 ppm), V (69 ppm) and Zn (537 ppm) are present in the sediments of Layari River outfall in Karachi Harbour. While concentration of Sr (339 ppm) is found in Layari River Kakkapir and U (0.975 ppm) is found in Layari River Shamspir side. The pollution load of trace metal in Layari River out fall in Karachi can be attributed due to untreated domestic and industrial waste drained through Layari river in Karachi Harbour.

TABLE 1. TOXIC/TRACE METAL CONCENTRATION IN BOTTOM SEDIMENTS OF LAYARI RIVER OUTFALL, KARACHI HARBOUR AND MANORA CHANNEL MAIN

Sediment Sample Location	Geological Locations	Mn %	Cr (ppm)	Ni (ppm)	Pb (ppm)	Sr (ppm)	U (ppm)	V (ppm)	Zn (ppm)
Layari River Outfall Area									
Layari River Outfall (Karachi Harbour)	24-51-01 66-58-25	0.03	293.00	48.78	49.46	192.00	0.883	69.80	537.60
Layari River Outfall (Shamspir Village Channel side)	24-50-34 66-55-39	0.04	106.00	32.40	22.41	297.00	0.975	64.80	111.40
Layari River Outfall (Kakapir Village Channel side)	24-50-05 66-55-35	0.04	89.00	36.99	21.88	339.90	0.658	60.00	85.00
	Average	0.04	162.67	39.39	31.25	276.30	0.84	64.87	244.67
Karachi Harbour Area									
KPT Shipyard (Butti) Karachi Harbour/ Close to Layari Outfall	24-49-59 66-58-02	0.03	92.12	1.53	18.93	449.05	1.041	45.64	83.94
Boat Building Area Karachi Harbour/ Close to Layari Outfall	24-50-21 66-58-03	0.04	319.84	56.46	33.84	307.77	1.660	88.26	666.28
Keamari Fish Harbour	24-50-59 66°58-39	0.03	102.00	25.56	29.36	313.90	0.791	39.00	581.00
	Average	0.03	171.32	27.85	27.38	356.91	1.16	57.63	443.74
Manora Channel Mains									
Bhit Island	24-49-00 66-58-03	0.05	70.00	30.60	21.68	348.50	0.433	55.60	96.20
Bhaba Island	24-49-27 66-57-53	0.04	80.00	27.54	20.56	393.40	0.550	48.80	95.60
Keamari Oil Terminal	24-48-08 66-59-13	0.06	82.00	39.06	23.71	262.20	0.408	67.80	524.00
Light House (Manora Channel Inner Exit)	24-47-33 66-58-54	0.03	14.00	7.04	9.00	581.30	0.383	15.80	15.60
	Average	0.045	61.500	26.060	18.738	396.350	0.444	47.000	182.850

Karachi harbour area: Karachi Harbour area comprises of Karachi Port Trust, Boat Building Area and Keamari Fish Harbour. Maximum concentration of Mn (0.04%) Cr (319 ppm), Ni (56 ppm), Pb (34 ppm), U (1.66ppm) V (88ppm) and Zn (666ppm) were found in boat building area. In General average concentration of Mn, Cr, Ni, Pb, Sr, U, V and Zn in Karachi Harbour were 0.034%, 171 ppm, 28 ppm, 27 ppm, 357 ppm, 1 ppm, 58 ppm and 444 ppm respectively.

Manora channel main: Bhit Island, Bhaba Island Keamari Oil Terminal and Manora Light house inner Exit were main location in Manora Channel Mains. Keamari Oil Terminal may had maximum concentration of Mn (0.06%), Cr (82 ppm) Ni (39 ppm) Pb (24 ppm) and V (68 ppm). Maximum Sr (393 ppm) and U (0.550 ppm) is noticed in Bhaba Island. Manora Lighthouse has minimum concentration of these metal.

Open sea profile

Table 2 shows the trace element concentrations in selective shallow sea bottom sediments of Karachi Sea South-East Coast, Manora Channel Exit and the North-West coast. Results described in the following section

South east coast: Five shallow sea sediment samples from North West Coast Karachi were analysed for trace metals. The locations include bet Oil Jetty/Oyster Rocks, Casino, between marina club/ Naval Jetty and Ghizri Coast. Oil Jetty/Oyster Rock Area with Mn (0.09%), Cr (85 ppm), Ni (59 ppm), Pb (27 ppm), V (118 ppm) and Zn (161 ppm) are the most polluted site on the North West Coast. However maximum Sr (218 ppm) and U (0.285 ppm) was observed at Ghizri Area.

Manora channel mains: Two sampling points between NIO and Manora Lighthouse and Manora Channel Exit were monitored for trace metal analysis. High concentrations of Mn (0.05%), Cr (70 ppm), Ni (44 ppm), Pb (23 ppm), Sr (216 ppm), U (0.19 ppm), V (97 ppm), and Zn (119 ppm) are present in the area between NIO and Manora Light House.

