

Impact of Industrial and Sewage Effluents on Karachi Coastal Water and Sediment Quality

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Abstract: Two main sewer systems Malir and Lyari Rivers receive a large amount of effluent discharge approximately 450,000 gallons per day of raw municipal as well as industrial effluents to multi branched tidal creek estuary along the Karachi coast. The impacts of raw sewage disposal on water and sediments quality in Karachi fish harbor and estuary along Karachi urban coast were assessed during the period of January to December 2010 using sewage pollution markers, enrichment, contamination and geo-accumulation factors. The contents of four elements Cd, Pb, Zn and Hg, have been determined in the surficial sediments of West Wharf Karachi Fish Harbor Estuary. The contamination of the sediments was assessed on the basis of geo-accumulation index, contamination factor and modified degree of contamination. The results revealed highly elevated Cd, Pb, Zn, Cr and Hg concentration (Cd, 987-1240 mg/ kg; Pb, 930-1230 mg/ kg; Cr, 428-706 mg/kg; Zn, 1260-1410 mg/kg; Hg, 118-242 mg/kg). The enrichment of metals in the sediments resulted from the contribution of the Lyari river sewage outfall through which the waste of the river basin ends up in Karachi harbor as well as from industrial and ship contaminants.

Key words: BOD % Hypoxia % Enrichment % Contamination % Geo-Accumulation % Surficial

INTRODUCTION

Sewage disposal has become a major problem of the urban world due to the increase in human population, urbanization and industrial complex establishment. The commonality of sewage related problems throughout coastal areas of the world is significant since these areas are inhabited by over 60% of the human population [1]. Consequently, domestic and industrial effluents discharges are considered one of the most significant threats of the coastal environments worldwide. Environmental effects associated with domestic wastewater discharges are generally local with trans-boundary implications in some areas [1, 2].

Coastal waters are facing a variety of pressure affecting both the ecosystem and human health through sewage effluents discharge and disposal practices that may lead to introduction of high nutrient loads, hazardous

chemicals and pathogens causing diseases. The adverse public health, environmental, socio-economic, food quality and security and aesthetic impacts from sewage contamination in coastal areas are well documented [1-5]. Pollution of the coastal water usually interferes with various water uses. Cultured bivalves are generally reared in areas that are often densely populated and are sensitive to heavy pollution from human activities. Pathogens transmitted by human feces are most commonly involved and the discharge of sewage polluted by human and animal pathogens into the sea represents the main source of bacterial pollution [3]. Every pathogen present in seawater may be trapped and concentrated in the tissues of the bivalves and so represents a potential health hazard.

Discharges of industrial and municipal sewage effluents with heavily contaminated pollutants into the aquatic environment are of great concern all over the world. Under certain environmental conditions, pollutants

like, persistent organic pollutants, nutrients and heavy metals may accumulate to a toxic concentration and cause ecological damage. Estuarine areas are complex and dynamic aquatic environments where depositional processes are predominant. They principally act as sink and/or transitional way of several chemical pollutants as well as nutrients between freshwater-land and the open sea. Estuaries with extensive intertidal zones are of great interest from a biological point of view. Estuarine flats provide vital feeding grounds for migrant and native birds as well as nursery zones for fish; in addition, these areas are usually assigned to both industrialization and urbanization processes [6]. After 1980, freshwater flow to the estuary has noticeably decreased, mainly due to the initiation of the industrial establishments at Malir and Lyari Rivers most important rivers of metropolitan. Contaminants used to be mostly found associated with fine sediment particles. Heavy metals concentrations in recently deposited surface sediments within the intertidal zone reflect updated water quality within the estuary and could also affect the bioassimilation and bioaccumulation of metals in aquatic organisms, resulting in potential long-term implications on human health and ecosystem [7, 8]. Many of these toxic chemicals, persistent organic pollutants (POPs) in particular, due to a combination of their physicochemical properties and toxicity, have been reported to pose long-term harmful effects to the human health and their movement within environmental compartments and long-range transport may result in a serious threat not only to organisms around the initial point of release, but also to organisms distant from the pollution source. The problem of persistent toxic substances pollution is a complex global environmental issue of increasing concern [9, 10]. Monitoring and control of POPs has been a challenge to environmental authorities worldwide, partially because of their low level of occurrence and associated high analytical cost [11]. The great production and use of chemicals in technologically advanced societies provokes the release of many xenobiotic substances in the aquatic environment [12-15]. Such materials could promote toxic effects even at low concentrations. In the past, the risk connected to xenobiotic substances was evaluated using chemical analysis. Nevertheless, chemical analysis by itself can only identify and quantify pollutants when the analyte in question is known; moreover, synergic and antagonistic effects between contaminated substances are not always established [16, 17]. Fine particle reactive metals enter estuarine waters, many are quickly adsorbed onto suspended particulate matter in the water column and

removed to the surface sediment layer at the bottom or even tend to be accumulated in places where waves and currents are absent or weak [6, 18]. Re-suspension of surface sediment by increased turbulence and during ebb tides has led to sediment-bound contaminants re-entering the water column and moving to the estuarine system into the marine zone [6] resulting in particulates that are transported down the estuary or exchanged between different depositional regions.

