Journal of Biodiversity and Environmental Sciences (JBES)
ISSN: 2220-6663 (Print) 2222-3045 (Online)
Vol. 8, No. 5, p. 219-232, 2016
http://www.innspub.net

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RESEARCH PAPER

OPEN ACCESS

Toxicity levels, Ecological risk assessment of Heavy metals and distribution in the surface sediment of Hub River, Hub River estuary and Gadani coast, Baluchistan, Pakistan

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Article published on May 27, 2016

Key words: Heavy metal; Contamination factor; Geo-accumulation Index; Potential Ecological Risk Index, Hub River Baluchistan.

Abstract

Fourteen sediment samples were collected from three sites (Hub River, Hub River estuary and Gadani coast) for examining the concentrations and toxicity levels of heavy metals (Cadmium, Chromium, Copper Lead, Cadmium, Zinc, Manganese and Iron) and their concentrations. Furthermore, some factors and indexes, Contamination Factor, MERM-Q, Geo-accumulation Index, and Potential Ecological Risk Index were used for their environmental assessment and pollution status of surface sediments of the study area. The present data has also been compared with the sediment quality guideline. All the values of heavy metals of the study sites lie in the LEL (Lowest Effect Level) except for Cadmium but its values were also below the ERL (Effects Range Low). The results of the Geo-accumulation index of Cadmium indicate that the sediments in most studied stations of the three sites were moderately to strongly polluted (1.72-2.99). According to Geo-accumulation index all studied stations were found unpolluted with respect to Mn, Cu, Zn and Fe, while Pb was found up to moderate values. The contamination factor of each metal was found in the following order Cd>Pb>Cu>Mn>Zn. The contamination factor of the study area shows that this area has Moderate to Considerable contamination. In the present study, the MERM-Q values range 0.08-0.16 with average values 0.11 which indicates that metal concentrations are approximately with 9-21% probability of toxicity to the benthic organisms. The values of the Potential Ecological Risk Index in the studied stations show considerable to very high risk from metal contamination in the following order: Hub River estuary>Hub River>Gadani coast.

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Introduction

Heavy metals play a key role in the health of the aquatic environment as well as human health but become toxic if their concentration exceeds prescribed limit, and have potential to bio magnification. An increase in the development and utilization of heavy metals in industries and contamination probability has been observed. With a growing public concern about heavy metal pollution and the threat to the ecosystem, scientists are developing tools as a Geo-accumulation index (Muller, 1981), Contamination Factor, Degree of Contamination ((Hakanson, 1980), Enrichment Factor (Buat-Menerd and Chesselt (1979), Potential Ecological Risk Index (Hakanson, 1980). The probability of sediment toxicity to benthic organisms was determined for contaminants using the mean ERM quotient (MERM-Q) approach (Long *et al.*, 1998). Scientists have also prepared sediment quality guidelines for toxicity of heavy metals, (Long and Morgan, 1990; O'Connor *et al.*, 1998; Long and MacDonald, 1998; Long *el al.,* 2000).

Gadani and Hub River are located in the south eastern part of Lasbela district of Baluchistan province. Lasbela district is arid and mostly consists of rocks and hilly area. According to Ahsan (1989) and Allen *et al.*, 1994 huge mineral deposits consisting of Zinc-Lead (14-16%) were found here. Huge deposits of Manganese were discovered in Kharrari Nai and Siro Dhoro in Lasbela District (Abbas, 1980; Nasim, 1996).

Hub River serves as the boundary between the provinces of Sindh and Baluchistan. Hub city is located along the Hub River and is one of the largest industrial estates of Baluchistan, which consist of more than one hundred and sixty six industrial units.

The major industries include textile, chemical, pharmaceutical, engineering, food/beverages and, steel etc. In addition, two power plants and one oil refinery are also located near the mouth of the Hub River (Lasbela, 2011). Gadani is a small town. Its population is estimated at ten thousand. The world's third largest ship breaking yard is located in Gadani beach. The yard consists of 132 ship-breaking plots located across a 10 km long beachfront at Gadani. Ship-breaking industry is the main source of pollution in the Gadani coastal area. Churna Island is a small uninhabited island located in the Arabian Sea, about 9 km (5.6 mi) west of the mouth of the Hub River. In the past Churna Island was mostly used as a firing range by the Pakistan Navy. Presently it is being use as a sports fishing site (Wikipedia: Churna Island).

The main objectives of the present study are to measure the concentrations and distribution of heavy metals (Cd, Cr, Cu, Fe, Mn, Pb, and Zn) in the sediments of Hub River, Hub River estuary and Gadani coast and to also determine the Potential ecological risk index using Contamination Factor (CF), Degree of Contamination, Geo-accumulation Index (I_{geo}). Moreover, the study also aims to find the risks of potential toxicity by comparison with the Sediment Quality Guidelines (SQGs) to determine the potential bioavailability and mobility of the metals with a view to provide a baseline data regarding the distribution and accumulation of heavy metals in the sediments and help in avoiding any metal contamination in future.