North west coast: Five shallow sea sediment samples from North West Coast Karachi were analysed for trace metals. The locations include PNS Himaliya, Sandspit, Buleji, Kakkapir seaside and Power house. Maximum concentration of Mn (0.13%) and U (0.95%) was found in the sediments of power house. Bulji is the most polluted site where Cr (80 ppm), Ni (938 ppm), Pb (25 ppm), Sr (375 ppm), V (88 ppm) and Zn (80 ppm) was noticed.

Concentration of Cr, Cu, Ni, Pb, V and Zn are higher in sediments of Manora Channel exit as compare to south east coast and northwest coast. However, sediments pertaining to the southeast coast off Karachi have relatively high concentrations of these toxic elements except (Pb, Sr, U) as compared to the northwest coast. The high concentrations of toxicity in sediments of southeast coast of Karachi are due to several factors. Firstly, Korangi- Phitti creek on southeast coast mostly receives domestic sewage, agrochemical wastes, industrial waste waters. Secondly, sediments along this coast have high contents of clayey matter which have in-turn high absorption or trapping capacity for metals. Thirdly, this distribution is due to the impact of monsoons. During the winter (October - February), the northwest monsoon winds are relatively weaker, resulting in diminishing upwellings. The seawater from the near shore and off-shore Indus Delta enters the coastal waters of Karachi from the southeast and moves along the coast towards the northwest or westwards and then to the western coast of Karachi.

TABLE 2: TOXIC/TRACE METAL CONCENTRATION IN BOTTOM SEDIMENTS ALONG THE SOUTH EAST COAST, MANORA CHANNEL EXIT AND NORTH WEST COAST OF KARACHI

Sediment Sample Location	Geological Locations	Mn %	Cr (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Sr (ppm)	U (ppm)	V (ppm)	Zn (ppm)
South East Coast										
Btw. Oil Jetty/ Oyster Rocks (Clifton Coast)	24-48-12 66-59-22	0.09	85.00	N.D.	58.86	27.03	193.10	0.241	118.20	161.00
Bhutto Casino) (Clifton Coast)	24-47-32 67-01-39	N.D.	33.01	16.09	46.06	22.4	N.D.	N.D.	N.D.	73.2
Naval Jetty (Clifton Coast)	24-47-04 67-03-01	N.D.	25.79	13.41	43.37	19.12	N.D.	N.D.	N.D.	51.9
Btw Marina Club & Naval Jetty (Defence Coast)	24-46-23 67-03-01	N.D.	26.54	13.49	46.46	10.61	N.D.	N.D.	N.D.	59.5
Ghizri Area	24-45-23 67-03-39	0.04	12.00	ND	18.80	16.94	217.80	0.283	41.80	41.40
	Average	0.065	36.468	14.330	42.710	19.220	205.450	0.262	80.000	77.400
Manora Channel Exit										
Btw. NIO & Manora Lighthouse	24-48-20 66-59-33	0.05	70.00	N.D.	43.65	22.92	216.00	0.191	97.60	119.60
Light House Manora Exit	24-47-53 66-59-04	N.D.	19.23	18.56	38.46	21.15	N.D.	N.D.	N.D.	48.68
	Average	0.05	44.62	18.56	41.06	22.04	216.0	0.191	97.6	84.14
North West Coast										
PNS Himaliya (Sea ide)	24-48-30 66-56-29	N.D.	23.69	15.63	37.91	21.5	ND.	ND.	ND.	49.25
Sandspit (Sea side)	24-49-15 66-55-23	0.04	33.00	N.D.	23.94	15.42	325.00	0.408	49.60.	49.80
Buleji (Sea side)	24-49-04 66-50-41	0.06	80.00	N.D.	38.13	25.10	375.30	0.358	88.50	80.40
Kakka pir (Sea side)	24-49-55 66-53-55	N.D.	18.18	8.78	36.66	17.71	N.D.	N.D.	N.D.	29.05
Power House (Sea side)	24-50-12 66-47-56	0.13	20.00	N.D.	12.48	25.10	ND	0.95	36.80	80.40
	Average	0.077	34.974	12.205	29.824	20.966	350.150	0.572	62.650	57.780

ND = Not Determined

Thus, it moves in the southwest direction to the offshore area. During this type of a circulation pattern in the open sea, small clockwise gyres are developed along the beach. During the southwest monsoon (May - September), the dominant direction of seawater flow in the coastal waters of Karachi remains clockwise, i.e. the major flux of

seawater from the offshore area enters the coastal waters of Karachi at the western part of the coast from the southwest direction (Rizvi et al., 1995). During this type of a circulation pattern in the open sea, small anticlockwise gyres are developed along the beach. Due to weak speed of water in the winter monsoon and the south-west direction water movement in the summer monsoon, the contaminated water plume is not effectively spread in the direction of northwest coast. Thus metal rich water accumulates in the sediments of southeast coast and the Manora channel exit zone.