MATERIALS AND METHODS

Description of the Region and Sampling Stations:

The Estuary with a spoon-shaped topography is located in the shoreline of Arabian Sea. The border of the basin extends to Korangi Creek in south and Hawksbay to west. Karachi metropolitan has a moderate climate. The annual average temperature is 21.15-30.78°C. The annual rainfall is 209.44mm. In the present study, sediments and surface water samples were taken from four stations, during January 2010 to December 2010. Samples were collected every month for a season and sets of eight surface water and bottom sediment samples were taken for each station during the study period. The locations of the sampling stations are depicted in Figure 1. The four sampling points (SP 1, SP 2, SP 3 and SP 4), were in the vicinity of discharges of the estuary.

Analytical Methods: Field and laboratory measurements of selected water and sediment parameters were made on eight dates during January 2010-December 2010, for samples taken from all four stations (Figure 1). Temperature and dissolved oxygen (DO) were measured at the field. Conductivity and pH measurements were made using a portable conductivity meter (HACH SenIon 95) and a pH meter (WTW FL 320), respectively. The other physical and chemical parameters were determined after transferring the samples to the laboratory.

Biochemical oxygen demand (BOD₅) chemical oxygen demand (COD) and heavy metals were measured by atomic absorption spectrophotometer (Thermo iCE3500-AAS) using standard methods [19, 20].

Bottom sediments were collected from four locations (Figure 1) using a steel spatula to avoid contamination, homogenized and then preserved in suitable polyethylene tubes. Sediments were stored at 4-6°C. Sediment samples were dried at 40°C for 24 hour, crushed and homogenized prior to analysis. Total concentrations of Cd, Cr, Cu, Pb, Ni, Mn, Zn, As and Hg in the sediments were measured by the same AAS after acid digestion of the samples

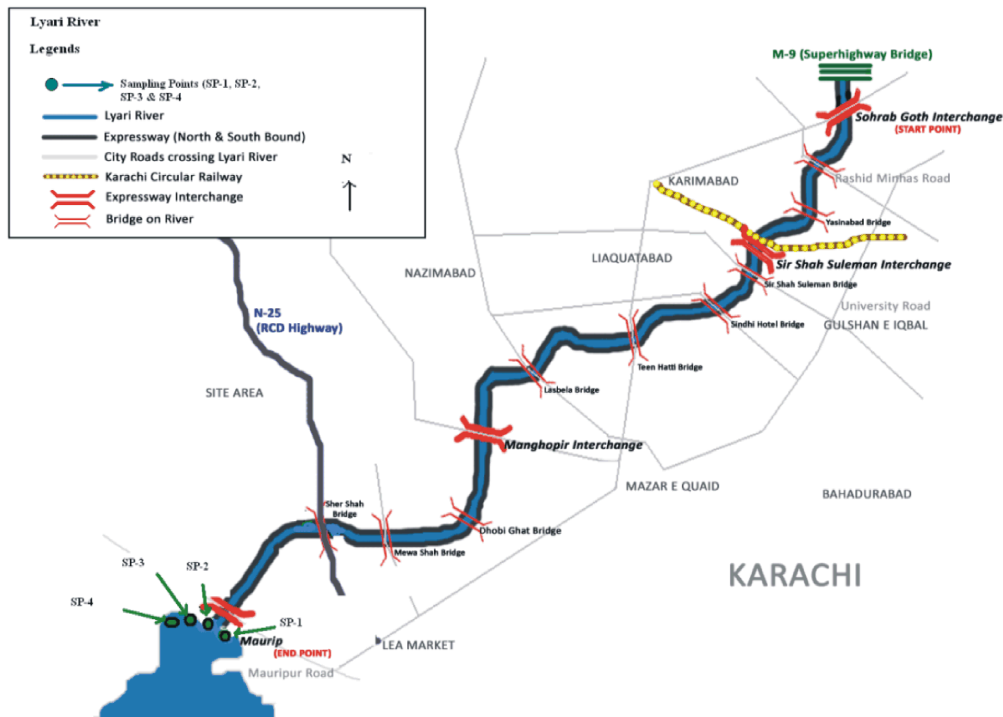


Fig. 1: Sampling Points at Lyari River and Estuary

using the Method 3050B [19, 20]. Replicate samples were analyzed separately and results for sediments were calculated on a dry weight basis. Approximately 0.25 g of sediment was subjected to microwave-assisted digestion of samples using the mixture of nitric, hydrofluoric and hydrochloric acids [21].