Materials and methods

Sediment sampling

Ten surface sediment samples were collected on 15th October 2014 by using fisherman boat from the Hub River and Hub estuary (St-5 to St-14) as shown in Fig.1. Three Gadani coastal surface sediment samples (St-2 to St-4) were collected on 10th June 2014, during low tide by hand using plastic scoop while one sample was collected from St-1 (Gadani coast) on the same day using Peterson grab at 5 meters depth.

Heavy metal analysis

Sediment samples were digested according to US-EPA method no. 3050B (1996). About 4-5 gram (dry weight) sediment sample was digested with repeated additions of nitric acid (HNO_3). Samples were

evaporated till dryness. Dried samples diluted with 5% nitric acid up to 25ml, were finally filtered through pre clean Whatman no 40 filter paper. Diluted extracts sample were analyzed on Flame Atomic Absorption Spectrometer (Perkin Elmer model analyst AA-700) for Zinc, Copper, Iron and Manganese while Cadmium and Lead were analyzed on the Graphite Atomic Absorption Spectrometer.

Total Organic Carbon

Five grams (5 g) of sediments that were passed through a sieve of 2 mm mesh were further dried at 105 °C. The samples were subjected to calcination for 5h at 300 °C (Miyazawa *et al*., 2000). Subsequently, the samples were weighed and the difference between the initial and final mass was corresponded to the organic matter of the sediments. Organic matter was converted in Total Organic Carbon with multiplication factor 1.73 applied as according to Nelson (1996).

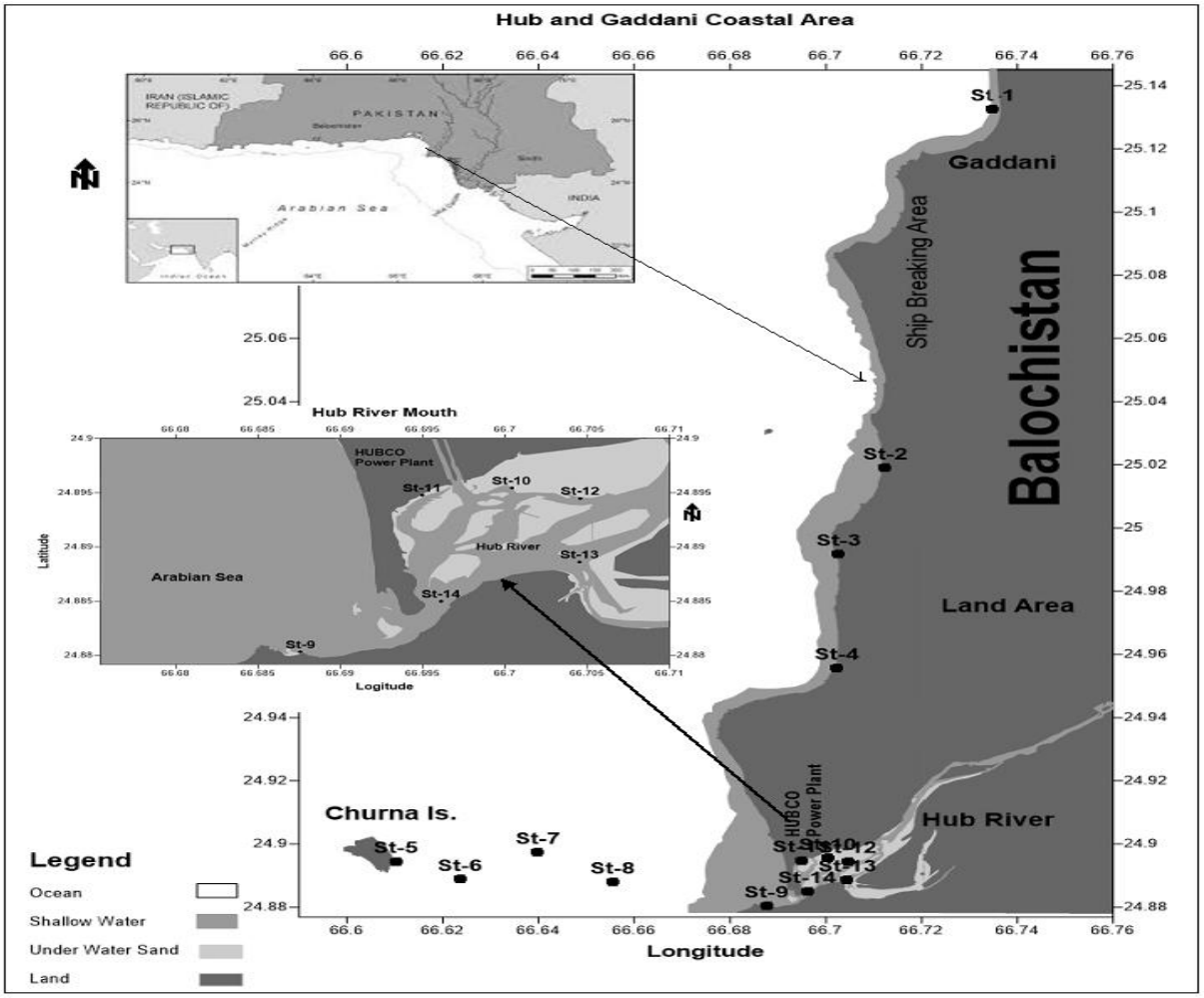

Fig. 1. Location of sampling sites in the Gadani coast, Hub River and HubRiver Estuary, Baluchistan.

