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By

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Introduction

Pakistan has an estimated 240,000 sq. km of marine area with a coastline of about 1,050 km on the Northern Arabian Sea, of which 250 km falling in the Sindh province and 800 km in Baluchistan. Karachi is the highly polluted, mega city population increasing day by day and threatened by pollution through industrial and domestic effluents (>262 million gallons per day), containing shipping, traffic, and associated pollutants discharged largely into the Lyari and Malir Rivers excluding urban runoff during the rainy monsoon season. Sandspit backwaters situated at the mouth of Karachi comprising a monospecific mangrove forest (*Avicennia marina*) (Farooqui et al., 2012) is flooded periodically with about 3.4 million m^3 of seawater from the Arabian sea through Manora Channel (Rizvi, 1997). Reported data suggest that 92% of urban wastewater and 99% of industrial effluents is discharged untreated in sewers, causing more stress to ecosystem (Azizullah et al., 2011). Backwater also receives discharge/freshwater from the Lyari River; and runoff during the monsoon and industrial and domestic effluents in the rest of the year (Rizvi, 1997). The Balochistan coast extends from Hub River to the Iranian border with mangroves occurring only in protected areas, located at Miani Hor, Kalmat Khor and Gwadar Bay. Miani Hor along the Balochistan coast is a protected lagoon with a mangrove cover of 31 km² and about 2%, the total mangroves of Pakistan (Siddiqui et al., 2008), where *A. marina*, *Ceriops tagal,* and *Rhizophora mucronata* co-exist (Saifullah and Rasool, 2002). Miani Hor receives runoff discharge during Monsoon rains from two ephemeral rivers, the Porali and Winder, locally named as "the rivers of sand" (Hussain, 1998). During 1988 to 2007 the population and commercial activities have raised almost three fold gradually making it polluted (Amjad and Jusoff, 2007). The Indus Delta, located at the east of Pakistan coast, extended up to the Indian border, is a mangroves enriched channel and ranked as the fifth largest (0.26 million hectares) mangrove forest in the world. These dense mangrove forests are dominated by *A. marina* (98%) with few small populations of *R. mucronata*, *C. tagal*, and *Aegiceras corniculatum* (Qureshi, 1993) spread over 0.26 million hectares' area. According to UNEP, yearly 54.7 km^3 of wastewater

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is poured into the Indus River, with 90% alone from the agricultural sector through five big rivers; the Beas, Sutlej, Jhelum, Ravi and Chenab (Iqbal, 2013). Mangrove ecosystems have special importance for coastal estuaries and wetlands, in tropical and subtropical regions providing protection against natural and anthropogenic disasters. Mangroves are rich source of valuable products like black tea, mosquitocides, gallotannins, microbial fertilizers, antiviral drugs, UV-screen compounds, etc. (European Commission, 2013; Defew et al., 2005; Nath et al., 2013). They also provide the shelter for the spawning of fisheries, shell fisheries as well as the source of nutrients for the microfauna (Khattak et al., 2012). The destruction of mangroves could be the cause of great loss of different beneficial compounds and blessings from human lives. Once Pakistan had eight mangrove species (*Bruguiera conjugata, Ceriops roxburghiana, C. tagal*, *Rhizophora apiculata, R. mucronata* Lam., *A. corniculata, A. marina* (Forsk.) Vierh and *Sonneratia caseolaris*) but now only four species (*A. marina, A. corniculatum, R. mucronata, C. tagal*) are present, out of these *A. marina* is the most abundant. Over-exploitation, over-harvesting, over grazing, pollution, decline in fluvial discharge in delta, and change in the environmental conditions has made remaining four extinct (Siddiqui et al. 2008). *A. marina,* consistently exhibited higher HM tolerance than the other species (Cheng et al., 2014).

Mangrove soils and/or sediment sequester heavy metals (HM) by providing organic ligands provided by mangroves and inorganic complexes present in it (Clark et al., 1998). HM impart adverse effects to the water quality, benthic biota and other organisms. HM penetrates into the sediments, resist decomposition and are persistent (Jain et al., 2008) and ultimately enters the food chain with serious risks to the environment (Yin et al., 2011; Karbasdehi et al., 2016). Dissolved HM can move everywhere easily via water channels and are absorbed and get accumulated into the mangroves' tissues posing long-term damaging effects.

In this study distribution of ten heavy metals (HM) mercury (Hg), cadmium (Cd), arsenic (As), lead (Pb), copper (Cu), chromium (Cr), zinc (Zn), iron (Fe), aluminium (Al), and selenium (Se) were investigated in seawater and sediments of three different mangroves enriched sites (Sandspit, Miani Hor, and Indus Delta) along Pakistan coast in three different seasons (monsoon, post-monsoon and pre-monsoon). Pollution risks of heavy metals, using multiple assessment e.g., contamination factor, pollution indices, etc., were also calculated. Hg, a highly toxic metal, causes neurological, cardiovascular collapse, renal failure and gastrointestinal damage (WHO, 2005). Its organic forms are more toxic than inorganic and

are fatal if entered in food chain. It accumulates easily in the fat and penetrates readily into the nerves and brain. Hg vapors are easily transported in the atmosphere and ultimately fall down to aquatic environment (Yokoyama, 2018; Bat and Özkan, 2019). Cd is a non-essential toxic heavy metals. As is a carcinogen and one of the hazardous elements not only for human life but also for other biota as it enters the food chain easily. As is carcinogenic especially in the youngsters of age 6 to 10 (USEPA, 1988). Pb is also among most toxic elements, accumulating with age in bones, kidney, liver and spleen. Cr stops the enzymatic activities in cell while Al affects the plasma membranes. Excessive Fe showed sever effect on gastrointestinal tract and biological fluids. Zn and Cu cause risk for human health and environment (Neff, 2005; Jaishankar et. al., 2014; WHO, 2005). Aquatic organisms, such as fish, benthic animals and phytoplankton are much more sensitive to Zn concentrations than those of terrestrial. Higher concentration of Zn causes the adverse effects to the organisms resulting in stunted growth (Wang et al., 2017). Cu has toxic effects on growth of algae and phytoplanktons, which are primary producers, affecting the whole of the marine food web negatively. Cu is highly reactive metal, has capacity to bind with organic compounds, displacing other metals from their associated binding sites within metalloproteins. Cu can easily bind with enzymes inhibiting its activities (Lopez et al., 2019). Se is one of the elements with the narrowest gap between deficiency and toxicity but it accumulates in the body of the marine biota. Se binds specifically to cysteine and ceased the activities of selenoproteins, e.g. glutathione peroxidases and thioredoxin reductases (Karthikeyan et al., 2019; Vicente-Zurdo et al., 2019).

Materials and Methods

Study sites included Indus Delta (24°93′33″ N, 67°27′43.54″ E), Sandspit backwater (24°49′49″ N, 66°55′41″ E), and Miani Hor Bay (25°30′55.76″ N, 66°32′29.41″ E). The locations of sampling sites were identified by a hand-held global positioning system (GPS). Both Indus Delta and Miani Hor are ramsar sites (Siddiqui et al., 2008). Sites are shown in the figure 2.1.

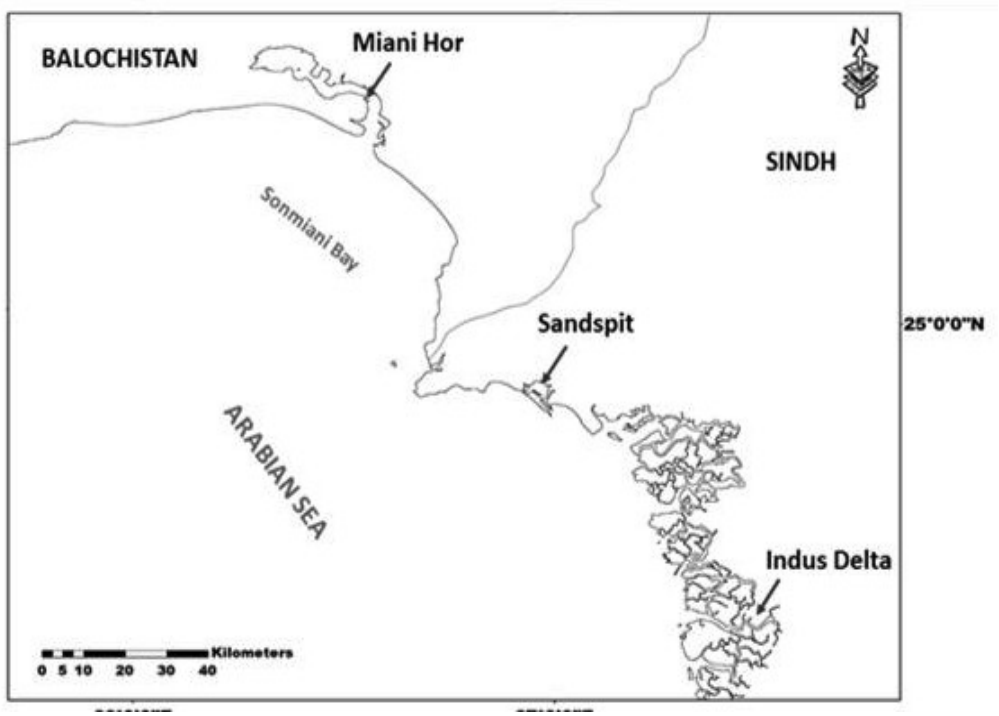


Figure-2.1: Pakistan coast; showing three study sites along Northern Arabian Sea

Replicates of samples of seawater and sediment from a depth of 5 to 7 cm, adhering to the pneumatophores were collected from the mangroves stands, during monsoon (Jun to Sep 2017), postmonsoon (Oct to Nov 2017) and then premonsoon (Mar to May 2018) season at start of ebbing during a single low tides. The seawater samples were collected in 1000 mL acid washed clean plastic bottles while the sediment were stored in clean polyethylene zip-locked bags. Samples were stored in ice box during travelling and in refrigerator before analyses. Known volumes of seawater samples were kept on water bath at 30 to 40°C for evaporation until salt is obtained, replicating the salt pan process. Weighed amount of air dried salt and sediments were ground to powder using mortar and pestle and digested in acid resistant vessels following USEPA, 3051A. Samples were filtered through Whatman filter paper no. 42, and then initial volume was made up to 50 mL with deionized water (USEPA, 2007). Concentration of metals was determined exploiting the atomic absorption spectrophotometer (AAS) (Agilent series 2000). Flame atomization (240 FS AA) was used for the detection of Cu, Fe and Zn; graphite tube atomization (240Z AA) for the analysis of Al, As, Cd, Cr, Pb and Se; and vapour generation accessory (77A) for the analysis of Hg. Standard solutions

obtained from Sigma Aldrich Hg (cat. no. 16482), Cd (cat. no. 51994), As (cat. no. 39436), Pb (cat. no. 16595), Cu (cat. no. 38996), Cr (cat. no. 02733), Zn (cat. no. 18827), Fe (cat. no. 16596), Al (cat. no. 39435), Se (cat. no. 89498), were used to prepare calibration curves.

Samples analysed achieved good precision (1 to 5% RSD). Data obtained from the analysis were expressed as mean ± S.D. HM were dependent variables while the three seasons and sites were independent variables. Data have been tested for homogeneity in variation before analyses for significance. The results were analysed using Microsoft Excel (ver. 10) and Multivariate Analysis of Variance (MANOVA) followed by Post Hoc Tukey test. Values of $P < 0.05$ calculated using SPSS® ver. 23.0 (Chicago, IL, USA) were considered statistically significant. Cluster analysis (PAST®, Version 3.21) was used to analyse similarity index and cluster analysis and MATLAB® was used for Principal Component Analysis (PCA) and similarity indices.