Enrichment Factor: The enrichment factor (*EF*) was based on the standardization of a tested element against a reference one. A reference element is the one characterized by low occurrence variability. The most common reference elements are Sc, Mn, Ti, Al and Fe [22-25]. Calculation methods have been put forward for quantifying the degree of metal enrichment in sediments [26]. Salomons and Förstner [27], Müller [28] and Hakanson [29] have proposed pollution impact scales or ranges to convert the calculated numerical results into broad descriptive bands of pollution ranging from low to high intensity.

Enrichment factor (*EF*) a common approach to estimating the anthropogenic impact on sediments is to calculate a normalized *EF* for metal concentrations above uncontaminated background levels [27, 30, 31]. The *EF* calculation seeks to reduce the metal variability associated with variations in mud/sand ratios and is a convenient tool for plotting geochemical trends across

large geographic areas, which may have substantial variations in the mud (i.e. clay rich) to sand ratios. The *EF* method normalizes the measured heavy metal content with respect to a sample reference metal such as Fe or Al [32]. In this approach the Fe or Al is considered to act as a “proxy” for the clay content [33, 34]. The *EF* is calculated according to the following equation:

$$EF = M_x \times Fe_a / M_a \times Fe_x$$

Where M_x and Fe_x are the sediment sample concentrations of the heavy metal and Fe (or low variability occurrence element), while M_a and Fe_a are their concentrations in a suitable background or baseline reference material [27].

Geo-Accumulation Index (I_{geo}): Müller [28] proposed the methods for enrichment of metal concentrations above background or baseline concentrations to calculate the I_{geo} . The method assesses the degree of metal pollution in terms of seven enrichment classes based on the increasing numerical values of the index. This index is calculated as follows:

$$I_{geo} = \log_2 C_w / 1.5B_n$$

Where C_n is the concentration of the element in the enriched samples and the B_n is the background or baseline value of the element. The factor 1.5 is introduced to minimize the effect of possible variations in the background values which may be attributed to lithologic variations in the sediments [35]. Müller [28] proposed the following descriptive classes for increasing I_{geo} values; Class 6 with value >5 : extremely contaminated, Class 5 with value 4-5: strongly to extremely contaminated, Class 4 with value 3-4: strongly contaminated, Class 3 with value 2-3: Moderately to strongly contaminated, Class 2 with value 1-2: Moderately contaminated, Class 1 with value 0-1: Uncontaminated to moderately contaminated, Class 0 with value 0: Uncontaminated.

Degree of Contamination (Cd): To proposed an overall indicator of contamination based on integrating data for a series of seven specific heavy metals and the organic pollutant PCB [29]. This method is based on the calculation for each pollutant a contamination factor (C_f). However the C_f requires that at least five surface sediment samples are averaged to produce a mean pollutant concentration which is then compared to a baseline pristine reference level, according to the following equation:

$$C_f = M_x/M_b$$

Where M_x and M_b refer to the mean concentration of a pollutant in the contaminated sediment and the preindustrial "baseline" sediment. Study of specified heavy metals (As, Cd, Cu, Cr, Hg, Pb, Zn) and the organic pollutants proposed that the numeric sum of the eight specific contamination factors express the overall degree of sediment contamination (Cd) using the following formula [29].

$$Cd = \sum_{i=1}^8 C_f^i$$

Cd defined as the sum of C_f for the eight pollutant specified species. The Cd is aimed at providing a measure of the degree of overall contamination in surface layers in a particular core or sampling site. Classification terminologies and calculation formula are based on and restricted to the seven metals plus PCB. Furthermore all eight species must be analyzed in order to calculate the correct Cd for the range of classes [29]. Abraham and Parker [36] presented the modified degree of contamination (mCd) as a result of the above limitations,

modified and generalized form of the Hakanson [29] equation for the calculation of the overall degree of contamination at a given sampling or coring site as follows.