Total phosphorous

To determine total phosphorus, sodium bicarbonate ($NaHCO_3$) extraction method was used as described by Schoenau and O'Hallora (2006) based on the ammonium molybdate–antimonyl potassium tartrate–ascorbic acid method described by Murphy and Riley (1962).

Results

Characteristic of sediments

Grain size of sediments

Distribution of grain size of the sediment samples is shown in Table 1. The grain size of the Hub River samples (St-10 to St-14) was from fine to fine sand. Grain size of Hub estuary sediments was coarse to

very fine sand. Sediments of St-5 and St-6 (close to the Churna Island) were coarse sand, while St-8 and St-9 sediment were fine to very fine sand towards Hub River mouth.

Gadani coastal sediments vary from very fine to coarse sand. St-3 sediments were mostly coarse sand and sediments of St-2 and St-4 sediment were very fine to fine sand, while sediments from St-1 were medium to coarse sand.

Table 1. Grain size distributions (in Percentage) in surface sediment from the Gadani coast, Hub River Estuary and Hub River Baluchistan (Pakistan).

Stations	Grain size distribution					
	1mm	0.5mm	0.250mm	0.125mm	0.063mm	<0.063mm
St-1	23.77	41.1	21.48	5.91	4.12	3.38
St-2	2.11	1.22	17.85	73.69	5.26	0.05
St-3	86.18	12.74	0.3	0.05	0.04	0.02
St-4	3.74	7.69	28.38	56.4	3.57	0.22
St-5	81.26	15.76	0.7	1.13	0.55	0.46
St-6	83.59	10.6	2.7	2.2	0.46	0.25
St-7	87.09	11.52	0.12	0.07	0.16	0.12
St-8	0.3	2.0	1.7	50.0	31.0	16.0
St-9	0.3	1.92	2.26	25.39	62.28	7.86
St-10	1.02	2.45	2.9	53.87	35.43	3.72
St-11	0.26	5.06	73.59	21.02	0.07	0
St-12	0.08	0.54	9.1	85.11	5.14	0.04
St-13	0.01	2.44	27.97	67.01	2.56	0.02
St-14	1.21	1.27	25.71	66.71	5.08	0.04

Table 2. Metal concentrations (ppm dry weight) TOC (percent) & total Phosphorous (mg/g) in Gadani coast, Hub River Estuary and Hub River sediments of Baluchistan (Pakistan).

Sampling sites	Stations	Cd	Pb	Cu	Zn	Mn	Fe	TOC	Tot. Phos.
	St-1	1.68	27.41	5.02	33.87	158.1	46040	3.11	0.0400
Gadani	St-2	1.99	23.51	5.93	8.80	106.4	67980	0.93	0.0320
	St-3	1.76	31.39	4.69	13.57	246.1	75488	2.30	0.0260
	St-4	1.39	18.42	3.12	13.01	205.7	73040	2.16	0.0380
Average		1.71	25.18	4.69	17.31	179.08	65637	2.12	0.034
	St-5	2.38	25.18	4.33	10.37	141.2	33950	2.80	0.0900
Hub River	St-6	2.32	25.14	4.61	18.55	146.0	34490	3.47	0.0800
Estuary	St 7	2.02	25.15	10.74	8.89	190.1	34340	4.01	0.0358
	St 8	1.33	13.65	5.63	24.08	182.0	34090	5.21	0.0400
	St 9	2.18	27.10	5.15	36.10	167.1	33720	3.02	0.0260
Average		2.05	23.24	6.09	19.60	165.28	34118	3.70	0.054
	St 10	1.69	14.58	2.89	5.68	130.7	32530	1.64	0.0290
Hib River	St 11	1.41	11.76	3.35	10.23	185.9	33370	1.35	0.0320
	St 12	1.53	12.88	3.23	11.15	151.5	33610	2.65	0.0420
	St 13	1.69	13.40	2.40	8.90	140.6	33400	1.86	0.0356
	St 14	1.75	14.50	3.21	16.98	158.8	33940	3.33	0.0381
Average		1.61	13.42	3.02	10.59	153.50	33370	2.17	0.035

Total Organic Carbon

Mean Total Organic Carbon contents in sediments at the Hub River, Hub estuary and Gadani coast were in the range of 2.12–3.55 % dry weight basis (Table 2). Highest values 4.01 and 5.21% of Total Organic Carbon were noted at St-7 and St-8 respectively. The mean values of Total Organic Carbon in the Gadani coast and the Hub River were found in the range of 2.1% and 3.11%.

Total Phosphorous

Total phosphorus concentration and their distribution in the surface sediments from fourteen (14) stations of three sites are given in Table 2. The highest concentration of total phosphorous was found at St- 4 and St-5 of Hub River estuary which was

recorded 0.08-0.09 mg/kg and its average was 0.044 mg/kg. Average concentration of total phosphorous of Gadani and Hub River sediments was found almost similar (0.035 mg/kg).

