REVIEW OF HEAVY METAL CONTENTS IN SEDIMENT OF KARACHI COAST, PAKISTAN

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ABSTRACT: *This paper reviews heavy metal contents in the sediments of Karachi coast in the past few years. The concentrations of heavy metals of the various sampling points are compared in different studies. The sampling procedures, digestion methods, measuring techniques and metals correlations are also reviewed. The heavy metal concentrations along the various points of the Karachi coastal area have been reviewed to assess the pollution level. It has been observed that the highest concentration for Pb in the Layari river mouth area among all the points. However the highest concentrations of Ni were observed in BTW Oil Jetty and Oyster Rocks, and for the elements Cr and Zn were observed in the KPT boat building area channel. Lowest values of the elements Cr and Pb was found in Rehri Creek, for Ni was found in KPT Shipyard channel and for Zn was found in Manora light house channel. In general higher concentrations of Cr, Ni and Zn were found in Layari River mouth area. Higher concentrations of Zn were found in fish harbour channel and Keamari oil terminal channel. The review of metals correlation indicates a good picture among various metals studied as strong and weak relations*.

Keywords: Sediment, heavy metal, Karachi coast, Pollution

INTRODUCTION:

Karachi is the largest city of Pakistan. Its location is on the north of the Arabian Sea. Karachi coast is extended up to 135 km. There is a huge domestic and industrial waste which is carried into the Karachi costal sea. Due to an increase in the Karachi population density there is an urgent need to setup more industrial units to meet the necessities of masses and hence there is an increase in industrial discharges as well. Heavy metal contamination in aquatic environment is a serious threat because of their environmental persistence, toxic nature and the ability to participate in the food chain [1]. The sediments are very good indicators for aquatic contamination measurements. The sediments can be polluted by a variety of harmful substances including heavy metals that may accumulate into the sediments. Sediment cores help in the measurement of changes in marine environmental quality in past years. The sediment cores draw good picture of pollution history [3].

MATERIAL AND METHODS:

The surface sediments have been sampled from shallow bottom using a grab sampler. Plastic spoon was also used to collect sediment from the grab sampler. The samples were then transferred to a polyethylene bag and stored at a low temperature. Samples were carried to the laboratory and dried at a temperature of 70 ^{o}C to achieve a constant weight of the sample. The samples were sieved to 0.5 mm by a mechanical method, homogenized and finally ground to fine powder. The various sampling points of Karachi coastal sea that have been tested for heavy metal contamination so far including Manora Channel, open sea coastal area.

In order to digest the sediment samples, aqua regia (HNO_3 and HCl; 1:3 ratio) is normally used (USEPA method 3050B). However, any other recommended method for sediment digestion may also be employed. The digested sample volume was made to 100 ml with the deionized water in a volumetric flask.

There are a number of techniques that can be used to measure metal content qualitatively as well as quantitatively. The most commonly techniques used in the measurement of heavy metals in sediment include, inductively coupled plasma optical emission spectrometry (ICP-OES), atomic absorption spectrometry (AAS) and the non-destructive technique Proton induced X-ray emission (PIXE).

Table 1. Concentration of Heavy metals in sediments along Karachi coast [1].

Sampling Location	Cr	Cu	Ni	Pb	Zn	Reference
Layari River Mouth Area	293.00	--	48.78	**49.46**	537.60	[1]
Kakapir Layari Channel side	89.00	--	36.99	21.88	85.00	[1]
Shamspir–Layari Channel side	106.00	--	32.40	22.41	111.40	[1]
Fish Harbour Channel	102.00	--	25.56	29.36	581.00	[1]
KPT Boat Building Area Channel	**319.84**	--	56.46	33.84	**666.28**	[1]
KPT Shipyard Channel	92.12	--	1.53	18.93	83.94	[1]
Baba Island Channel	80.00	--	27.54	20.56	95.60	[1]
Bhit Island Channel	70.00	--	30.60	21.68	96.20	[1]
Keamari Oil Terminal Channel	82.00	--	39.06	23.71	524.00	[1]
Manora Light House Channel	14.00	--	7.04	9.00	15.60	[1]
BTW Oil Jetty and Oyster Rocks	85.00	--	**58.86**	27.03	161.00	[1]
BTW NIO/Manora Lighthouse	70.00	--	43.65	22.92	119.60	[1]
Gizri Area Seaside	12.00	--	18.80	16.94	41.40	[1]
Sandspit Seaside	33.00	--	23.94	15.42	49.80	[1]
Buleji Seaside	80.00	--	38.13	25.1	80.40	[1]
Paradise Point	20.00	--	12.84	13.64	27.80	[1]