- C The modified formula is generalized by defining the degree of contamination (mCd) as the sum of all the contamination factors (C_f) for a given set of estuarine pollutants divided by the number of analyzed pollutants.
- C The mean concentration of a pollutant element is based on the analysis of at least three samples of the impacted sediments (taken from either the uppermost layers of a core or from the associated surface sediments).
- C The baseline concentrations are determined from lower core concentrations or from similar nearby uncontaminated sediments. The modified equation for a generalized approach to calculating the degree of contamination is given below:

$$mCd = \sum_{i=1}^n C_f^i / n$$

Where n = number of analyzed elements and i = n th element (or pollutant) and C_f = contamination factor. Using this generalized formula to calculate the mCd allows the incorporation of as many metals as the study may analyze with no upper limit. The expanded range of possible pollutants can thus include both heavy metals and organic pollutants should the latter be available for the studied samples. For the classification and description of the modified degree of contamination (mCd) in estuarine sediments the following gradations are proposed [36] <1.5 : Nil to very low degree of contamination, $1.5 \# 2$: Low degree of contamination, $2 \# 4$: Moderate degree of contamination, $4 \# 8$: High degree of contamination, $8 \# 16$: Very high degree of contamination, $16 \# 32$: Extremely high degree of contamination, >32 : Ultra high degree of contamination.

RESULTS AND DISCUSSION

Results of the waste water quality parameters measured at the four selected stations of the estuary were shown in Tables 1, 2, 3 and 4 for four seasons. The results were as follows: Temperature values ranged from 28.87 to 30.5°C during the sampling period. Minimum and maximum temperatures were higher than reported previously (16.6°C and 26.8°C) for water samples collected

Table 1: Summary of Analysis of Surface Water Samples at SP1

Sr. #	Parameters <i>N= 16</i>	Units	Results				Median	Mean±SD
			Spring 2010	Autumn 2010	Summer 2010	Winter 2010		
1	Temperature	°C	28.8	30.9	37.8	24.5	29.85	30.5±5.54
2	pH	SU	6.94	8.28	10.22	8.68	8.48	8.53±1.35
3	DO	mg/L	1.6	2.04	0.4	2.18	1.82	1.56±0.808
5	BOD5	mg/L	370.0	427.0	612.0	398	412.5	451±109
6	COD	mg/L	649	772	1160	682	727	815±235
7	Cd	mg/L	0.154	0.307	0.836	0.109	0.2305	0.352±0.33
8	Cr	mg/L	0.186	0.235	0.532	0.098	0.2105	0.263±0.188
8	Pb	mg/L	0.244	0.178	0.405	0.157	0.211	0.246±0.112
9	Zn	mg/L	4.554	6.283	8.397	7.206	6.7445	6.61±1.6
10	Hg	mg/L	0.0307	0.1875	0.01643	0.1037	0.0672	0.085±0.07

Table 2: Summary of Analysis of Surface Water Samples at SP2

Sr. #	Parameters <i>N= 16</i>	Units	Results				Median	Mean±SD
			Spring 2010	Autumn 2010	Summer 2010	Winter 2010		
1	Temperature	°C	26.3	27.6	39.4	26.2	26.95	30.04±6.26
2	pH	SU	7.87	9.13	9.87	7.93	8.53	8.87±0.83
3	DO	mg/L	2.25	1.02	0.24	1.97	1.495	1.18±0.738
5	BOD5	mg/L	289.0	487.0	528.0	367.0	427	452.25±70.35
6	COD	mg/L	427.0	788.0	718	529.0	623.5	664.63±112
7	Cd	mg/L	0.207	0.116	0.457	0.213	0.21	0.249±0.146
8	Cr	mg/L	0.0937	0.1685	0.5893	0.1104	0.13945	0.252±0.226
8	Pb	mg/L	0.1856	0.2063	0.3929	0.0867	0.19595	0.220±0.127
9	Zn	mg/L	5.116	3.937	10.184	6.035	5.5755	6.433±2.67
10	Hg	mg/L	0.0179	0.2034	0.0107	0.1418	0.07985	0.109±0.08

Table 3: Summary of Analysis of Surface Water Samples at SP3

Sr. #	Parameters <i>N= 16</i>	Units	Results				Median	Mean±SD
			Spring 2010	Autumn 2010	Summer 2010	Winter 2010		
1	Temperature	°C	29.8	25.6	41.14	24.17	27.7	29.65±7.79
2	pH	SU	5.75	8.38	10.54	8.76	8.57	9.06±0.99
3	DO	mg/L	1.06	1.33	0.08	1.08	1.07	0.89±0.55
5	BOD5	mg/L	496.0	513.0	726.0	356.0	504.5	524.88±152
6	COD	mg/L	595.0	759.0	1136.0	461.0	677	758.25±281
7	Cd	mg/L	0.146	0.365	0.173	0.339	0.256	0.283±0.08
8	Cr	mg/L	0.1744	0.2653	0.348	0.0974	0.21985	0.233±0.105
8	Pb	mg/L	0.2638	0.0738	0.9115	0.05518	0.1688	0.302±0.041
9	Zn	mg/L	7.643	5.374	8.483	4.537	6.5085	6.226±1.71
10	Hg	mg/L	0.0079	0.0458	0.0072	0.0345	0.0212	0.027±0.017