Spatial distribution of heavy metals

Heavy metal concentrations, ranges and averages in the surface sediments of three sites are given in Table 2. Metal contents were found in the following ranges Cd (1.33-2.38 mg/kg), Copper (2.4-10.74), Zinc (5.68-33.87), Lead (11.76-31.39), Iron (32530.0-75488.0) and Manganese (106.4-246.1), while mean concentration were 1.72, 4.59, 14.49, 19.57, 428.56, 165.01mg/kg for Cd, Pb, Cu, Zn, Fe and Mn respectively. Highest mean concentration of iron and Manganese found (65,637 and 179.08 ppm) respectively were found in the Gadani coastal surface sediments, High concentration most likely due to wastes from ship breaking industries. Highest mean concentrations of Cadmium, Lead, Copper and Zinc (2.05, 23.24, 6.09, and 19.60 ppm respectively) were recorded in Hub River estuarine sediments (Table 2).

Table 3. Classification of Geo-accumulation Index (I_{geo}) Values.
(Muller G. 1969)

Geo-accumulation Index (I_{geo}) Value	Class	Sediment Quality
≤0	0	Unpolluted
0 - 1	1	From unpolluted to moderately polluted
1 -2	2	Moderately polluted
2 - 3	3	From moderately to strongly polluted
3 - 4	4	Strongly polluted
4 - 5	5	From strongly to extremely polluted
>6	6	Extremely polluted

Table 4. Geo-accumulation index study stations sites (Gadani coast, Hub River Estuary and Hub River) of Baluchistan (Pakistan).

Study area	Station	Cu	Pb	Cd	Zn	Mn	Fe
Gadani Coast	St-1	-3.75	0.55	2.49	-1.63	-3.17	-0.88
	St-2	-3.51	0.33	1.72	-3.58	-3.74	-0.31
	St-3	-3.85	0.74	2.55	-2.95	-2.53	-0.16
	St-4	-4.44	-0.03	2.21	-3.01	-2.79	-0.21
Hub River estuary	St-6	-3.87	0.42	2.95	-2.50	-3.29	-1.29
	St-7	-2.65	0.42	2.75	-3.56	-3.34	-1.30
	St-8	-3.58	0.34	2.15	-2.12	-3.29	-1.31
	St-9	-3.71	0.53	2.86	-1.54	-3.34	-1.32
	St-10	-4.55	-0.36	2.49	-4.21	-3.45	-1.30
Hub River	St-11	-4.33	-0.67	2.23	-3.36	-2.94	-1.31
	St-12	-4.39	-0.54	2.35	-3.24	-3.23	-1.32
	St-13	-4.81	-0.48	2.49	-3.56	-3.34	-1.34
	St-14	-4.39	-0.37	2.54	-2.63	-3.17	-1.32

Assessment of heavy metal pollution

Geo-accumulation Index (I_{geo})

Geo-accumulation Index (I_{geo}) has been used widely to evaluate the degree of metal contamination or pollution in terrestrial, aquatic and marine environment sediments. The Geo-accumulation Index (I_{geo}) of a metal in sediments of the study area is calculated with formula according to the equation $I_{geo} = \log_2 (C_n/1.5B_n)$,

B_n =geochemical background value of the earth crusts of element.

n = is the background matrix correction in factor due to lithogenic effects:

The Geo-accumulation index is classified into seven classes from unpolluted to extremely polluted as shown in Table 3.The result of the Geo-accumulation Index (I_{geo}) values of the present study is shown in Table 4. The values of Geo-accumulation Index of Cd

showed that the sediments were moderately to strongly polluted (1.72-2.95). In most of Hub estuarine stations the values of Geo-accumulation Index of Pb showed that the sediments were unpolluted to moderately polluted (0.33-0.74). The Geo- accumulation Indices of Cu, Zn, Mn and Fe showed that the sediments were unpolluted and their values were found < 0 or negative at all the stations.

Mean Effect Range Median Quotient (MERM-Q)

Effect Range Median–empirically derived sediment quality guideline (SQG) is based on co-occurrence of toxicity on a certain chemical concentration threshold. Contaminants rarely occur in sediments as single chemicals. To assess the adverse effects of mixtures of chemicals, mean ERM quotients (MERM-Qs) have been developed by normalizing the concentration of each substance for its ERM value, summing the quotients for each substance, and dividing the sum by the number of chemicals used.

Table 5. Enrichment factor of metals in the surface sediments from the Gadani coast,Hub River Estuary and Hub River of Baluchistan (Pakistan).

Stations	Cd	Pb	Cu	Zn	Mn
St-1	10.27	2.68	1.36	0.59	0.20
St-2	8.24	1.56	1.09	0.10	0.09
St-3	6.56	1.87	0.78	0.14	0.19
St-4	5.36	1.14	0.53	0.14	0.17
St-5	19.73	3.34	0.16	0.25	0.25
St-6	18.94	3.28	0.17	0.43	0.25
St-7	16.56	3.30	0.39	0.21	0.33
St-8	10.98	3.12	0.21	0.57	0.32
St-9	18.20	3.62	0.19	0.86	0.29
St-10	14.62	2.02	0.11	0.14	0.24
St-11	11.89	1.59	0.13	0.25	0.33
St-12	12.81	1.73	0.12	0.27	0.27
St-13	14.24	1.81	0.09	0.21	0.25
St-14	14.51	1.92	0.12	0.40	0.28
Average of Sites					
Gadani Coast	7.61	1.81	0.94	0.25	0.16
Hub River Estuary	16.88	3.33	0.22	0.46	0.29
Hub River	13.62	1.81	0.11	0.25	0.27

Table 6. Classification of Enrichment factor (EFs).