Ecological and environmental indices and factors were estimated; including those related to HM in water and sediment*: Heavy metal pollution index (HPI), Pollution Level Index (PLI), Enrichment Factor (EF)*, Geo-accumulation Index (Igeo)*, Contamination Factor (C_f) Contamination degree (C_d) Modified Degree of Contamination (C_d),; related to Biota health: Potential Ecological Risk Index (Er^i)* and Requested Potential Ecological Risk Index (RI); and related to variation from standards: distribution between two phases Relative % difference (%Δ) and Partition coefficient (Kd)*.

HPI rates the composite influence of individual heavy metal on the overall quality of water (Horton, 1965); EF rates HM in sediments (Chester and Stoner, 1973); I_{geo} evaluate the intensity of metal contamination (Müller, 1981); C_f compare the metal concentration in the matrix (Turekian and Wedepohl, 1961); C_d estimate polymetallic contamination for each sampling site (Hakanson,1980); mC_d calculate overall degree of contamination (Abrahim and Parker, 2008); PLI assesses the level of metal contamination (Tomlinson et al., 1980); Er^i is a quantitative terms to calculate the potential ecological risk of individual HM to the biota in direct contact with sediment (Hakanson, 1980); RI: is a quantitative terms used to calculate the potential ecological risk of total HMs to the biota in direct contact with sediment (Hakanson, 1980); $\%_\Delta$ calculate inter-analytical difference between HM concentration in water and sediment; and K_d expresses the ratio of the concentrations of a particular matter adsorbed on solids to its concentrations in the seawater (Merrikhpour and Jalali, 2015).

Results

The concentrations of HM in the seawater and sediment samples in three different seasons and at three different sites are given in tables 2.1 and 2.2 along with average and total values. All analyses were done in triplicate or more. Result obtained from the calculations of C_f, PLI, C_d and mC_d for the seawater are given in table 2.3. HPI calculated, with details for the seawater given in the table 2.4. Indices calculated for the sediment i.e., C_f, EF, I_{geo}, Er^i, and RI values of HM in three seasons at three sites are given in the table 2.5 and 2.6. The variations in K_d values of HM are given in the table 2.7. The metals are arranged in the table in the descending order of their toxicity.

Table 2.1: Concentration of heavy metal in seawater samples collected from three sites in three different seasons ($mg.L^{-1}$; Mean ± SD)

HM	Sandspit				Miani Hor				Indus Delta			
	Monsoon	Post-monsoon	Pre-monsoon	Average	Monsoon	Post-monsoon	Pre-monsoon	Average	Monsoon	Post-monsoon	Pre-monsoon	Average
Hg	16.5 ±0.12^{a}	14.7 ±0.14^{b}	11.47 ±0.20^{c}	14.22 ±2.55	13.5 ±0.18^{a}	12 ±0.16^{b}	9.58 ±0.16^{c}	11.69 ±1.98	15.9 ±0.13^{a}	13.9 ±0.36^{b}	13.1 ±0.17^{c}	14.33 ±1.46
Cd	Chart Area ±0.19^{a}	2.01 ±0.14^{a}	1.31 ±0.08^{b}	1.92 ±0.57	1.14 ±0.08^{a}	0.88 ±0.06^{b}	0.56 ±0.03^{c}	0.86 ±0.29	0.64 ±0.02^{a}	0.47 ±0.02^{b}	0.40 ±0.01^{c}	0.50 ±0.12
As	29.5 ±0.25^{a}	21.4 ±0.22^{b}	17.1 ±0.18^{c}	22.66 ±6.27	18.6 ±0.27^{a}	17.2 ±0.24^{b}	15.2 ±0.26^{c}	17.00 ±1.66	19.4 ±0.16^{a}	18.7 ±0.13^{b}	16.5 ±0.11^{c}	18.20 ±1.53
Pb	15.9 ±0.22^{a}	10.7 ±0.12^{b}	10.12 ±0.18^{c}	12.24 ±3.18	1.68 ±0.16^{a}	1.39 ±0.18^{b}	1.04 ±0.09^{c}	1.37 ±0.32	0.87 ±0.03^{a}	0.79 ±0.02^{b}	0.73 ±0.03^{c}	0.80 ±0.07
Cu	3.9 ±0.13^{a}	2.9 ±0.10^{b}	1.84 ±0.05^{c}	2.89 ±1.04	1.7 ±0.13^{a}	1.03 ±0.06^{b}	0.77 ±0.03^{c}	1.17 ±0.49	1.53 ±0.1^{a}	1.11 ±0.12^{b}	0.93 ±0.03^{c}	1.19 ±0.31
Cr	49.3 ±0.37^{a}	43.6 ±0.32^{b}	41.9 ±0.20^{c}	44.91 ±3.87	4.28 ±0.08^{a}	3.71 ±0.15^{b}	1.33 ±0.09^{c}	3.11 ±1.56	1.38 ±0.12^{a}	0.99 ±0.07^{b}	0.84 ±0.03^{c}	1.07 ±0.28
Zn	4.7 ±0.17^{a}	3.61 ±0.09^{b}	3.00 ±0.11^{bc}	3.77 ±0.89	1.33 ±0.1^{a}	1.26 ±0.13^{b}	0.78 ±0.03^{c}	1.12 ±0.30	0.86 ±0.02^{a}	0.71 ±0.02^{b}	0.55 ±0.02^{c}	0.71 ±0.16
Fe	49.2 ±0.24^{a}	45.6 ±0.34^{b}	40.97 ±0.11^{c}	45.27 ±4.15	0.97 ±0.06^{a}	0.84 ±0.04^{b}	0.51 ±0.02^{c}	0.77 ±0.24	1.41 ±0.14^{a}	1.16 ±0.14^{b}	1.01 ±0.05^{c}	1.19 ±0.20
Al	20.3 ±0.35^{a}	17.4 ±0.27^{b}	16.7 ±0.10^{c}	18.14 ±1.92	12.7 ±0.14^{a}	12.2 ±0.24^{a}	10.6 ±0.22^{b}	11.84 ±1.12	10.0 ±0.12^{a}	6.63 ±0.14^{b}	4.24 ±0.16^{c}	6.97 ±2.90
Se	0.086 ±0.005^{a}	0.068 ±0.008^{b}	0.068 ±0.008^{b}	0.074 ±0.01	0.028 ±0.007^{a}	0.023 ±0.005^{a}	0.014 ±0.005^{b}	0.02 ±0.01	0.08 ±0.005^{a}	0.07 ±0.008^{a}	0.04 ±0.008^{b}	0.06 ±0.02
Σ	192	162	144	166	56	51	40	49	52	45	38	45

^{a}p <0.001, ^{b}p <0.01, ^{c}p <0.05

Table 2.2: Concentration of heavy metal in sediment samples collected from three sites in three different seasons (mg.Kg^{-1}; Mean ± SD)

HM	Sandspit				Miani Hor				Indus Delta			
	Monsoon	Post-monsoon	Pre-monsoon	Average	Monsoon	Post-monsoon	Pre-monsoon	Average	Monsoon	Post-monsoon	Pre-monsoon	Average
Hg	12.8 ±0.18^{a}	10.8 ±0.09^{b}	10.1 ±0.19^{bc}	11.2 ±1.40	11.1 ±0.19^{a}	10.8 ±0.09^{b}	8.4 ±0.11^{c}	10.1 ±1.46	13.1 ±0.14^{a}	11.5 ±0.13^{b}	10.8 ±0.09^{c}	11.8 ±1.17
Cd	2.8 ±0.08^{c}	2.9 ±0.12^{b}	4.2 ±0.08^{a}	3.31 ±0.76	1.50 ±0.17^{c}	1.77 ±0.14^{b}	2.2 ±0.17^{a}	1.82 ±0.35	0.75 ±0.01^{c}	0.92 ±0.03^{b}	1.33 ±0.18^{a}	1.00 ±0.30
As	20.5 ±0.27^{b}	16.8 ±0.13^{c}	21.8 ±0.11^{a}	19.70 ±2.62	14.4 ±0.36^{b}	13.6 ±0.28^{c}	18.4 ±0.24^{a}	15.48 ±2.60	16.1 ±0.12^{b}	15.3 ±0.12^{c}	17.3 ±0.13^{a}	16.24 ±1.03
Pb	21.4 ±0.30^{c}	25.6 ±0.24^{b}	31.7 ±0.22^{a}	26.23 ±5.20	1.73 ±0.12^{c}	2.1 ±0.14^{b}	2.53 ±0.13^{a}	2.12 ±0.40	1.03 ±0.06^{c}	1.48 ±0.11^{b}	1.74 ±0.07^{a}	1.42 ±0.36
Cu	4.8 ±0.08^{c}	5.6 ±0.12^{b}	6.1 ±0.16^{a}	5.50 ±0.65	1.82 ±0.1^{c}	2.02 ±0.08^{b}	2.23 ±0.13^{a}	2.02 ±0.21	1.88 ±0.13^{b}	2.03 ±0.17^{b}	2.24 ±0.14^{a}	2.05 ±0.18
Cr	27.6 ±0.26^{c}	35.1 ±0.19^{b}	39.6 ±0.36^{a}	34.08 ±6.03	2.59 ±0.08^{c}	2.86 ±0.07^{b}	3.21 ±0.06^{a}	2.89 ±0.31	0.90 ±0.01^{c}	1.15 ±0.12^{b}	1.51 ±0.14^{a}	1.18 ±0.32
Zn	4.9 ±0.15^{c}	5.7 ±0.14^{b}	9.1 ±0.22^{a}	6.57 ±2.22	1.78 ±0.13^{a}	1.71 ±0.11^{a}	1.8 ±0.1^{a}	1.76 ±0.05	1.08 ±0.05^{b}	1.11 ±0.07^{a}	1.74 ±0.13^{b}	1.31 ±0.38
Fe	2001 ±11.05^{a}	1822 ±8.60^{b}	1772 ±12.42^{c}	1865 ±120.5	1356 ±11.37^{a}	1292 ±12.41^{b}	1278 ±3.79^{c}	1309 ±41.67	1114 ±11.6^{a}	1045 ±8.06^{b}	1010 ±8.49^{c}	1056 ±53.15
Al	24.2 ±0.22^{c}	25.6 ±0.32^{b}	33.5 ±0.35^{a}	27.74 ±5.00	13.1 ±0.21^{bc}	13.8 ±0.16^{b}	17.7 ±0.17^{a}	14.88 ±2.47	29.1 ±0.12^{c}	33.2 ±0.14^{b}	35.7 ±0.19^{a}	32.68 ±3.34
Se	0.063 ±0.005^{b}	0.074 ±0.005^{b}	0.085 ±0.005^{a}	0.074 ±0.01	0.022 ±0.008^{b}	0.026 ±0.005^{a,b}	0.032 ±0.008^{a}	0.03 ±0.01	0.06 ±0.008^{b}	0.08 ±0.005^{a}	0.08 ±0.009^{a}	0.07 ±0.01
Σ	2120	1950	1928	1999	1404	1341	1335	1360	1178	1112	1082	1124

^{a}p <0.001, ^{b}p <0.01, ^{c}p <0.05

Table 2.3: Comparison of concentration (mg.L^{-1}; Mean ± SD) of heavy metal with standards in seawater samples and sediments collected from three sites in three different seasons