Figure 2 shows average concentration of Cr, Ni, Pb, Sr, U, V, Zn in the studied area. It is clear from this figure that Karachi harbor is most polluted site as compare to the other areas. The presence of high concentration of these toxic metals in harbour sediments is attributed to input of industrial waste effluents related to leather tanning industries, electroplating industries, battery material, waste from Karachi shipyard and Naval dockyard into the Karachi harbour area. The results obtained are consistent with the studies carried out by National Institute of Oceanography (NIO)-Karachi (Ali & Jilani, 1995). A small scale study in the Korangi-Phitti Creek, IAEA-Marine Environment Laboratory (Monaco) has reported that the concentration of Cr in the range of 2-19 ppm, Ni in the range of 3-7 ppm, Pb in the range of 3-13 ppm and V in the range of 4-13 ppm (IAEA, 1987). Similar concentrations of Cr, Ni, Pb, V and Zn have been reported in the literature for Oman Harbour, Kuwait Harbour, Bahrain Harbour and Bombay Harbour (Saleem & Qazi, 1995).

Over the last decade, chemical contamination of aquatic sediments has been recognized as a serious problem in coastal waters. In Puget Sound, hot spots of toxic chemicals have been shown to alter and reduce the bottom-dwelling community, to interfere with cellular and physiological processes, and to cause disease in fish (NOAA, 1987). Other adverse economic impacts of contaminated sediments include delaying or raising the cost of maintenance dredging of navigational waterways due to the potential dangers of re-suspending toxic chemicals into the water column or the need to find disposal sites for the sediments.

Toxic metal contaminants lead to a severe reduction in the diversity of bottom dwelling organisms that live in affected estuaries or coastal regions and adverse effects can spread, via the food chain, to fish, birds, and mammals that feed on contaminated sea life. Those species that persist despite contamination may be subject to chronic ailments including diseases, deformities, and reproductive maladies. Because they often contain high concentrations of toxic metals in their tissues, these organisms become a threat to human health. Organisms

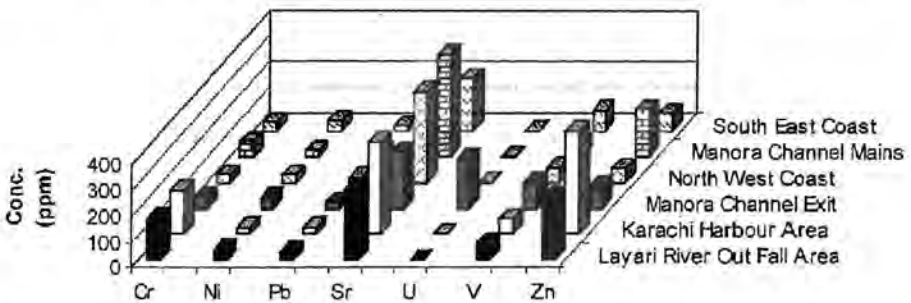

Fig. 2. Comparison of average toxic concentration of metals (ppm) in Karachi Coast.

may accumulate contaminants from water, sediments, or food in their tissues. This can result in concentrations of the contaminant many times higher than those found in the environment. The degree of bioaccumulation depends on the level of exposure and the mechanisms by which the organism expels, stores, or metabolically breaks down the contaminant. The contamination of marine sediments becomes an important political issue when ports are dredged and contaminated dredged materials have to be dumped at someplace, and it becomes a human health issue when fisheries are affected due to contaminated or diseased fish.

CONCLUSIONS

Good environmental quality is essential to sustaining coastal and marine ecosystems, commercial and recreational fisheries, and economic growth in coastal communities. The health of coastal and marine ecosystems is affected by water and sediment quality. The present results indicate that the inshore shallow sea waters off Karachi coast are polluted by untreated disposal of industrial and domestic waste water into the Karachi sea via Layari River outfall. The toxic metal analysis have given a rough evaluation of the aerial extent of the polluted zone in the Karachi harbour area and the Manora Channel Mains in response to mixing of Layari River water with the Arabian Sea water. The continuous pollution inventories along the coast of Karachi will have adverse effects in terms of (i) increase in toxicity levels of marine food chain; (ii) considerable stress on fish habitat and mangroves; (iii) corrosion of cargo ships and navel vessels; and (iv) significant ill effects on the health of bathing tourists and inhabitants of Bhaba & Bhit islands, naval dockyard and Manora channel. The environment and the economic health of marine and coastal waters are linked at the individual, community, state, regional, national and international levels. Government agencies and private industry in partnership should adopt technologies to prevent and reduce the impacts of pollution.

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