Enrichment factor (EFs)	Classification
EFs < 1	No enrichment
EFs < 3	Minor enrichment,
EFs = 3 to 5	Moderate enrichment
EFs = 5 to 10	Moderately severe
EFs = 10 to 25	Severe enrichment
EFs = 25 to 50	Very severe enrichment
EFs > 50	Extremely severe enrichment

The present result of spatial distribution with the combination of four heavy metals (Cd, Pb, Cu and Zn) of MERM-Quotient of the surface sediment samples are shown in Figure 2.

The MERM-Quotient varied within the range 0.08-0.16. According to MERM-Quotient classification , sediment samples of Hub River and Gadani coast fell in the range 9-21% probability of studied metal toxicity (based on amphipod survival test), while Hub estuary has a slightly higher probability of toxicity than the Hub River and Gadani coast.

Enrichment factor (EF)

A number of scientists use Enrichment Factor for evaluating the influence of anthropogenic contamination of heavy metals. The following equation was used to calculate metal enrichment factor:

EF = (Ms) / (Fes)/ (Mcr / (Fecr)

(Ms) / (Fes) is the metal to iron ratio in the sample of interest while, (Mcr / (Fecr) is the background value of metal to iron ratio.

The calculated EFs values for selected metals in the study area of fourteen stations are shown in Table 5. The EFs of the cadmium ranging between 5.36 to19.73, indicates moderate to severe enrichment, while EFs values of the lead element ranged 1.14-3.62 can be categorized as with nil to moderate enrichment (Table 6). In the Hub Estuary area highest average EFs of the cadmium (16.88) were found amongst the Hub River and Gadani coast (Table 5). Similar patterns of average EFs of the element lead was found 3.33 in the Hub Estuary, while average values (1.81) were recorded in both areas Hub River and Gadani coast.

No enrichment of Cu, Zn, Mn and Fe in the study area was found. Almost all the values were observed <1 at all stations except St-1 for copper. Its value was 1.36.

Contamination Factor and Degree of Contamination

Contamination Factor is the basic tool used for the sediment pollution levels. The classification of pollution levels is given in Table 7.

Table 7. Classification of Contamination factor and Degree of Contamination.

Contamination Factor CF	Degree of Contamination Dc	Description Classification
CF < 1	Cd < 6	Low degree of contamination
1 < CF < 3	6 ≤ Cd < 12	Moderate degree of contamination
3 < CF < 6	12 ≤ Cd < 24	Considerable degree of contamination
CF > 6	Cd ≥ 24	Very high degree of contamination

Table 8. Contamination factor and Degree of Contamination of metals in the surface sediments from the Gadani coast, Hub River Estuary and Hub River of Baluchistan (Pakistan).

Sampling sites & Average	Contamination Factor							Degree of Contamination Dc
	Stations	CFs (Cd)	CFs (Pb)	CFs (Cu)	CFs (Mn)	CFs (Zn)	CFs (Fe)	
	St-1	8.4	2.19	0.11	0.17	0.48	0.82	12.17
Gadani Coast	St-2	9.95	1.88	0.13	0.11	0.13	1.21	13.41
	St-3	8.8	2.51	0.1	0.26	0.19	1.34	13.21
	St-4	6.95	1.47	0.07	0.22	0.19	1.3	10.19
	St-5	11.9	2.01	0.1	0.15	0.15	0.6	14.91
Hub River	St-6	11.6	2.01	0.1	0.15	0.27	0.61	14.74
Estuary	St-7	10.1	2.01	0.24	0.2	0.13	0.61	13.29
	St-8	6.65	1.09	0.13	0.19	0.34	0.61	9.01
	St-9	10.9	2.17	0.11	0.18	0.52	0.6	14.47
	St-10	8.45	1.17	0.06	0.14	0.08	0.58	10.48
Hub River	St-11	7.05	0.94	0.07	0.2	0.15	0.59	9
	St-12	7.65	1.03	0.07	0.16	0.16	0.6	9.67
	St-13	8.45	1.07	0.05	0.15	0.13	0.59	10.44
	St-14	8.75	1.16	0.07	0.17	0.24	0.6	10.99
Average		8.97	1.62	0.10	0.17	0.22	0.76	11.86
Gadani Coast (Avg.)		8.53	2.01	0.10	0.19	0.25	1.17	12.25
Hub River Estuary (Avg.)		10.23	1.86	0.14	0.17	0.28	0.61	13.28
Hub River (Avg.)		8.07	1.07	0.06	0.16	0.15	0.59	10.12

$CF = C_m/C_b$

C_m # Concentration of metal

C_b # Background concentration of metal

Degree of contamination (D_C) was defined as the sum of all contamination factors.