HM	Sea water							Sediments						
	NEQS	Sandspit		Miani Hor		Indus Delta		AVCSR	Sandspit		Miani Hor		Indus Delta	
	1997	Average	%Δ#	Average	%Δ#	Average	%Δ#	2010	Average	%Δ#	Average	%Δ#	Average	%Δ#
Hg	<0.01	14.22 ±2.55	142100	11.69 ±1.98	116800	14.33 ±1.46	143200	0.4	11.24 ±1.40	2710	10.1 ±1.46	2425	11.8 ±1.17	2850
Cd	<0.1	1.92 ±0.57	1820	0.86 ±0.29	760	0.50 ±0.12	400	0.42	3.31 ±0.76	688	1.82 ±0.35	333	1.00 ±0.30	138
As	<1.0	22.66 ±6.27	2166	17.00 ±1.66	1600	18.20 ±1.53	1720	13	19.70 ±2.62	51	15.48 ±2.60	19	16.24 ±1.03	25
Pb	<0.5	12.24 ±3.18	2348	1.37 ±0.32	174	0.80 ±0.07	60	80	26.23 ±5.20	-67	2.12 ±0.40	-97.3	1.42 ±0.36	-98.2
Cu	<1.0	2.89 ±1.04	189	1.17 ±0.49	17	1.19 ±0.31	19	250	5.50 ±0.65	-97.8	2.02 ±0.21	-99.2	2.05 ±0.18	-99.2
Cr	<1.0	44.91 ±3.87	4391	3.11 ±1.56	211	1.07 ±0.28	7	90	34.08 ±6.03	-62	2.89 ±0.31	-96.8	1.18 ±0.32	-98.7
Zn	<5.0	3.77 ±0.89	-25	1.12 ±0.30	-78	0.71 ±0.16	-86	165	6.57 ±2.22	-96.0	1.76 ±0.05	-98.9	1.31 ±0.38	-99.2
Fe	<8.0	45.27 ±4.15	466	0.77 ±0.24	-90	1.19 ±0.20	-85	65000	1865 ±120.5	-97.1	1309 ±41.67	-97.9	1056 ±53.15	-98.4
Al	<0.5*	18.14 ±1.92	3528	11.84 ±1.12	2268	6.97 ±2.90	1294	84000	27.74 ±5.00	-99.9	14.88 ±2.47	-99.9	32.68 ±3.34	-99.9
Se	<0.5	0.074 ±0.01	-85	0.02 ±0.01	-96	0.06 ±0.02	-88	0.17	0.074 ±0.01	-56	0.03 ±0.01	-82	0.07 ±0.01	-59
ΣM		166		49		45			1999		1360		1124	

*taken from ASQG, 2010, not available in NEQS, 1997. #%Δ is calculated by comparing average observed values with the limits described in NEQS 1997 or AVCSR, 2010. ^{a}p <0.001, ^{b}p <0.01, ^{c}p <0.05.

Table 2.4: Contamination factor (C_f), pollution load index (PLI), contamination degree (C_d), modified contamination degree (mC_d) for seawater samples of three sites in three seasons

HM	Sandspit				Miani Hor				Indus Delta			
	Monsoon	Post-monsoon	Pre-monsoon	Average	Monsoon	Post-monsoon	Pre-monsoon	Average	Monsoon	Post-monsoon	Pre-monsoon	Average
C_f (Hg)	1650	1470	1147	1422	1350	1200	958	1169	1590	1390	1310	1430
C_f (Cd)	31	20.1	13.1	21.4	11.4	8.8	5.6	8.6	6.4	4.7	4.0	5.03
C_f (As)	29.5	21.4	17.1	22.7	18.6	17.2	15.2	17.0	19.4	18.7	16.5	18.2
C_f (Pb)	31.78	21.41	20.24	24.48	3.36	2.78	2.08	2.74	1.74	1.58	1.46	1.59
C_f (Cu)	3.9	2.9	1.8	2.9	1.71	1.03	0.77	1.17	1.53	1.11	0.93	1.19
C_f (Cr)	49.33	43.61	41.90	44.91	4.28	3.71	1.33	3.11	1.38	0.99	0.84	1.07
C_f (Zn)	0.94	0.60	0.72	0.75	0.36	0.25	0.16	0.25	0.17	0.14	0.11	0.14
C_f (Fe)	6.1	5.7	5.1	5.7	0.12	0.10	0.06	0.09	0.17	0.14	0.12	0.15
C_f (Al)	40.6	34.8	33.4	36.3	30.4	24.4	21.2	25.3	20.0	13.3	8.5	13.9
C_f (Se)	0.172	0.148	0.136	0.152	0.056	0.046	0.028	0.043	0.163	0.141	0.080	0.13
PLI	14.36	11.17	9.61	11.71	3.72	2.99	2.03	2.90	3.05	2.46	1.98	2.49
C_d	1843.36	1620.64	1280.55	1581.52	1420.27	1258.32	1004.42	1227.67	1640.95	1430.76	1342.52	1471.41
mC_d	184.34	162.02	128.1	158.15	142.11	125.84	100.41	122.73	164.13	143.11	134.27	147.17

Reference values (C_r) for HM were taken from NEQS, 1997 except that the value for Al is taken from ASQG, 2010

Table 2.5 Heavy metals pollution indices (HPI) in seawater

Metals	Monsoon			Post-monsoon			Pre-monsoon			Average
	V_n	q_n	$W_n q_n$	V_n	q_n	$W_n q_n$	V_n	q_n	$W_n q_n$	
Sandspit										
Hg	16.5	165,000	138,287	14.7	147,000	123,201	11.47	114,700	96,130	119,206
Cd	3.1	3100	260	2.01	2010	168	1.31	1310	110	179
As	29.5	2950	25	21.4	2140	18	17.1	1710	14	19
Pb	15.9	3180	53	10.7	2140	36	10.12	2024	34	41
Cu	3.9	390	3.26	2.9	290	2.43	1.84	184	1.54	2.41
Cr	49.3	4930	41	43.6	4360	37	41.9	4190	35	38
Zn	4.7	94	0.15	3	60	0.10	3.61	72.2	0.10	0.12
Fe	49.2	615	0.64	45.6	570	0.60	40.97	512	0.54	0.59
Al	20.3	4060	68	17.4	3480	58	16.7	3340	56	61
Se	0.086	17.2	0.29	0.074	14.8	0.25	0.068	13.6	0.23	0.26
ΣHPI			138,738			123,521			96,382	119,547
Miani Hor										
Hg	13.5	135,000	113,143	12	120,000	100,572	9.58	95,800	80,290	98,002
Cd	1.14	1140	96	0.88	880	74	0.56	560	47	72
As	18.6	1860	16	17.2	1720	14	15.2	1520	13	14
Pb	1.68	336	5.63	1.39	278	4.66	1.04	208	3.49	4.59
Cu	1.7	170	1.42	1.03	103	0.86	0.77	77	0.64	0.97
Cr	4.28	428	3.58	3.71	371	3.11	1.33	133	1.11	2.59
Zn	1.78	35.6	0.05	1.26	25.2	0.04	0.78	15.6	0.02	0.04
Fe	0.97	12.1	0.01	0.84	10.5	0.01	0.51	6.4	0.01	0.01
Al	15.2	3040	51	12.2	2440	41	10.6	2120	36	43
Se	0.028	6.6	0.11	0.023	4.6	0.08	0.014	2.8	0.05	0.08
ΣHPI			113,316			100,710			80,390	98,139
Indus Delta										
Hg	15.9	159,000	133,258	13.9	139,000	116,496	13.1	131,000	109,791	119,848
Cd	0.64	640	54	0.47	470	39	0.4	400	34	42
As	19.4	1940	16	18.7	1870	16	16.5	1650	14	15
Pb	0.87	174	2.92	0.79	158	2.65	0.73	146	2.45	2.67
Cu	1.53	153	1.28	1.11	111	0.93	0.93	93	0.78	0.99
Cr	1.38	138	1.16	0.99	99	0.83	0.84	84	0.70	0.89
Zn	0.86	17.2	0.03	0.71	14.2	0.02	0.55	11	0.02	0.02
Fe	1.41	17.6	0.02	1.16	14.5	0.01	1.01	12.6	0.01	0.01
Al	10	2000	34	6.63	1326	22	4.24	848	14	23
Se	0.08	16	0.27	0.07	14	0.23	0.04	8	0.13	0.21
ΣHPI			133,367			116,578			109,857	119,934

Table 2.6: Pollution and Risk Indices (Cf, Er^i, EF and Igeo) and Risk Indices (RI) of Sediment three Season, in three sites.

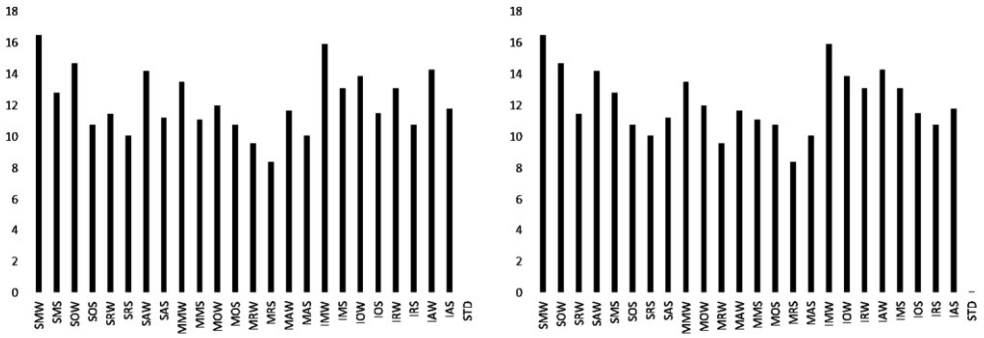
HM	Sandspit				Miani Hor				Indus Delta			
	C_f	Er^i	EF	I_{geo}	C_f	Er^i	EF	I_{geo}	C_f	Er^i	EF	I_{geo}
Monsoon												
Hg	51.200	2048.000	1173.815	4.415	44.400	1776.000	1330.199	4.209	52.400	2096.000	1910.907	4.448
Cd	2.800	84.000	244.5448	2.152	1.500	45.000	171.1968	1.252	0.750	22.500	104.1934	0.252
As	1.367	13.667	57.84424	0.072	0.907	9.067	50.14749	-0.52	1.073	10.733	72.26212	-0.276
Pb	0.306	1.529	9.812359	-2.487	0.025	0.124	1.036597	-6.12	0.015	0.074	0.751234	-6.864
Cu	0.112	0.560	0.82167	-6.065	0.036	0.182	0.348968	-7.687	0.038	0.188	0.438779	-7.64
Cr	0.307	0.613	11.24906	-2.29	0.029	0.058	1.379466	-5.704	0.010	0.020	0.570517	-7.261
Zn	0.029	0.029	1.111567	-5.629	0.008	0.008	0.386386	-7.54	0.006	0.006	0.381916	-7.84
Fe	-	-	1	-5.782	-	-	1	-6.168	-	-	1	-6.452
Al	-	-	0.012489	-12.11	-	-	0.005764	-13.606	-	-	0.020214	-12.08
Se	-	-	13.59381	-2.017	-	-	6.203366	-3.535	-	-	20.59352	-2.087
RI	2148				1830				2129			
Postmonsoon												
Hg	43.200	1728.000	963.2272	4.16	43.200	1728.000	1358.359	4.17	46.000	1840.000	1788.278	4.261
Cd	3.000	90.000	254.822	2.252	1.770	53.100	212.019	1.49	0.920	27.600	136.2497	0.546
As	1.120	11.200	46.10318	-0.215	0.960	9.600	55.72755	-0.437	1.020	10.200	73.20574	-0.35
Pb	0.366	1.829	11.41603	-2.229	0.030	0.150	1.320627	-5.837	0.021	0.106	1.150718	-6.341
Cu	0.096	0.480	0.684962	-6.288	0.040	0.202	0.406502	-7.536	0.041	0.203	0.505072	-7.529
Cr	0.390	0.780	13.91328	-1.943	0.032	0.064	1.598727	-5.561	0.013	0.026	0.79479	-6.875
Zn	0.033	0.033	1.232412	-5.44	0.010	0.010	0.52139	-7.177	0.010	0.010	0.655937	-7.152
Fe	-	-	1	-5.742	-	-	1	-6.238	-	-	1	-6.544
Al	-	-	0.010872	-12.266	-	-	0.008265	-13.15	-	-	0.024584	-11.89
Se			14.27003	-1.907	-	-	7.694409	-3.294	-	-	29.27104	-1.672

Table 2.7 Partition Coefficient (K_d) values of studied metals in three seasons in three sites.