Table 4: Summary of Analysis of Surface Water Samples at SP4

Sr. #	Parameters <i>N= 16</i>	Units	Results				Median	Mean±SD
			Spring 2009	Autumn 200	Summer 2009	Winter 2009		
1	Temperature	°C	27.4	24.7	39.2	25.25	26.32	28.87±6.9
2	pH	SU	7.84	7.79	9.83	8.18	8.01	8.45±0.93
3	DO	mg/L	1.39	1.04	0.17	1.02	1.03	0.82±0.43
5	BOD5	mg/L	387.0	487.0	821.0	467.0	477	563.0±172
6	COD	mg/L	501.0	788.0	1165	639	713.5	826.38±233
7	Cd	mg/L	0.093	0.157	0.118	0.239	0.1375	0.163±0.05
8	Cr	mg/L	0.0938	0.3218	0.1844	0.1476	0.166	0.205±0.079
8	Pb	mg/L	0.1182	0.7364	0.4537	0.02817	0.28595	0.334±0.321
9	Zn	mg/L	9.334	6.4116	10.622	5.729	7.8728	7.659±2.16
10	Hg	mg/L	0.0108	0.0224	0.0127	0.1957	0.01755	0.062±0.08

Table 5: Summary of Analysis (Mean and Standard Deviation) of Surface Water Samples

Sr. #	Parameters <i>N= 64</i>	Units	Results			
			SP 1	SP 2	SP 3	SP 4
1	Temperature	°C	30.5±5.54	30.04±6.26	29.65±7.79	28.87±6.9
2	pH	SU	8.53±1.35	8.87±0.83	9.06±0.99	8.45±0.93
3	DO	mg/L	1.56±0.808	1.18±0.738	0.89±0.55	0.82±0.43
5	BOD5	mg/L	451±109	452.25±70.35	524.88±152	563.0±172
6	COD	mg/L	815±235	664.63±112	758.25±281	826.38±233
7	Cd	mg/L	0.352±0.33	0.249±0.146	0.283±0.08	0.163±0.05
8	Cr	mg/L	0.263±0.188	0.252±0.226	0.233±0.105	0.205±0.079
8	Pb	mg/L	0.246±0.112	0.220±0.127	0.302±0.041	0.334±0.321
9	Zn	mg/L	6.61±1.6	6.433±2.67	6.226±1.71	7.659±2.16
10	Hg	mg/L	0.085±0.07	0.109±0.08	0.027±0.017	0.062±0.08

from the Lyari River in 2004 [37]. In general, pH was on the alkaline side, ranging from 8.45-9.06. The highest pH value was observed during the summer of 2004 at sampling point (SP 3) shown in Table 5. This high pH could be due to the discharge of alkaline materials from textile industrial effluent that caused a high pH value in the river. This might lead to disruption of the pH buffer system of the river and reduction of its potential to kill harmful microorganisms [38]. Most aquatic organisms survive best within a limited pH range. Even small changes in pH can be harmful to pH sensitive species. Most fish can tolerate pH values in the range of 5.0 and 8.5 [39]. The pH values outside this range can create problems for reproduction and survival. High pH levels 9-14 can harm living species by denaturing cellular membranes. Because alkalinity and pH are so closely related, changes in pH can also affect alkalinity, especially in poorly buffered waters.

Biochemical oxygen demand (BOD5) load from the sewage and industrial effluent cause a decrease in dissolve oxygen [40]. Concentrations of DO were in the range of 0.82-1.56 mg/L, having the lowest value at sampling point 2 (SP 2) in summer given in Table 2. Various oxidizing and reducing agents, such as the ammonia, nitrite, nitrate and sulfate and organic contaminants discharged from various sources can cause oxygen depletion. This not only decreases the nutritional value of the water but also causes foul odor and microbial growth. On the other hand, the ideal dissolved oxygen concentration for many fish is between 7 and 9 mg/L. The high DO concentrations (2.04 and 2.25 mg/L) were observed in autumn and spring for SP 1-2. Abrupt changes in dissolved oxygen can induce stress and subsequently make fish more susceptible to disease [41].

The concentrations of COD were in the range of 664-824 mg/L given in Table 5 much higher than the threshold level (150 mg/L) specified in the Pakistan Environmental Protection Act (NEQS for municipal and

industrial effluent) and control regulations [42]. The COD results in the effluent samples indicated excess pollution in terms of organic (COD) parameter. Mahmood [37] reported 4000 industrial plants including textile, metal, leather, pharmaceutical, rubber and plastic, etc. manufacturing in ten categories based on their effluent discharges to Lyari River. This wide range of industries, more than 3500 are located in Sindh Industrial Trading Estate (SITE) and more than 1000 were located in Federal B and New Karachi Industrial Area on mouth of Lyari River. The Karachi Metropolitan Municipality dumped their sewage and solid wastes in Lyari and Malir Rivers. Average biochemical oxygen demand (BOD5) concentrations ranges were 451-563 mg/L given in Tables 1-4, in all four seasons study. Average concentrations were much higher than the threshold limits given in NEQS limits for 80 mg/L. BOD concentrations depicts that the organic loads is being discharged by the industrial process without any pretreatment. Treatment Plants at SITE and Maripure having the capacity of 25 and 55mgd are not fully functional [37], due to high organic load of sewage and industrial effluents being discharge in Lyari River stream.