$D_c = \Sigma CF$

In the present study Contamination Factor (CF) values describe the contamination level as shown in table 8. The contamination factor of each metal was found in the following order Cd>Pb>Fe>Zn>Mn>Zn>Cu and their mean values were 8.97, 1.62, 0.76 0.22, 0.17 and 0.10 respectively. Maximum CF was observed at station No. 5, i.e. CF>6 (which indicates very high contamination). High contamination factor was mainly due to the high concentration of cadmium and lead recorded in the study area.

Table 9. Classification of Potential Ecological Risk (PER) Hakanson (1980).

Potential Ecological Risk (PER)	Classification
PER<40	Low
40≤PER<80	Moderate
80≤PER<160	Considerable
160≤PER<320	High
PER≥320	Very high

The calculations of Degrees of Contamination (Dc) in this study were based on concentrations of six elements (Cd, Pb, Cu, Zn, Mn and Fe). Dc in the study area was found in the following order: Hub Estuary>Gadani coast>Hub River.

Their values were noted as 13.28, 12.25 and 10.12 respectively (Table 8). The results of degree of contamination in the study area show moderate to considerable contamination.

Potential Ecological Risk (PER) and Potential Ecological Risk Index (PERI)

Potential Ecological Risk (PER) and Potential Ecological Risk Index (PERI) are one of the best tools to control the heavy metal pollution. PERI is a comprehensive potential ecological index, which equals the sum of all the PER values. It represents the sensitivity of biological community to toxic substances.

Potential Ecological Risk (PER) is determined by the formula:

$PER = TRf^* CF$

Trf^*# Toxic Response Factor, depends on the sedimentological toxic factor and Trf^* is calculated for each metal as follows: $Hg = 30\times5/BPR^{1/2}$; $Cd = 30\times5/BPR^{1/2}$; $Cu = 5\times5^{1/2}/BPR^{1/2}$; $Pb = 5\times5^{1/2}/BPR^{1/2}$; $Cr = 2\times5^{1/2}/BPR^{1/2}$; $Zn = 1\times5^{1/2}/BPR^{1/2}$.

BPR = ([TP in mg/g]/(TOC in %)×100

CF is contamination factor.

Potential Ecological Risk assessment can be classified into four categories which are shown in Table 9.

PERI is the sum of all PER calculated for each metal inside one area:

$PERI = \sum PER$.

Spatial distribution of single risk indices (PER), sum of PERI of four metals and average of three sites (Gadani coast, Hub Estuary and Hub River) of PERI are shown in Table 10. It was found that the single PER of heavy metals was ranked in the order of Cd >Cu>Pb>Zn. The average Potential Ecological Risk (PER) of Cd in the three studied areas (Gadani coast, Hub Estuary and Hub River) were 440.8, 540.3, 420.3 respectively, indicating that Cd posed a very high risk.

Table 10. Potential Ecological Risk and Potential Ecological Risk Index for the single heavy metal in the sediments from Gadani coast, Hub River estuary and Hub RiverBaluchistan, Pakistan.

Study Area	Stations	PER (Cd)	PER (Pb)	PER (Cu)	PER (Zn)	PERI ΣPER	PERI Average of sites
	St-1	497.1	21.6	88.4	4.1	611.3	
Gadani	St-2	359.4	11.3	45.7	9.6	425.9	
coast	St-3	555.6	26.4	101.0	10.9	693.9	
	St-4	351.1	12.4	121.4	9.1	494.0	
Average		440.8	17.9	89.1	8.4		556.3
	St-5	445.0	12.6	64.8	8.4	530.7	
	St-6	512.1	14.8	71.8	5.6	604.3	
Hub River Estuary	St-7	720.0	23.9	95.0	6.9	845.8	
	St-8	509.0	13.9	111.5	5.0	639.4	
	St-9	515.6	17.1	33.0	12.4	578.2	
Average		540.3	16.5	75.2	7.7		639.7
	St-10	426.9	9.8	131.1	20.8	588.6	
	St-11	307.6	6.8	97.7	10.0	422.0	
Hub River	St-12	408.0	9.2	123.8	11.2	552.2	
	St-13	410.1	8.7	151.7	12.7	583.2	
	St-14	548.7	12.1	146.5	8.6	715.9	
Average		420.3	9.3	130.2	12.7		572.4

The results of Potential Ecological Risk Index (PERI) are shown in Table 10. The values recorded were 639.7, 572.4 and 556.3 from Hub estuary, Hub River and Gadani coast respectively. According to the PERI classification (Table 11) Hub River and Gadani coast showed considerable ecological risk, while Hub estuary showed high ecological risk.

Table 11. Classification of Potential Ecological Risk Index (PERI) Hakanson (1980)

Potential Ecological Risk Index (PERI)	Classification
PERI<150	Low
150≤PERI<300	Moderate
300≤PERI<600	Considerable
PERI≥600	Very high

Discussion

Spatial distribution of heavy metals shows that highest concentration of Cd, Pb, Zn and Mn in the Hub Estuary area while iron and copper were found at Gadani coasts, lowest concentrations of and heavy metals (Cd, Pb, Zn, Cu, Mn and Fe) were found in the sediments of Hub River.