	Sandspit				MianiHor				Indus Delta			
Metals	Monsoon	Post-monsoon	Pre-monsoon	Average	Monsoon	Post-monsoon	Pre-monsoon	Average	Monsoon	Post-monsoon	Pre-monsoon	Average
Hg	0.78	0.73	0.88	0.79	0.82	0.90	0.88	0.86	0.82	0.83	0.82	0.82
Cd	1.17	1.44	3.21	1.72	1.32	2.01	3.93	2.12	1.17	1.96	3.33	2.00
As	0.69	0.79	1.27	0.87	0.77	0.79	1.21	0.91	0.83	0.82	1.05	0.89
Pb	1.35	2.39	3.13	2.14	1.03	1.51	2.43	1.55	1.18	1.87	2.38	1.78
Cu	1.23	1.93	3.32	1.90	1.07	1.96	2.90	1.74	1.23	1.83	2.41	1.72
Cr	0.56	0.81	0.95	0.76	0.61	0.77	2.41	0.93	0.64	1.16	1.80	1.10
Zn	1.04	1.58	3.03	1.75	1.34	1.36	2.31	1.57	1.26	1.56	3.16	1.85
Fe	40.67	39.96	43.25	41.20	1397.94	1538.10	2505.88	1700.00	790.07	900.86	1000.00	887.39
Al	1.19	1.47	2.01	1.53	1.03	1.13	1.67	1.26	2.91	5.01	8.42	4.69
Se	0.73	1.09	1.25	1.00	0.79	1.13	2.29	1.50	0.75	1.14	2.00	1.17

Discussion

Hg was found higher in seawater than those of sediment samples (Figure 2.2), irrespective of sites and seasons. Both seawater and sediment samples reflected the similar pattern in all of the three studied sites, i.e., highest concentration was observed during monsoon gradually decreasing to lowest during premonsoon. Average Hg content of these sites were comparable to one another but exceeding the standard limits.



(i) Seawater v/s sediments in different seasons.

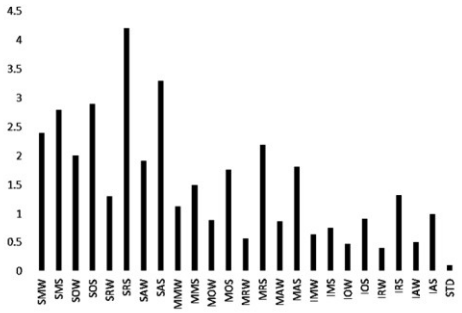
(ii) Seasons v/s seawater and sediments.

Figure-2.2: Average content of Hg at Sandspit (S), Miani Hor (M) and Indus Delta (I), (denoted by the first letter in the three letter code), in three seasons, monsoon-2015 (M), post-monsoon-2015 (P) and pre-monsoon-2016 (R) (the middle letter in code),in seawater (W) and sediments (S), (the last letter in code).(A) represents overall average of three season in studied sites.

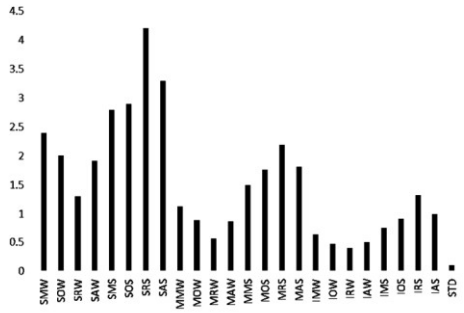
%Δ was found very high in seawater from NEQS and in sediment from AVCSR at Sandspit, Indus Delta and Miani Hor, respectively. The critical value for HPI is 100. Excessively high values of HPI reflect very poor seawater quality. The worst HPI was calculated for Sandspit in all three seasons. Exceedingly high of Hg was alone major contributor in HPI in seawater at Sandspit. Miani Hor during pre-monsoon was found to be the least polluted reference to HPI. The similar trend with slightly low values was reflected by Miani Hor and Indus Delta. Here again Hg was the main contributor. The case was supported by other calculated values of Hg. At Sandspit the Cf value of Hg during premonsoon was lower than that of Indus Delta (1310) during same season. During premonsoon, the Hg content in the seawater of Sandspit was smaller than that of Indus Delta. The higher content of Hg also affected the values of C_d and mC_d, at same sites and seasons. Coastal regions and estuaries are particularly vulnerable to Hg

contamination, produced by; industrial, minerals and anthropogenic activities. Hg can contaminate the marine environment *via* atmospheric deposition or directly from water bodies discharging therein. However, the main source of Hg pollution is the direct discharge of mercury (waste material) into seawater without proper treatment rather than its atmospheric deposition (Gworek et al., 2016). The results are consistent with the findings in previous study where the concentrations of Hg in the sediment samples were showing an understandable trend (Liang et al., 2010). The K_d in current study was showied more retention of Hg in seawater in comparison to sediment (Merrikhpour and Jalali, 2015). Almost similar pattern of results in K_d have also been reported by Liang et al (2010) and Byrd (1990). High Hg content, irrespective of sites and seasons, is quite alarming and has already been reported by various groups (Holmes et al., 2008; Hamza et al., 2014; Shahab et al., 2016). A lot of data is available on the Hg assessment in seawater, ranging as high as 3 ppm (Hasan et al., 2013; Kumar et al., 2013; Mohiuddin and Naqvi, 2014; Naqvi et al., 2002). Globally the assessment of Hg along within the total suspended solids (TSS) or total particulate matter (TPM) have shown values as high as 150 $mg.kg^{-1}$ (Hosek et al., 2019; Wilken and Hintelmann, 1991; Cranston and Buckley, 1972). These are sites where anthropogenic interference specially of industrial origin are in direct contact with coasts, analogous to Karachi. Comparatively a little work has been done on the Hg conc. in total particulate matter in Indian Ocean (Chakraborty et al., 2019). However, no work on the assessment of Hg and other HM in the TPM and TSS has been done along Pakistan coast. Moreover, Pakistan is rich in minerals, including barite and cinnabar. Its production has recently been increased to 75,000 metric tons per year, ranking Pakistan 8th globally (Shahab et al., 2016; Ozbas and Hicyilmaz, 1994).

In contrast to Hg, Cd showed higher content in all of the samples of sediment compared to the seawater (Figure 2.3). The trend of content was similar in three sites. Irrespective of sites, considering seawater, the highest concentration of Cd was observed during monsoon, which gradually decreases resulting in lowest during pre-monsoon. Unlike Hg, exactly opposite trend was observed in sediment samples, where Cd content was found lowest during monsoon while highest during pre-monsoon season. Probably the subtropical rains as well as peak agricultural activities (Thilagavathi et al., 2011) are bringing and pouring more Cd via agricultural and industrial run-off in seawater, which later get accumulated onto the soil during downwelling and winter (Dec-Feb). Cd was much higher than limits at Sandspit, as well as was crossing limits at two other sites.



(i) Seawater v/s sediments in different seasons.

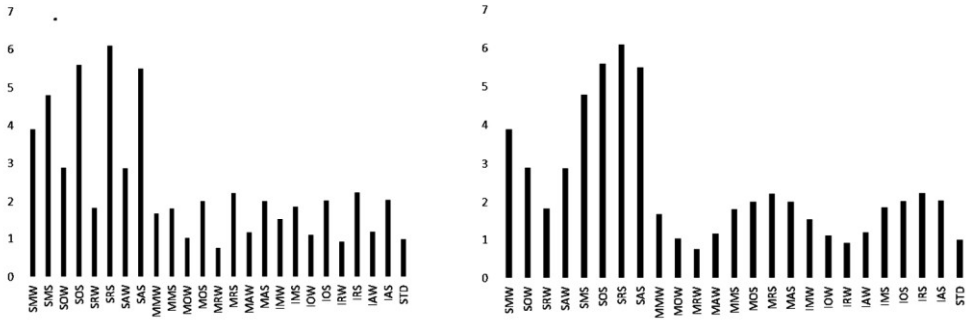


(ii) Seasons v/s seawater and sediments.

Figure-2.3: Average content of Cd. Keys are similar to Figure 2.2

In premonsoon, immediately after downwelling, lesser input of fresh water and relatively resting seawater let Cd to chemisorbed onto sediments while upwelling (Jun-Sep) caused desorption (Cao et al., 2009; Ding et al., 2016; Zang et al., 2017). %Δ for Cd was much higher than the described limits in seawater at Sandspit i.e., 1820. Comparatively, Sandspit seawater was three times more polluted as compared to the other two sites, which were found just crossing over the limits. The K_d values (table 2.7) of Cd at Miani Hor and Indus Delta were comparable, while at Sandspit K_d was relatively low, showing that Sandspit is receiving more anthropogenic Cd in seawater (Merrikhpour and Jalali, 2015) and is most contaminated with it. Sandspit is most while Indus Delta is least contaminated with Cd. As far as accumulation is considered, Cd has shown similar biogeochemical behaviour in soil and sediment (Chaney, 2010; Ghrefat and Yusuf, 2006; Jain and Sharma, 2002), organisms and in aquatic food web (Hooda, 2010; Chaney, 2010; Mebane et al., 2017; Wesner et al., 2017). Various aquatic organisms spend majority of their life-cycle living in or around sediments (Fletcher et al., 2017). Thus most of Cd discharged into water bodies either got fixed onto sediments or bio-accumulated and bio-magnified. The K_d of Cd is indicating that it has more ability to bind with the sediment (Merrikhpour and Jalali, 2015).

Like Cd, Cu was higher in sediments than the seawater samples (Figure 2.4). In seawater concentration of Cu has been reached highest during monsoon season and gradually decreased to lowest value in pre-monsoon. Exactly opposite trend was observed in sediments where minimum Cu was recorded during monsoon gradually increasing to maximum in pre-monsoon. Comparatively, Sandspit was three times more polluted as compared to the other two sites (Figure Cu).



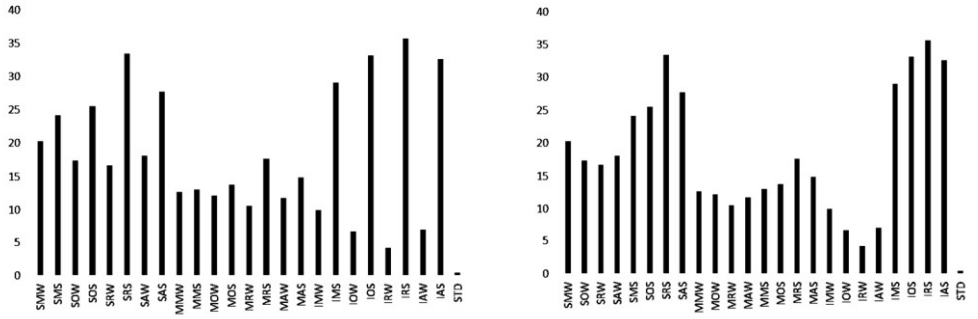
(i) Seawater v/s sediments in different seasons.