The results of the heavy metal analyses of water samples from the four sampling sites (SP 1-4) were presented in Tables 1-4. There were some high values (see maximum levels of Cd, Cr, Pb, Zn and Hg) which are not typical of natural waters. Some relatively high values of standard deviation and correspondingly high variance levels were also found in the successive sampling period. This situation suggests a strong variability possibly due to the presence of different anthropogenic and non-point sources. The classification of inland waters with respect to metal concentrations according to the Pakistan environmental act 2000 was given in Table 6. The concentrations of Cd, Cr, Pb, Zn and Hg reported for all seasons at all sampling points (SP 1-4) given in Table 5

Table 6: National Environmental Quality Standards ^a for Municipal and Liquid Industrial Effluent (mg/L, Unless Otherwise Defined)

Sr. #	Parameters	Revised Standards			
		Existing Standards	Into Inland Waters	Into Sewage Treatment	Into Sea
1	Temperature/Temperature increase	40°C	≤3°C	≤3°C	≤3°C
2	pH Value	6-10	6-9	6-9	6-9
3	5-days BOD at 20°C ⁽¹⁾	80	80	250	200
5	Chemical Oxygen Demand (COD) ⁽¹⁾	150	150	400	400
6	Cadmium (Cd) ⁽²⁾	0.1	0.1	0.1	0.1
7	Chromium (trivalent and hexavalent) ⁽²⁾	1.0	1.0	1.0	1.0
8	Lead (Pb) ⁽²⁾	0.5	0.5	0.5	0.5
8	Mercury (Hg) ⁽²⁾	0.01	0.01	0.01	0.01
9	Zinc (Zn)	5.0	5.0	5.0	5.0

^aNational Environmental Quality Standards as defined in Pakistan Environmental Protection Act, 1997.

1. Summing minimum dilution 1:10 on discharge, lower ratio would attract progressively stringent standards to be determined by the Environmental Protection Agency. By 1:10 dilution means for example, that for each one cubic meter of treated effluent the recipient body should have 10 cubic meter of water for dilution of this effluent.

2. Subject to total toxic metals discharge.

Table 7: Summary of Metals Analysis in Sediments Samples

Sr. #	Parameters <i>N=16</i>	Units	Results			
			SP 1	SP 2	SP 3	SP 4
1	Cadmium (Cd)	mg/Kg	1108	987	1060	1240
2	Lead (Pb)	mg/Kg	930	1230	987	1020
3	Chromium (Cr)	mg/Kg	517	428	706	654
4	Zinc (Zn)	mg/Kg	1380	1260	1276	1410
5	Mercury (Hg)	mg/Kg	197	118	204	242
6	Organic Carbon	%	4.28	3.96	4.49	2.84

were higher than the threshold value. Of the potential multiple sources of Cd, Cr, Pb, Zn and Hg are metal plating, petrochemical steel and foundries. These sources have a very high impact on the metal concentrations in effluent and the sedimentation of estuary [22]. On the other hand, industrial activities may represent a primary source for Cd, Cr, Zn, Pb and Hg, extensively used in paint, chemical factories, tanning, leather manufacturing and textile works which are operational in the area [37].

To estimate the environmental status of sediments, several quality guidelines were issued [43, 44]. The group of Canadian researchers developed chemical concentrations recommended to support and maintain healthy aquatic life associated with bed sediments. These values are derived from available information on biological effects of sediment associated chemicals. Among the heavy metals studied, the following concentration ranges were recorded i.e., Cd (987-1240 mg/kg), Pb (930-1230 mg/kg), Cr (428-706 mg/kg), Zn (1260-1410 mg/kg), Hg (118-242 mg/kg) and organic carbon (2.84-4.49%). The average concentrations of metals in sediments taken from the four sampling (SP 1-4) locations were given in Table 7. Since there is no standard established for the sediments in Pakistan, the concentrations of the metals in