High concentrations of heavy metals were recorded in Gadani and Hub estuary which is most probably due to the influence of ship breaking industries along the Gadani coast while, power plants and an oil refinery in Hub estuary surround the land area. Gadani coastal belt is continually facing strong winds creating long-shore currents and strong waves, especially

during the summer monsoon period, which help the sediment flux from north to south (Gadani beach to Hub estuarine area). As mentioned by Rao *et al*., 2001, heavy mineral concentrations in coastal areas depend on the hydrodynamic condition like hinterland, wave energy, and its velocity, long-shore current and wind speed which control the littoral transport.

The studied heavy metals were compared with Sediment quality guideline Canada, US- NOAA and Australian and New Zealand Environment and Conservation Council (ANZECC) for Interim Sediment Quality Guideline, (ISQG), Probable Effect Level (PEL), Effect Range Low (ERL), Effect Range Mean (ERM), $ISQG_{Low}$ and $ISQG_{High}$ respectively (Buchman, 2008; ANZECC, 2000.). Compared results of cadmium in the sediments of the study area exceeded the limit of ERL or $ISQG_{Low}$, while lead values are close to the limit of ERL or $ISQG_{Low}$ at some stations of Gadani coastal area and most stations of the Hub River Estuary (Table 12).

Table 12. Comparison between the averages values of elements in surface sediment from Gadani coast, Hub River estuary and Hub River (µg/g d.w, for Fe g/100g d.w) with the guidelinessuggested by Canada, USA NOAA, and ANZECC.

Guideline / Study area	Cd	Pb	Cu	Zn	Mn	Fe
ISQG (CANADA)	0.7	30.2	18.7	124	-	-
PEL (CANADA)	4.2	112	108	271	-	-
ERL (US- NOAA)	1.2	46.7	34	150	-	-
ERM (US- NOAA)	9.6	218	270	410	-	-
$ISQG_{Low}$ (ANZECC)	1.5	50	65	200	-	-
$ISQG_{High}$ (ANZECC)	10	220	270	410	-	-
Present study sites						
Gadani coast	1.71	25.18	4.69	17.31	179.08	6.56
Hub River Estuary	2.05	23.24	6.09	19.6	165.28	3.41
Hub River	1.61	13.42	3.02	10.59	153.5	3.33

.ANZECC) # Australian and New Zealand Guidelines for Fresh and Marine Water Quality
ISQG # Interm Sediment Quality Guidelines
PEL # Probable effect low
ERL # Effect range low.

Positive correlations of cadmium were found with lead, copper and zinc (0.085-0.647), while Iron was found in negative correlation (–0.156), as shown in table13. Lead was found in strong positive correlation with copper, Iron, zinc and manganese. Similar strong and positive correlation was found in the sediments of New York Hudson–Raritan Estuary (Wolfe *et al*., 1996) and Karachi on-shore area (Monawwar *et al*., 1988). Iron oxide plays a major role in absorption of heavy metal in the marine environment (Sadiq, 1992). Similar positive correlation of manganese and lead with Iron was observed by Agah *et al*; 2012 in the Northern Persian Gulf and ROPME sediments respectively.

The Geo-accumulation index, Contamination Factor, Degree of contamination and Enrichment Factor were used for the assessment of anthropogenic input or naturally derived metals in the study area. The values of the Geo-accumulation index, Contamination factor and Degree of contamination of cadmium show that this area is moderately to strongly polluted, while values of lead show that the Gadani coast and the Hub estuary area are unpolluted to moderately polluted as observed by Abrahim and Parker 2008 in Tamaki Estuary, Auckland New Zealand.

Table 13. Correlation matrix between metal, organic matter and total phosphorous in surface sediments.

	Cd	Pb	Cu	Zn	Mn	Fe	OM	TP
Cd	1	0.647	0.336	0.085	-0.345	-0.156	-0.079	0.57
Pb		1	0.495	0.367	0.235	0.424	-0.017	0.18
Cu			1	0.098	0.167	0.01	0.404	-0.032
Zn				1	0.124	-0.097	0.219	-0.065
Mn					1	0.395	0.236	-0.291
Fe						1	-0.294	-0.274
OM							1	0.336
TP								1

OM # (Organic matter), TP # (Total Phosphorous).

Results of Enrichment factor indicate moderate to severe enrichment of cadmium, while minor enrichment of lead. The Enrichment Factors of lead and cadmium indicate that both are anthropogenic origin as observed by Wang *et al*., 2007, Azhar *et al*., 2009 Szefer *et al*., 1996 in the Jiaozhou Bay, Karachi coast and Southern Baltic Sea respectively. Similar values were observed (Zhang *et al*., 2007) in western Xiamen Bay and Aprile & Bouvy (2008) in Tapacura River basin, Northeastern Brazil where Enrichment factor values exceeded to 1.5 at most of the sites, suggesting that metals originate most likely from anthropogenic sources.