(ii) Seasons v/s seawater and sediments.

Figure-2.4: Average content of Cu. Keys are similar to Figure 2.2

Cu was much higher than limits at Sandspit, although it was also crossing limits at two other sites. %△ for Cu was much higher than the described limits in seawater at Sandspit. Comparatively, Sandspit seawater was three times more polluted as compared to the other two sites, which were found just crossing over the limits. In premonsoon, immediately after downwelling, lesser input of fresh water and relatively resting seawater let Cu to chemisorbed onto sediments while upwelling (Jun-Sep) have been causing desorption (Cao et al., 2009; Ding et al., 2016; Zang et al., 2017; Kongsuwan et al., 2009; Dezfoli et al., 2013; Escudero et al., 2013). This pattern was similar in all of the three sites. All the sediments sample collected in current study were clay in nature (Majeed et al. 2010; Ahmed, 2016; Syed et al., 2019). The high Cu percentage in the Sandspit sediments is because of the fact that Cu can fix onto sediments specially it is chemisorbed on the clay minerals easily. One of the reasons is presence of more Fe-Mn oxide and hydroxide in clay, which was found rich in Fe in this study (Ghrefat and Yusuf, 2006; Jain and Sharma, 2002; Pickering, 1986). The Kd is also indicated the ability of Cu to bind with the sediments (Merrikhpour and Jalali, 2015).

Al also showed the similar trend as was observed for Cu and Cd (Figure 2.5). It was high in sediment as compared to seawater. In sediments Al was found gradually increasing from monsoon to pre-monsoon while in seawater the trend was exactly reverse. This was due to chemisorption of Al on the sediments during premonsoon and desorption during upwelling (Jun-Sep). Same kind of pattern of Al was observed in all three sites. The seawater samples of Sandspit had higher concentration of Al (during all the seasons) than the rest of the two sites (Cao et al., 2009; Ding et al., 2016; Zang et al., 2017).



(i) Seawater v/s sediments in different seasons.

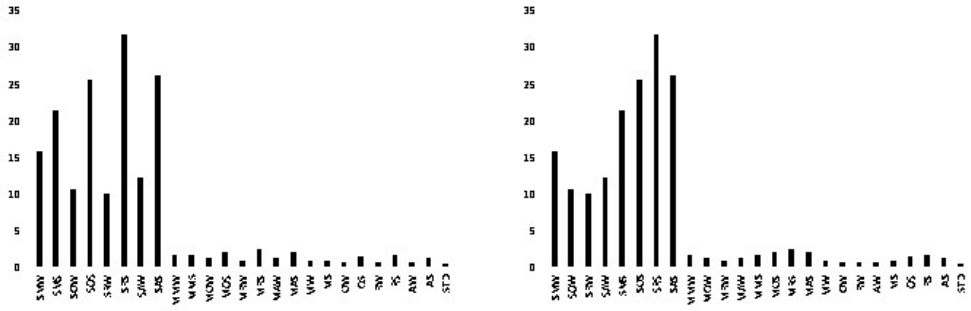
(ii) Seasons v/s seawater and sediments.

Figure-2.5: Average content of Al. Keys are similar to Figure 2.2

Like Cr and Fe, Al is also present mainly in the residual phase of clay tightly bounded to its structure (Staley and Haupin, 1992; Guzman et al., 2010; Ho et al., 2012; Carroll, 1958; Collinson, 1968). Similarly, Barite, an abundant ore of Paksitan, also contain <10% impurities including alumina (Al_2O_3) (Ozbas and Hicyilmaz, 1994). Large amount of Al in seawater might be due to anthropogenic activities, as discussed by Wilson and Hyne (1997) and Angel et al. (2012). One of the reason is the acidic soil near human and industrial settlements as in case of Sandspit (Rizvi, 1997), resulting in release of more Al in the seawater compared to the rest of the two sites. Thus seawater samples of Sandspit had higher concentration of Al than the two other sites, might be due to the comparatively low pH (7.25), rendering Al in dissolved form. This might be due to anthropogenic activities, as discussed by Angel et al. (2012). Al was also found crossing SEQS limits (14 to 36 times). U.S. Al concentration 0.5 µg/L was considered as acute (Golding et al., 2015). Dissolved Al in marine waters is adsorbed on the compatible functional groups on the plasma membrane of seaweeds compromising their integrity and porosity (Monteiro et al., 2012). Al, like Fe, is a normal constituent of soil/sediment and is usually not studied as contaminant. Concentration of Al is also very small compared to pure clay (Pulford and Bakhsh, 1989; Turekian and Wedepohl, 1961). Al is lithophile, and most abundant metal found in the lithosphere. Al has been the normal constituent of most soils (soil with abundant Al is called clay), biota is not affected by soil Al. It can only affect biota when it moves into a soluble or exchangeable form (Hiradate, 2004; Boes et al., 2011; Ho et al., 2012; Korte et al., 2017). All the sediments samples collected in current study were found physically closer to clay in appearance but the content of Al was very low (Pulford and Bakhsh, 1989; Turekian and Wedepohl, 1961; Giosan et

al., 2006; Holmes and Western, 1969; Ahmed, 2016; Syed et al., 2019). The K_d of 4.69 showed that the sediment at Indus Delta is rich in bound Al. High Al content produces antagonistic effects in nutrient uptake, yielding a potential risk of phytotoxicity (Adams and Lund, 1966; Pavan and Bingham, 1982; Blamey et al., 1983; Alva et al., 1986; Sucoff et al., 1990; Godbold, 1994). Moreover, Al species may be involved in acidification of drainage waters and toxicity to fish (Monterroso, et al., 1999). Al in non-crystalline form influences physico-chemical properties as does the Fe (Monterroso, et al., 1999; Schwertmann and Taylor, 1989).

Pb also showed the same trend as that of Cd, Cu, and Al, except the values observed in three seasons in the seawater of Indus Delta, were very close, and need further studies for interpretation. Pb was found higher in sediment than seawater in all sites. Seawater showed highest concentration in monsoon while lowest during pre-monsoon season. In the sediment Pb was lowest in monsoon and highest during pre-monsoon season. The graphical trends of concentration were similar but the magnitudes of Pb clearly reflected that Sandspit is more polluted with Pb than Miani Hor and Indus Delta (Figure 2.6).



(i) Seawater v/s sediments in different seasons.

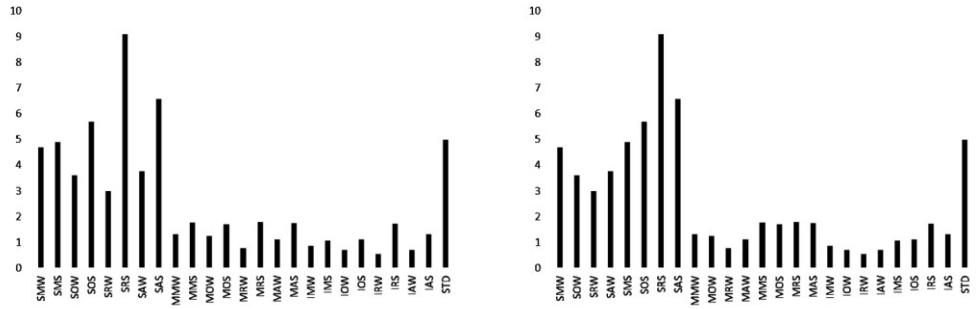
(ii) Seasons v/s seawater and sediments.

Figure-2.6: Average content of Pb. Keys are similar to Figure 2.2

The %Δ in seawater showed Pb is also 25 times higher at Sandspit and ±2 times at other two sites, comparing to NEQS. The K_d for Pb in the pre-monsoon season at Sandspit, Miani Hor, and Indus Delta was higher than the annual average of three seasons, showing more Pb binding with the sediments specifically in pre-monsoon. Pulford and Bakhsh have shown that the higher concentration of Pb is associated mainly with oxides of Fe-Mn, as these are able to form stable complexes. Such correlations have already been discussed (Pulford and Bakhsh, 1989; Ramos et al., 1994; Merrikhpour and Jalali, 2015). The current study showed a high

concentration of Fe in sediment and so does the Pb get associated. The possible major sources of contamination are the intensive anthropogenic activities such as; agricultural and industrial wastes running off without treatment (Monbet, 2006) and exhaust emission from the heavy traffic (Adriano, 1986). Sandspit Beach is highly contaminated probably with persisting Pb used in past, despite of ban on leaded gasoline. Upto 10% of Pb in gasoline is released from auto-exhausts (U.S. EPA, 2013). The total number of all types of motorized vehicles on the road in the megacity of Karachi is estimated to be 2,614,580 (URC, 2017), and are among major contributor in the anthropogenic pollution. Besides posing an immediate risk lead-emission also accumulate in the water and soil and ultimately enter the food web (Amjad and Rizvi, 1999). A continuous monitoring is thus recommended. Higher concentration of Pb at Miani Hor compared to Indus Delta might be due to Barite excavation in the vicinity (Shahab et al., 2016; Jewell and Kimball, 2015). Pakistan is rich in minerals, including barite, galena, orpiment, realgar, niccolite, etc. which are rich with Pb and As (Ozbas and Hicyilmaz, 1994).

Zn has also showing same trend as that of Cd, Cu, and Al (Fig. 2.7). However, Considerable and interpretable difference was not observed in three seasons among the concentration in sediments at Miani Hor and Indus Delta. In seawater, highest concentration has been observed in monsoon which decreased gradually and reached lowest level during pre-monsoon season while in sediments the trend was reverse. Minimum Zn concentration has been observed in monsoon season, increasing gradually to maximum during pre-monsoon in sediments of Sandspit backwater and Indus Delta, however, no significant difference was observed in the samples of Miani Hor.



(i) Seawater v/s sediments in different seasons.

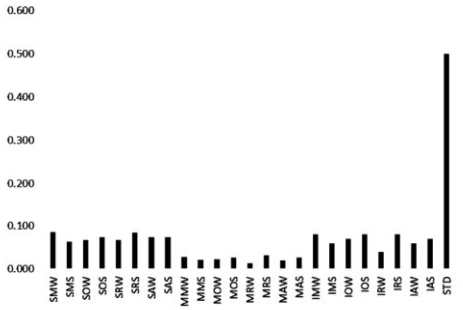
(ii) Seasons v/s seawater and sediments.

Figure-2.7: Average content of Zn. Keys are similar to Figure 2.2

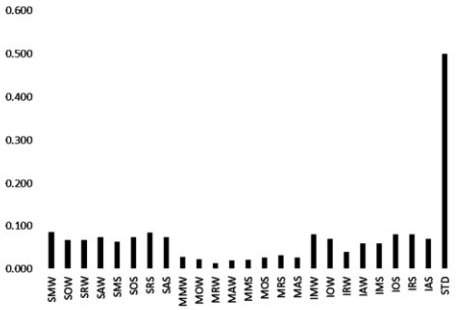
The study is correlating strongly with the recommendation of Hooda (2010), Chaney (2010), Pulford and Bakhsh (1989), and Ramos et al., (1994). Zn showed similar biogeochemical behaviour in sediments like Pb and Cd. High Fe content, observed in the current study may also occlude Zn in the lattice structures, a possible reason for high retention of Zn in sediments (Banerjee 2003). The higher concentration of Zn is also associated mainly with oxides of Fe-Mn, as discussed earlier (Pulford and Bakhsh, 1989; Ramos et al., 1994; Merrikhpour and Jalali, 2015). Zn is a micronutrient. Various mineral phosphate fertilizers typically contain Zn, Cd, and other elements as micronutrient, in relatively high concentrations. Agricultural application of such fertilizers can directly increase the concentration of P, Cd and Zn in the fertilized land and hence their runoff may increase their content in marine sediments (Mortvedt, 1996; Lambert et al., 2007). The Kd is also > 1 and was found correlating with the clay and $CaCO_3$ content (Merrikhpour and Jalali, 2015).