the sediments were compared to the recommended lowest levels for protection and management of aquatic sediments quality in Ontario, Canada [45, 46]. Such guidelines are based on potential negative effects of metal contents on the growth and distribution of flora and fauna in the impacted water bodies. The concentration of heavy metals in sediments varied significantly among all sampling sites. The striking heavy metals are Cd and Zn. The concentration of Cd and Zn was highly elevated at all sites in the estuary, by hundred times higher than the sediment quality level (SQL), SP 1 and 4, representing the two extreme ends of the range. The Pb concentrations were observed at all sampling points. Release and adsorption of metals in the Lagoon sediment would be dependent on the characteristics of the latter, saltwater inflow, freshwater contribution and accumulation and degradation rates of organic matter [47]. Additionally, the indicators such as the color of the sediments and decreasing living species suggest that the situation is getting worse. High accumulation of heavy metals in sediments could pose a potential risk for fishery. Total Hg contents were much lower than those corresponding to previous reports during the 1980s and 1990s [48, 49]. On the other hand, Cd, Pb and Cr have presented higher

concentrations in the finest fraction sediments in the inner sites principally affected by wastewater. As regards the industrial zone, only Cd has shown a similar behavior because both Pb and Cr were slightly more concentrated in the sediments. Earlier studies of semi enclosed docks area, reported similar trends to those included here for Cd and Cr, but found higher Pb values, probably because one of the sites receives a direct input of industrial effluents with a high load of fine material [50]. According to the results provided by other authors for different estuaries or coastal areas [6, 51, 52] Cd, Cr and Pb contents herein found were below those levels recognized as characteristic of polluted environments.

Two important increases were simultaneously observed at the three sampling sites and that would be an indication of an Hg-specific input into this environment. The values of this element have changed along the whole considered region, from levels lower than the detection limit of the applied analytical method to maximum ones near the area most influenced by industries and traffic of cargo vessel. Another source may be the internal cycling/recycling of older contaminated sediments or introduction from the atmosphere.

Elevated Cd concentrations found in estuarine sediments are related to the fact that this element is more ubiquitous in the environment due to the variety and congregation of anthropogenic activities, which provide different sources of metals to intertidal sediments, supported by atmospheric deposition, urban runoff, or different discharges [53]. Keeping in mind that these metals are highly toxic even at low concentrations, its accumulation within tidal flat sediments may be largely important as they can act as a metal reservoir and so a potential Cd source for the estuary. But sub-tidal sediments more influenced by vessels and ships can also act as an important sink at first and then source to the surrounding environment. Previous records on sub tidal sediments have shown values slightly higher but similar in samples from nude tidal flats in the medium region of the estuary (Table 5).

There is scarce information linked to this topic in our country. Our results are higher than those reported as typical for moderate to largely contaminated sites (Table 7). On the other hand, Cd geochemical partitioning has shown the maximum percentages for the inner region in the same fraction (carbonatic). These results are different from those reported by Marcovecchio and Ferrer [54] who determined that Cd was not as high (range between 3.8% and 13.4% vs. 13% and 40%) over the Principal Channel (sub-tidal area). Thus, it seemed

that processes occurring mainly within the carbonatic fraction take on a significant role in the biogeochemical distribution of cadmium in the nude tidal flats, hindering the transference to more mobile fractions which could be incorporated by organisms. The accumulation of cadmium in sediments could represent a potential risk to sediment-dwelling organisms living within these tidal flats. Concerning this, specific studies directed to evaluate this topic have not at present been developed, even though the Canadian guidelines for marine/estuarine sediment quality point out concentrations greater than 0.7 mg/kg as a limit where this kind of processes could start [43]. Recorded concentrations of Pb on tidal flat sediments were higher within the input areas as well as near the industrial one. The main Pb contribution to the system should be the sub-tidal sediments with high concentrations [54], which suggest that tidal flats would not be acting as a sink of this element. As far as the partitioning of lead is concerned, a significant increase was observed in the fraction FII (oxidizable) at all the studied area. So, organic complexes and sulfides appeared to be a more important sink for lead than the other mobile phases. Besides, it was the unique element that reached the highest amounts associated to FIV (reducible compounds). This fraction represents metals absorbed on iron or manganese oxides which are excellent scavengers for trace metals. These results are consistent with the observations of other researchers, particularly those who have worked on uncontaminated areas [51]. The observed levels are similar to or higher than those reported for other coastal areas in the country as well as in the world (Tables 7-8). The fact that its concentration was higher within the intertidal sediment suggests the occurrence of a transport process from land to the coastal marine environment.