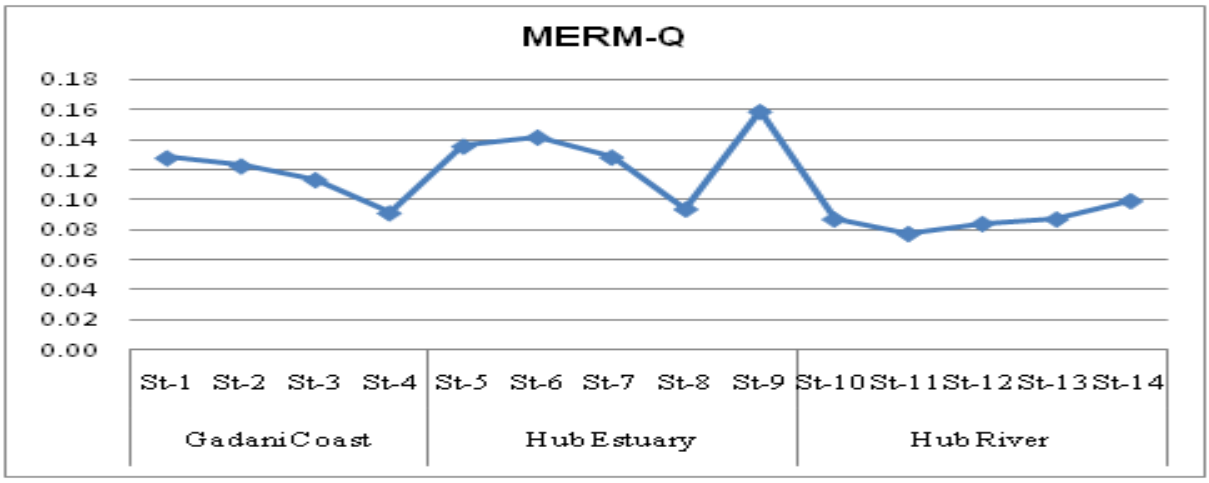

Fig. 2. Spatial distribution of mean effect range medium quotient (MERM-Q) values in Gadani coast, Hub River Estuary and Hub River, Baluchistan**.**

For the probability of toxicity of metals in sediments MERM-Q was used which confirms the assessment of metal contamination. This test was successfully used in the past (Gavin *et al* 2008, Usman 2014, Long & McDonald 1998b). It was found that MERM-Qs are an effective indicator of ecosystem health. In the current investigation the values of MERM-Q ranged 0.08-0.16, which indicates that the probability of toxicity was found in the range 9-21% (Based on amphipod survival test Long *et al*., 1998, Gao and Chen, 2012). Two stations from the Hub River Estuary had the highest MERM-Q (≥0.14), indicating the highest concentrations of metals in the sediments Higher values are most probably due to the power plant and an oil refinery located around the Hub river mouth. A similar study conducted by Usman *et al*., 2014 along the Baluchistan coastal sediments nearest to the Sonmiani Bay where MERM-Q were found 0.266, while in the present study MERM-Q average values observed 0.13 in the Hub Estuary therefore this site is not very toxic.

Comparisons of Potential Ecological Risks assessment and Index of four heavy metals in the sediments of Gadani coast, Hub River Estuary and Hub River show that cadmium was causing a very high ecological risk in the sites of Gadani coast at station 1, Hub River Estuary at stations from 6 to 9 and Hub River at station 14. Its values touched > 500, which is alarming. Based on the Hakanson classifications (1980), cadmium poses a very high potential risk. Similar high ecological potential risk was observed by Cheng-De *et al*., (2012) in Jen-Gen River Estuary, Taiwan. The values of potential risks of copper (40≤PER<80, 80≤PER<160) show moderate to considerable risk in most of the stations at all the sites while, Zinc and lead were found PER<40 at all the sites, indicating low potential ecological risk.

The highest average PERI of five stations of the Hub River Estuary was 639.7 and higher average value noted in the Hub River was 572.4, while lowest average PERI was 556.3 at Gadani coast. According to the PERI Hub River Estuary was at a very high ecological risk (PERI≥600) and the other nine stations of Gadani coast and Hub River were at considerable potential ecological risk having PERI 300≤PERI<600.

Conclusion

This study provides a baseline data of six heavy metals in the fourteen surface sediments collected from Gadani coast and Hub River Estuary and Hub River of Baluchistan.

Based on Enrichment Factor (EF), Contamination Factor (CF), Degree of Contamination (D_c), Geo-accumulation Index (I_{geo}) it was found that there was moderate to severe enrichment of cadmium in surface sediments whereas contamination factor was found moderate to high. Nil to moderate enrichment was found in lead values, while Contamination Factor was found from low to moderate. No enrichment and contamination were found in copper, zinc, manganese and iron. Conclusively high contamination of Cadmium and lead can be attributed to the ship breaking industry, the power plant and the oil refinery.

Mean ERM-Quotient (MERM-Q) values of the surface sediments of the study area classified as probability of toxicity to benthic organisms was found in range 9-21%.

Based on Potential Ecological Risk Index (PERI) the values of Cd, Cu, Pb and Zn in the surface sediments show that this study area is at considerable to high ecological risk. Government organizations (Baluchistan Environmental Protection Agency, Coastal Development Authorities' and Local Administration etc.) can benefit from the present study in formulating precautionary action to control heavy metal pollution and to regulate the industrial and urban wastes and other pollutants into the rivers and the sea.

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