Concentration of Se was found very low irrespective of season and sites and thus need further evaluation (Fig. 1). Overall the trend of Se was similar to Cd, Cu, and Al. All values of Se were found less than NEQS and AVCSR limits but unfortunately it is a micronutrient, needed by various biota as a micronutrient (Wang et al., 2017) and could enter in the aquatic environment through anthropogenic sources as well as natural source such as mineralization, sediment resuspension, erosion, etc. (Ghani, 2015).

The seasonal trend of concentration for Cr was similar to Cd, Cu, Al, Pb, Zn, and Se. Except that its concentration was found higher in seawater than sediments irrespective of sites and seasons. The trend was similar to Cu, i.e., highest concentration of Cr in monsoon while lowest during pre-monsoon in seawater and lowest concentration during monsoon and highest during pre-monsoon season in sediment samples. The average concentration of Cr was showing a reversal in trend with higher content in sediment relative to seawater at Indus Delta. These values are quiet closer and small and cannot be interpreted with confidence (Fig. 2.9).

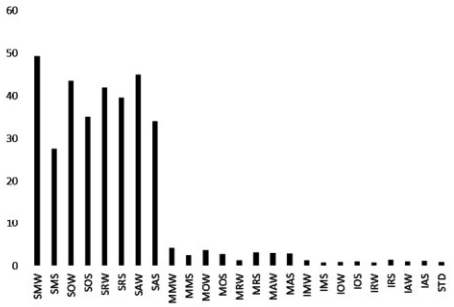


(i) Seawater v/s sediments in different seasons.

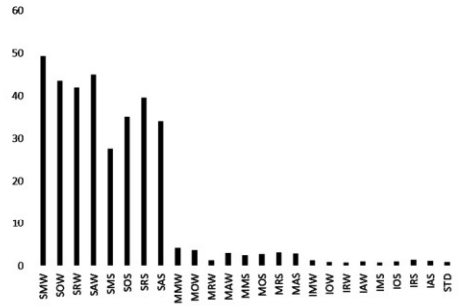


(ii) Seasons v/s seawater and sediments.

Figure-2.8: Average content of Se. Keys are similar to Figure 2.2



(i) Seawater v/s sediments in different seasons.

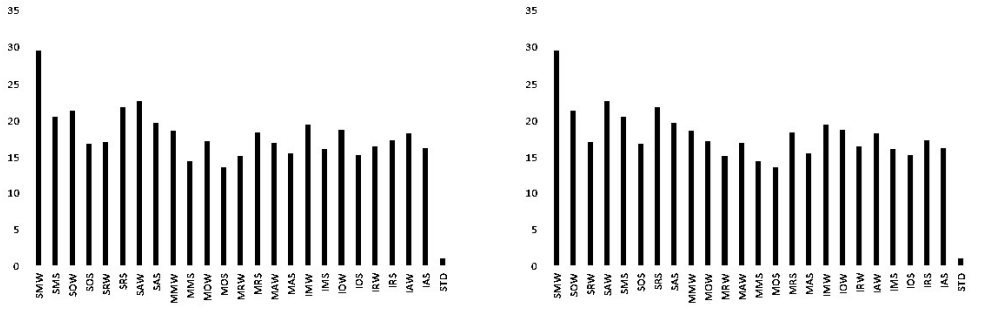


(ii) Seasons v/s seawater and sediments.

Figure-2.9: Average content of Cr. Keys are similar to Figure 2.2

Sandspit showed manifold Cr content compared to the Miani Hor and Indus Delta. Sandspit received more Cr. from Lyari River as well as Korangi Creek, which are receiving the industrial waste from dozens of tanneries from industrial areas. As a result, Sandspit is highly polluted with Cr. The %Δ with NEQS in seawater at Sandspit was found roughly 45 times higher than Miani Hor and Indus Delta. Cr at Indus Delta was 3 times to NEQS limits. These higher values of Cr are due to the effluents from tanneries. Cr at Indus Delta was 3 times to SEQS limits. Cr (VI) compounds are usually more soluble, mobile, and bioavailable, maximizing their toxic effects as well as availability in seawater. Chromium in the oxidised form (Cr IV) is very soluble and is not adsorbed strongly to suspended particles in natural waters (Jabłońska-Czapla, 2015). Most of the physicochemical behaviour discussed for Cu also stand true for Co as well, including binding to clay (Guzman et al., 2010; Ho et al., 2012).

Like Hg and Cr, overall concentration of As was found higher in seawater than those of sediment both in monsoon and post-monsoon seasons while, As concentration became higher in sediment, during pre-monsoon season. The %Δ being 2166, 1720, and 1600 in seawater at Sandspit, Indus Delta and Miani Hor, respectively, compared to NEQS. The trends of concentrations of As was similar to Hg, Cd, Cu, Al, Pb, Zn, Cr, and Se in seawater. Thus the concentration patterns of all sites reflect that As in seawater samples was decreasing from monsoon to pre-monsoon irrespective of sites. In case of sediments, highest As was observed in premonsoon, which gradually decreases to minimum in postmonsoon (Figure 2.10).



(i) Seawater v/s sediments in different seasons.

(ii) Seasons v/s seawater and sediments.

Figure-2.10: Average content of As. Keys are similar to Figure 2.2

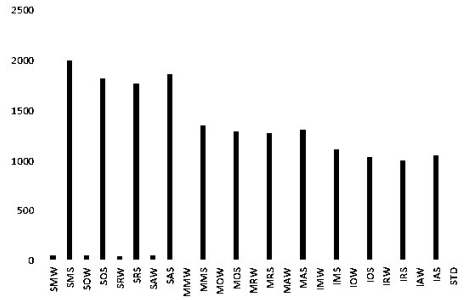
Concentrations of inorganic As in some estuaries and coastal waters facing anthropogenic interference have been reported higher than those in the open ocean. primarily due to runoff from land. Conversely, concentrations of As in seawater gradually increases in the estuaries due to progressive mixing of As-poor fresh water with As-rich seawater (Byrd, 1990; Tremblay and Gobeil, 1990; Froelich et al., 1985). Indus alluvial plains are being naturally eroded by rains, ground water suction, drilling, mining, irrigation network, etc. As a result, water and sediment of Indus River become As rich, through runoff from drilling, mining, agricultural lands, irrigated with As rich ground waters, and raining during the monsoon season led these minerals to marine sink, increasing As concentration in sweater (Edmunds et al., 2015; Giosan et al., 2006; Cao et al., 2009; Husain, 2009; Naseem, 2012; Husain et al., 2012). As discussed earlier, Pakistan is rich in minerals, including barite, orpiment, realgar, niccolite, etc., which are rich in As (Ozbas and Hicyilmaz, 1994; Shahab et al., 2016; Jewell and Kimball, 2015; Engle and Rowan, 2014; Edet et al. 2014). Moreover, Calcite

depositions and mineralised carbonates in the sediment and in adjoining marine sampling sites are also potential As sinks (Edmunds et al., 2015; Roman-Ross et al., 2003). Average K_d also supporting the presence of more As in the seawater then sediments. However, the Pre-monsoon season reflected the K_d ranging from 1.05 to 1.27, justifiable by the low tides and downwelling. In short, As was found crossing the NEQS limits (17 to 23 times).

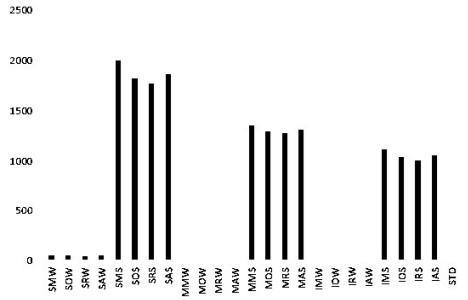
Fe was remarkably high in sediments of Pakistan coasts in comparison to seawater. The concentration patterns were similar in seawater and sediment irrespective of seasons and sites. The concentration was highest during monsoon and decline gradually to lowest during pre-monsoon season (Figure 2.11).

In seawater Fe followed the trend of Cd, Cu, Al, Pb, Zn and Se while in sediment it's trend was individual to sampling sites and season. Among the analysed HM concentration of Fe was found exceptionally high with an average of 1865, 1309, and 1056 $mg.Kg^{-1}$ in sediment at Sandspit, Miani Hor and Indus Delta, respectively. Fe, like Al is the most common lithogenic element in the earth's crust (Korte et al., 2017; Boes et al., 2011) and is present in considerably lower amount in the water bodies but gets accumulated in the sediment through terrestrial runoff. Fe is present in considerably lower amount in the seawater. The oxides and oxy-hydroxides of Fe, present in sediments are chemisorbing considerable quantities of Zn, Cd, and Pb in its lattice (Banerjee, 2003, Pulford and Bakhsh, 1989, Ramos et al., 1994). These non-crytalline Fe compounds also influence the physico-chemical properties of sediments e.g., aggregate stabilization, cementing effect, phosphorus, and heavy metals adsorption by getting involve in the soil buffering systems (Monterroso, et al., 1999; Schwertmann and Taylor, 1989). Comparative to the surrounding marine bodies the relatively higher content in Sandspit seawater may be attributed to a very large steel mill and several other iron industries and mills, mines, in the adjoining areas of sampling sites, specially the Sandspit and Indus Delta and ship breaking industries and ship breaking industries at Gadani. The suspended load of Fe in sea water has been reported 250 to 300 $mg.L^{-1}$ at Sandspit, which is mostly consisting of Fe-oxide dust (Saifullah et al., 2004; Khan 1995). In contrast to Sandspit, Fe content at Miani Hor and Indus Delta was found 6 times to NEQS limits in seawater, contributing more than 50% of total heavy metal analysed. Barite, an ore of $BaSO_4$, mined from Pakistan, contain iron (Fe_2O_3) as impurities. These impurities are main constituents of the waste from mining industry, which ultimately dumped to the sea (Ozbas and Hicyilmaz, 1994). The concentrations of Fe is very small

if the sediment is referred as pure clay. Therefore, the sediments at Sandspit, are neither pure clay nor sand. This need a separate study. (Pulford and Bakhsh, 1989; Turekian and Wedepohl, 1961; Naidoo and Raiman, 1982).



(i) Seawater v/s sediments in different seasons.



(ii) Seasons v/s seawater and sediments.