Concentrations were quite different to Cr values reported in sediments from estuary, Argentina where the determined higher contents reflected the influence of the most industrialized and mining [55]. In addition, our results are equal or higher than those from environments recognized as polluted ones (i.e., Mexico, Spain and China). Thus, sediments showed chromium enrichment with respect to other coastal areas. Chromium is used in the tinning process seemed to be an explanation of the high concentration. Moreover, there were no differences between sites at industrial area and others; it also suggests a narrow adsorption to organic matter within sediments, which is also, related with the high occurrence of suspended particulate matter [56]. The geochemical partitioning of Cr in the estuary reflected an increase in

Table 8: Selected Metals World Average Concentrations in Marine Sediments and Crust [59]

Sr. #	Analytes	Average Shale	Average Crust
1	Cd	0.2	0.1
2	Pb	20	14.8
3	Cr	90	NA
4	Zn	95	65
5	Hg	NA	NA

Table 9: Summary of Average Enrichment Indices for Metals in Estuary Sediments Calculated Using Various Methods

Sr. #	Analytes	Average I_{geo}	Average EF	Average Cf	mCd
1	Cd	12.18	6.2	13.0	9.8
2	Pb	5.4	6.0	12.6	8.5
3	Cr	4.8	3.5	5.8	4.9
4	Zn	6.3	6.6	13.4	10.2
5	Hg	1.8	2.4	1.3	1.8

(I_{geo} = index of geoaccumulation, EF = enrichment factor using Fe as normalizer and baseline values, mCd = modified degree of contamination)

three fractions (exchangeable, oxidizable and reducible) compared with previous results on the sub tidal sediments [54]. Keeping in mind that most of Cr was geochemically linked to the lithogenous fraction; results allow sustaining that this metal preferentially appeared associated with the oxidizable fraction within the studied coastal sediments has similar trends at different eutrophicated estuarine system [57]. In this sites recognized as highly contaminated, the carbonatic fraction has demonstrated to be the more important one [58]. The results showed synergistic interaction between organic and metal contamination, since the partial reducing conditions of these areas allow the remobilization of metals from the reducible form [57]. The evaluation of the estuary for the three evaluated metals has shown significant percentages, mainly in the cases of lead and chromium, a fact that indicated they could be assimilated by the organisms within this environment.

The results of the various methods for calculating heavy metal enrichment in Karachi fish harbor and estuary sediments were summarized in Table 9. The average results demonstrated that, using the continental shale as a reference concentration (Table 8), the EF factor is very high. By contrast the results for EF and mCd were similar (Table 9) with their mean indicating an average four folds enrichment compared to pristine "base line" sediment at depth in the cores. The I_{geo} factor was not readily comparable to the other indices of metal enrichment due to the nature of the I_{geo} calculation, which involves a log function and a background multiplication of 1.5. Based on the classification system proposed for I_{geo} factors, Estuary cores were classed on average as uncontaminated to moderately contaminated. The I_{geo} "uncontaminated" designation was clearly inappropriate as part of an overall description of the heavy metal results for cored sediments

from this estuary. The modified degree of contamination, mCd as proposed in the present study, is based on integrating and averaging all the available analytical data for a set of sediment samples. This modified method can therefore provide an integrated assessment of the overall enrichment and contamination impact of groups of pollutants in sediments. In considering the average mCd results, it should be noted that compared to baseline data, Pb, Cr and Zn were significantly enriched in estuary sediments (Table 9). This will allow the determination of realistic baseline values for the target area. This approach will work best in areas that have only suffered relatively recent contamination such as in countries that have relatively young industrial histories, where it is possible in most cases to get below the level of first anthropogenic impact. Studies of estuary sediments draw attention to the considerable depth to which metal contamination may exist in old heavily industrialized countries such as in Europe [26]. In these countries it may not be possible to get below the anthropogenic impact unless deep vibra-cores are used to penetrate several meters into the sediments. However for samples from these extended depths, the direct sedimentological and mineralogical similarities with surface sediments become less reliable and hence their comparability and suitability more tenuous as good reference samples. This difficulty in establishing good baseline reference samples in old heavily industrialized countries is a reminder of the role of average continental shale and crustal data for reference purposes. Alternatively, due to shortcomings in using average shale and crustal data, reference environmental concentrations may need to be more focused with the reference data based on regional and/or worldwide compilations of pristine or near-pristine estuarine sediment metal compositions derived from cored sediment

samples in which clear baseline trends are indeed visible. To this end the baseline data for cored fine fraction sediments in Karachi fish harbor and Estuary made a useful contribution.

The results of the chemical analysis of the Lyari River and harbor surficial sediments showed that the sediments contained highly elevated Cd, Cr, Pb, Zn and Hg concentrations. Based on the *EF*, *CF*, *mCd* and *Igeo* indices, these sediments could be characterized as heavily polluted in regard to Cd, Cr, Pb, Zn and Hg, highly contaminated concerning Cr and Pb. Moreover, according to the SQG the concentrations of Cd, Pb, Zn, Cu and Cr of most of the sediments exceeded the toxic effect range.

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