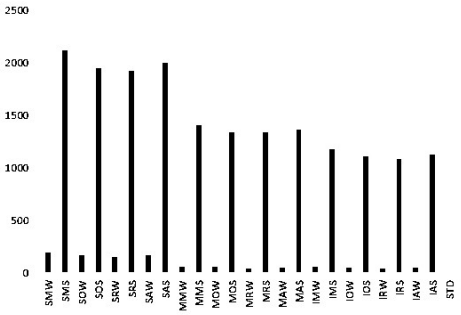
Figure-2.11: Average content of Fe. Keys are similar to Figure 2.2

The HM content in seawater and sediment were significantly ($p \leq 0.05$) different from one season to another (Tables 2.1 and 2.2 and Figure 2.12 and 2.13). At Sandspit seawater the order of HM content (in $mg.L^{-1}$) was Cr ~ Fe > As > Al > Hg > Pb > Zn > Cu > Cd > Se compared to Fe > Zn > Cu = As = Cr > Al = Pb = Se > Cd > Hg, as per order described in NEQS while %Δ was found to be Hg > Cr > Al > Pb > As > Cd > Fe > Cu > Zn > Se (table 2.3). Only Se and Zn were within the limits of NEQS. The order of HM content at Miami Hor were Hg > Al > As > Cd > Cr > Pb > Cu > Zn > Fe > Se. Fe, Se, and Zn were found within the limits of SEQS, while Cu was found crossing the limits. The order of HM content Indus Delta Hg > As > Al > Cd > Pb > Cu > Cr > Fe > Zn > Se. Fe, Se, and Zn were found within the limits of SEQS, similar to Miani Hor. In addition, Cr and Cu were slightly higher than standard limits.

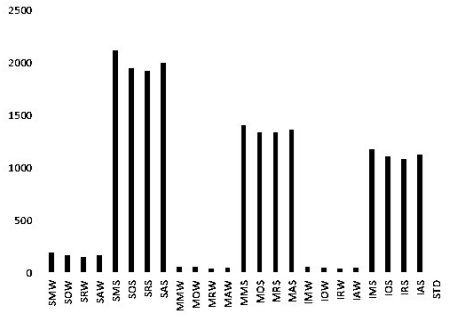
Comparing levels of heavy metals in three seasons, i.e., monsoon season (Jun to Sep 2017), post-monsoon (Oct to Nov 2017) and pre-monsoon (Mar to May 2018), study at these sites showed collectively that HM content was found highest during monsoon in the seawater (table 2.1), which was found gradually decreasing from postmonsoon to premonsoon. The reason of dilution is the rain water, which bring various pollutants from high altitude (Cao et al., 2009). Highest average of HM content was observed in seawater samples of Sandspit (166 $mg.L^{-1}$), as expected from water bodies of mega cities, while it was 50 and 44 $mg.L^{-1}$ at Miani Hor and Indus Delta, respectively. Al, Cd, Cr, Cu and Zn concentrations have been

remained higher in Miani Hor. As, Fe, Hg and Se showed higher concentration in Indus Delta than Miani Hor.

The order of the HM content in sediments in mg.kg^{-1} at Sandspit was Fe > Cr > Al > Pb > As > Hg > Zn > Cu > Cd > Se compared to Al > Fe > Cu > Zn > Cr > Pb > As > Cd > Hg > Se, (order declared in AVCSR), while %Δ was found to be Hg > Cd > As > Se > Cr > Pb > Zn > Fe > Cu > Al, showing that the HM having the higher concentration in sediments are Cr and Fe while those having lower concentrations are Se, Zn, Cd and Cu. In Sandspit sediments, the concentration of Al, As, Cu, Hg, were found decreasing from monsoon to postmonsoon while in premonsoon, the concentration of these HM were highest. In contrast, Cd, Cr, Fe, Pb, Se, and Zn all showed change in the concentration in the order monsoon < postmonsoon<premonsoon.



(i) Seawater v/s sediments in different seasons.



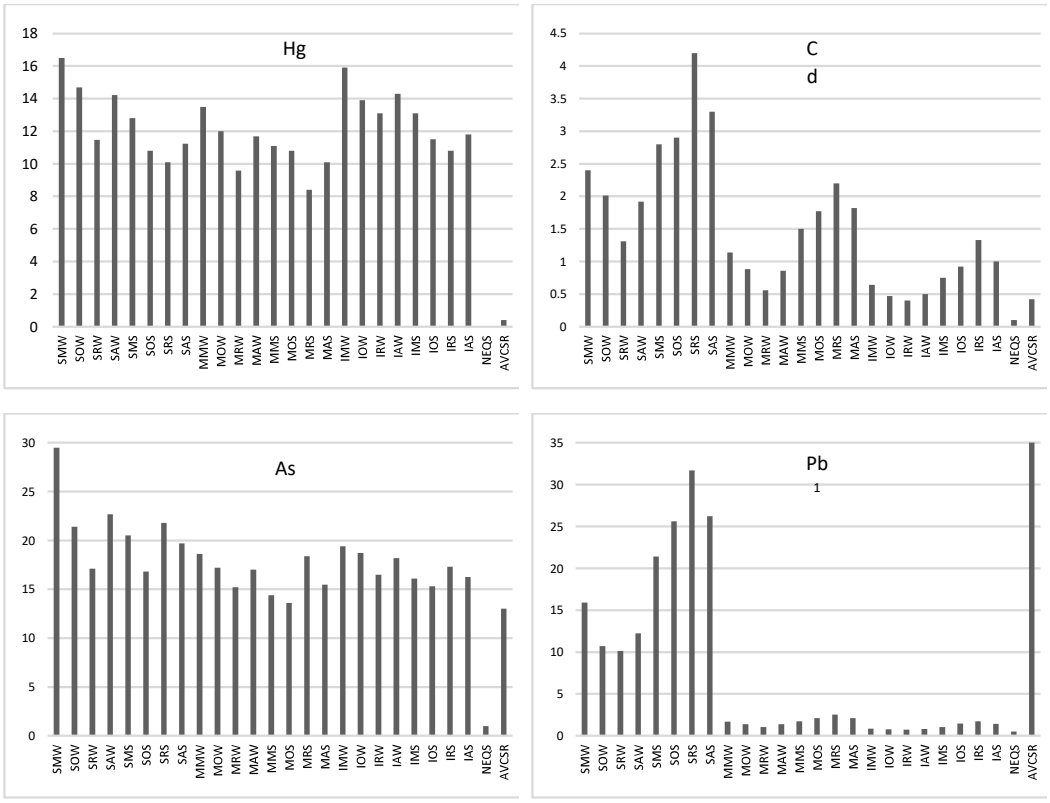
(ii) Seasons v/s seawater and sediments.

Figure-2.12: Average content of analysed metals. Keys are similar to Figure 2.2

The order of concentration in mg.kg^{-1} at Miani Hor was found to be Fe > As > Al > Hg > Cr > Pb > Cu > Cd > Zn > Se, while the %Δ was Hg > Cd > As > Se > Cr > Pb > Fe > Zn > Cu > Al. Except for Fe and Zn all metals were following same trend as was in adjoining seawater. Pb and Cu were found swapping the adjacent places in order. Fe and Hg in sediment of Miani Hor showed concentration order monsoon > postmonsoon > premonsoon while all the other heavy metals showed order of concentration as monsoon < postmonsoon < premonsoon.

The order of concentration in mg.kg^{-1} was Fe > Al > As > Hg > Cu > Pb > Cr > Cd > Zn > Se at Indus Delta while %Δ was Hg > Cd > As > Se > Pb > Fe > Cr > Cu > Zn > Al. When compared with seawater (As > Hg > Al > Cu > Fe > Cr > Pb > Zn > Cd > Se) the order was found changed for the metals having higher concentrations, the metals at lower concentration

were showing a slight interchange i.e., between Pb and Cr, and Cd and Zn. Similar to Miani Hor, Fe and Hg in soil samples of Indus Delta showed descending order from monsoon < postmonsoon < premonsoon while all the other heavy metals concentration showed ascending order. Exceptionally the concentration of As was found higher (16.1 mg.Kg^{-1}) in monsoon, decreased to lower (15.3 mg.Kg^{-1}) in post-monsoon season and then became highest (17.3 mg.Kg^{-1}) during pre-monsoon. In general, HM content in sediment were highest in premonsoon. A few HM showed highest concentration in monsoon.



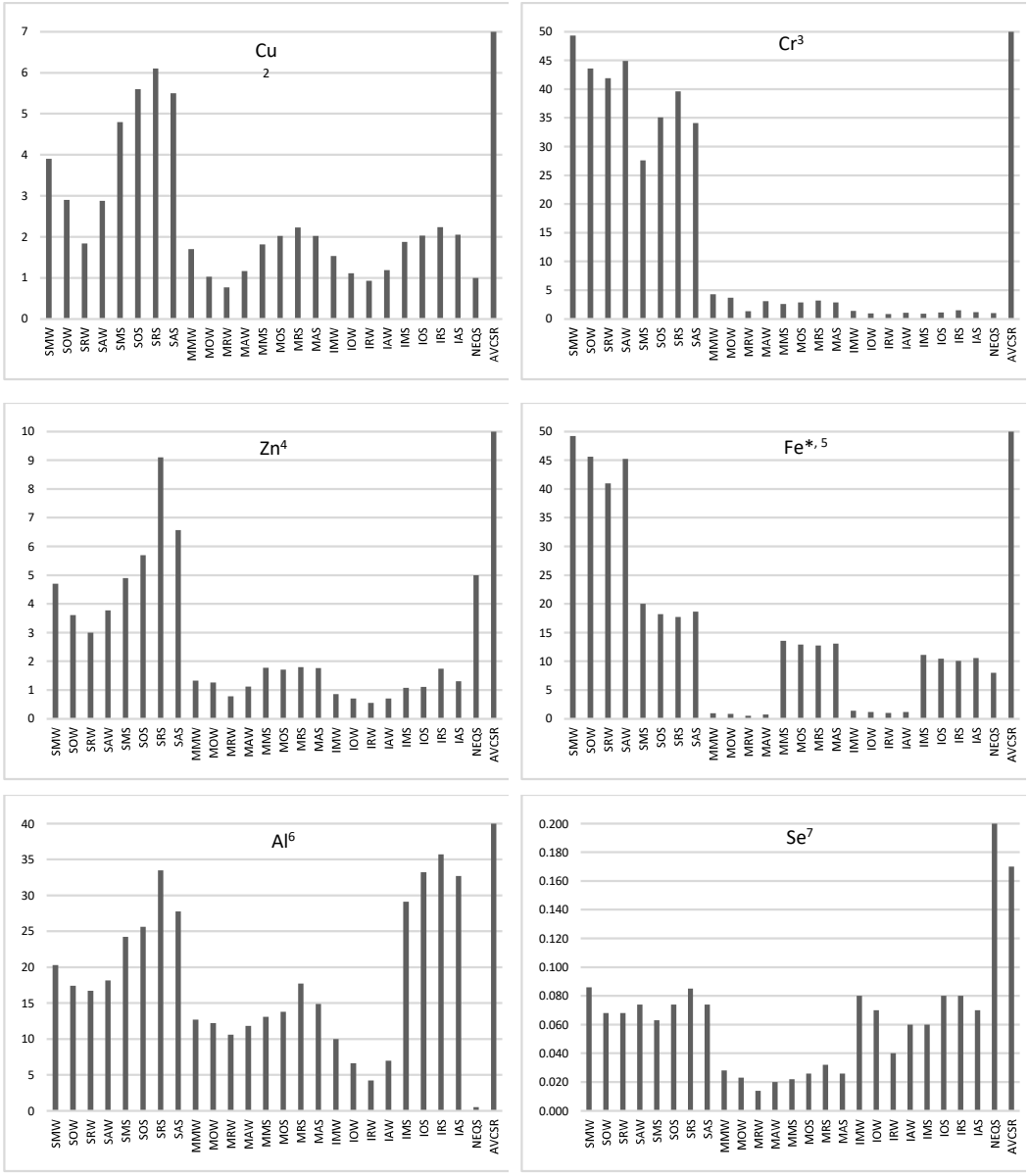


Figure-2.13: Average content of HM in seawater (mg.L^{-1}) and sediment (mg.kg^{-1}) in three seasons at three sites. Key: S) Sandspit, M) Miani Hor, and I) Indus Delta (sites are denoted by the first letter in the three letter code), M) monsoon-2015, P) postmonsoon-2015, and R) and pre-monsoon-2016 (seasons, denoted by the middle letter), W) seawater and S) sediments (matrix, denoted by the last letter), and A) average of three season at given site. *values of sediments are divided by a factor of 100 for better presentation. Off-scaled values are [1)]80, [2)]250, [3)]90, [4)]165, [5)]65000, [6)]84000, and [7)]5.0. continued to next page

The critical value for HPI is 100. Excessively high values of HPI reflect very poor seawater quality. The worst HPI was calculated for Sandspit as 138738, 123521, and 96382 during monsoon, post-monsoon, and pre-monsoon season, respectively. Similar trend with slightly low values was reflected by Miani Hor and Indus Delta in respective order. Concentration of Hg is one of the main cause of higher HPI because the value of ($W_n.q_n$) is turn out to be higher with low concentration of Hg (table 2.5). The C_f value of each HM was individually calculated. At Sandspit the C_f value of Hg during pre-monsoon season was greater than that of Indus Delta during same season. During premonsoon, the concentration of Hg in the seawater samples of Sandspit was smaller than that of Indus Delta. The higher concentration of Hg in seawater samples of Indus Delta during premonsoon, adding more contribution, dropping the water quality at the worst level. This higher concentration of Hg also affected the values of C_d and mC_d, at same sites and seasons. Overall result from the calculations of HPI, C_f, PLI, C_d and mC_d, proved that the water quality of these sites, specially of Sandspit is badly affected by the HM pollution. EF and I_{geo} were used to assess the accumulation of HM by anthropogenic activities so the reference values for these equations were taken from the preindustrial period (pristine values; AVCSR; Earth's average values of clay from sedimentary rocks) (Turekian and Wedepohl, 1961). The EF values of Hg, As and Cd as well as I_{geo} value is higher in three of the study sites and seasons were higher, showing that these three HM are polluting the natural environment by anthropogenic activity (Yang et al., 2014).

The data observed for sediment was compared using Sediment Quality Guidelines (SQGs) to assess the environmental quality, and degree of contamination, considering various SQGs (Sany et al., 2011). Sediment chemistry of this coast has not been evaluated nor the rainfall, run-off, quality of sediment, origin of pollution, direction of current, type of mineral bonding HM, geochemical conditions, etc. HM are known to effect the aquatic quality. So far this report is providing the comprehensive information on HM status of sediment. It is clear that these sites were moderately polluted with As and Cd and less polluted with reference to Cr, Zn and Cu. Sites are heavily polluted with Hg. As per sub levels of various SQGs, Hg, Cd, and As are at SQG-H while Zn, Cr, Cu, and Pb are at SQG-L level (Sany et al., 2011).

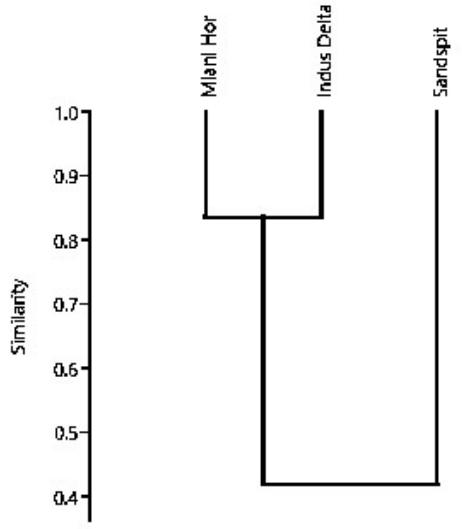
The results from this study have been treated through cluster analysis and have been presented as a complete linkage dendrogram. The cluster analysis made a cluster between Miani Hor and Indus Delta in sediment analysis showing similarity index of 0.89. Sandspit showing a

value of 0.76 and 0.68 with Miani Hor and Indus Delta respectively. The same observation is true with seawater analysis as shown in dendrogram (Figure 2.13). On the basis of this dendrogram, the three study sites have been classified into two clusters. One of these cluster consists of Miani Hor and Indus Delta while second cluster is Sandspit. Cluster pattern present Sandspit at a combined level of HM pollution. Relating this cluster pattern to the ambient pollution concentrations (of HM) may enable us to say that Cluster 2 representing, Sandspit with the highest level of heavy metals pollution.

In case of seawater, strong positive Pearson correlation has been found in Zn (post-monsoon with monsoon) while negative correlation was found in Se (Post-monsoon with monsoon) at Sandspit. At Miani Hor, negative correlation found in Hg (pre-monsoon with pre-monsoon) and Cu (monsoon with monsoon) while positive correlation was observed in Cr (monsoon with post-monsoon) and Cu (post-monsoon with post-monsoon). At Indus Delta, negative correlation was found only in Cu (pre-monsoon with post-monsoon) while following three metals showed positive correlations: Cu (monsoon-post-monsoon), As (monsoon with pre-monsoon) and Zn (pre-monsoon with pre-monsoon). These statistics showed that the sites are not correlated with one another, owing to the geographical distance. Other usual positive and negative correlations observed were not significant. No significant correlations were observed in the case of Sediments samples. This might be due to high level of pollution at this site. Noteworthy among these were positive correlation found in Cr (during pre-monsoon and monsoon) at Sandspit and negative correlation of As (post monsoon with monsoon season) at Miani Hor. However, at Indus Delta, negative correlation of two metals Cu and Pb (pre-monsoon with monsoon) were observed.

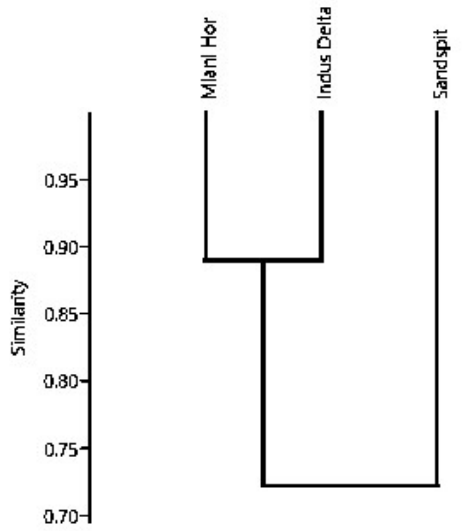
Mangroves stands are usually get rich in litter (Elliot et al., 1986; Connel et al., 1984) and so get contaminated with most of the HM. The levels of the HM in water and sediment were significantly ($p \leq 0.05$) different from one season to another (Tables 2.1 and 2.2). A few metals showed higher concentration in monsoon. During monsoon tides are very frequently changing directions, become aggressive and the reservoirs receive heavy inputs from rain and in consequence of more consumption during this hot season. Not only water but the fuel consumption is also higher during this season and thus disposal of load of pollutants to seawater increases. Sediments also release the chemisorbed HM. Premonsoon is somehow drought season during which pollution load decreases to the lowest level as compare to the monsoon. The concentrations at each of the site and

season, have crossed the national standard (SEQS) limits. In the case of sediment totally different pattern of HM was observed; at Sandspit, the concentration of HM gradually increases from monsoon to postmonsoon and attain highest level during premonsoon. The higher levels of HM observed during the non-monsoon months than the monsoon may be attributed to the HM content in the stagnant water during the non-monsoon months (Holmes, 1986). However, Ouseph (1987) felt that the increased levels of HM during the premonsoon season may be due to the intrusion of seawater.



	Sandspit	Miani Hor	Indus Delta
Sandspit	1.00	0.44	0.40
Miani Hor	0.44	1.00	0.84
Indus Delta	0.40	0.84	1.00

(A)



	Sandspit	Miani Hor	Indus Delta
Sandspit	1.00	0.76	0.68
Miani Hor	0.76	1.00	0.89
Indus Delta	0.68	0.89	1.00

(B)

Figure-2.14: Dendrograms based on UPGMA hierarchical cluster analysis among three sites using paired group Bray-Curtis in water (A) and Sediments (B) for similarity measure, cophenetic coefficient indicate the value 0.9972 and 0.9141 respectively. Next table showing the correlation of similarity index among 4 seasons

During weathering processes or premonsoon, HM got concentrated in the sediments of the study area. Sediment shows abundance trend as Fe

> Pb > Cr > Cu > Zn > Cd in relevance with Bela Ophiolite (BO) of cretaceous age along with sedimentary rocks of jurassic age (Hamza, 2011). The Cr, Cu, and Cd in the sediment are mainly supplied by ophiolitic rocks while high Fe and Zn can be contributed both from ophiolite and sedimentary rocks. Mineralogically it contains high quartz and calcite along with variable proportions of clay minerals and Fe-oxides. Presence of these clay fractions were responsible for mobilizing Cr, Cu, Zn and Cd, as during mineralization, oxides of these metals have been formed in excess (Naseem et al., 2012a).

The untreated waste water together with fresh seawater is fulfilling the need of natural monospecific *A. marina* jungle situated at Sandspit backwaters. Mangrove stands like Sandspit backwater has always been a nursery ground for many species of shellfish and fish. The decline in mangroves' species diversity is indicating that the area is under severe pollution stress. Thousands of industrial units, from six major industrial estates, and millions of Karachiites are dumping untreated industrial and house hold wastes ultimately into the Northern Arabian Sea (Rizvi, 1997). Reported data suggest that only 92% of urban wastewater and 99% of industrial effluents is discharged untreated in sewers, causing more stress to ecosystem (Azizullah et al., 2011). *A. marina*, *C. tagal* and *R. mucronata* coexist at Miani Hor. Saifullah and Rasool (2002) reported once this heavenly lagoon free from any kind of anthropogenic involvement. Increasing levels of pollution is subjecting the pristine lagoon to stress and mangroves are undergoing stunning growth (personal observation However, besides HM stress other factors e.g., low freshwater intake and high salinity are also influencing their growth. This lagoon is also a hotspot for dolphins sighting, attracting many tourists and now gradually becoming polluted. Increasing water pollution has also burdened the Indus Delta. Natural processes as well as other anthropogenic activities e.g., agriculture, industry, mining, and other activities are charging surface and groundwater resources with synthetic chemicals, including many dangerous pollutants such as fertilizers, pesticides, toxic metals, etc. So both natural and anthropogenic activities can be the main cause of HM pollution in the mighty river (Indus River) of Pakistan, which finally run to flow all the heavy pollution into the Arabian Sea at Indus Delta (Geneviève et al., 2008, Iqbal, 2013). Indus Delta is the only coast in Pakistan where four species of mangroves have been naturally available now, despite of increasing pollution. Probably the continuous downstream supply of freshwater from the mighty Indus River is causing dilution in the pollution at the perforation of the delta. The freshwater within itself contain lot of pollutants but yet the mangrove population is growing gradually. The increase in concentration

during monsoon could be attributed to the peak agricultural and industrial activities and release of sewage waste waters to the fresh water, having higher level of HM pollution (Thilagavathi et al., 2011).

Declaration

Parts/contents of this article submitted to one day Pakistan Engineering Congress, Lahore held on 12.04.2025 on the occasion of World Water Day, Theme: Glacier Preservation have been submitted for publications in an esteemed journal “Scientific Review”, and/or reproduced from the Ph.D. dissertation of one of the co-authors.

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