Mean	96.75	--	31.39	23.24	204.79	[1]
Korangi Creek	44.90	25.27	33.72	--	108.37	[2]
Rehri Creek	5.82	2.88	8.18	4.36	38.51	[3]
Layari River Outfall Area	162.67	-	39.39	31.25	244.67	[5]
Karachi Harbour Area	171.32	-	27.85	27.38	443.74	[5]
Manora Channel Mains	61.500	-	26.060	18.738	182.850	[5]
Industrial and Sewage Effluents on Karachi coast	517	-	-	930	1380	[6]

Table 2: Digestion method and Instrumental analysis of heavy metals (mg/kg) in sediments of Karachi, Korangi Creek, Rehri Creek Coast.

Sampling location	No of samples	Core Depth(cm)	Digestion Method	Instrumental technique	Reference
Karachi Coast	16	--	HCl and HNO_3, hydrogen peroxide	Inductively coupled plasma OES	[1]
Korangi Creek	--	73	--	Proton induced X-rays emission (PIXE)	[2]
Rehri Creek	4	37.5	Acid digestion	Inductively coupled plasma OES	[3]
Karachi coast	22	--	HF and 5 ml $HN0_3$, perchloric acid	(ICP-OES Model 3580,	[5]
Industrial and Sewage Effluents on Karachi coast	--	--	HNO_3, HF, HCl	atomic absorption spectrophotometer	[6]

RESULTS:

The inter-metal relationship was studied using co-relation co-efficient. The tables indicate weak, strong and poor correlations. The numbers with double star indicate strong correlations between metals in Table 3.

Table 3: Pearson correlation matrix between metals and TOC among metals in sediments of Karachi Coast [1]

	Fe	Mn	Cr	Mo	Ni	Pb	Se	Sr	U	V	Zn	Zr	TOC
Fe	1.00	0.32	0.21	0.60	0.79**	0.43	0.63	−0.45	−0.23	0.87**	0.31	−0.16	0.07
Mn		1.00	−0.28	−0.21	0.07	−0.22	−0.07	0.62	−0.09	0.23	−0.22	0.11	−0.37
Cr			1.00	0.71**	0.61**	0.87**	0.30	−0.34	0.69**	0.40	0.77**	0.38	0.79*
Mo				1.00	0.84**	0.76**	0.84**	−0.69	0.23	0.78**	0.52	0.001	0.45
Ni					1.00	0.70**	0.74**	−0.55	0.05	0.87**	0.52	−0.16	0.25
Pb						1.00	0.43	−0.49	0.36	0.51	0.75	0.04	0.62
Se							1.00	−0.66	−0.18	0.83**	0.12	−0.21	0.03
Sr								1.00	0.23	−0.49	−0.34	0.31	−0.30
U									1.00	−0.07	0.50	0.68	0.75**
V										1.00	0.24	0.02	0.11
Zn											1.00	0.11	0.77**
Zr												1.00	0.54

	Mg	**Al**	**S**	**K**	**Ca**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Ni**	**Cu**	**Zn**	**pH**	**TOC**	**Sand**	**Silt**	**Clay**
Mg	1.00	0.85	0.74	0.82	0.61	0.48	0.90	0.80	0.77	0.71	0.89	0.85	0.89	0.39	0.35	−0.53	−0.43	0.55
Al		1.00	0.77	0.78	0.29	0.32	0.75	0.41	0.40	0.78	0.86	0.82	0.85	0.43	0.40	−0.57	−0.48	0.62
S			1.00	0.66	0.56	0.53	0.70	0.70	0.75	0.78	0.71	0.72	0.90	0.59	0.59	−0.43	−0.19	0.35
K				1.00	0.49	0.66	0.84	0.93	0.87	0.82	0.87	0.93	0.82	0.38	0.44	−0.78	−0.43	0.71
Ca					1.00	0.47	0.60	0.56	0.47	0.40	0.56	0.49	0.67	0.11	0.51	−0.45	−0.21	0.37
Ti						1.00	0.46	0.71	0.68	0.73	0.66	0.69	0.59	0.32	0.24	−0.46	−0.25	0.42
V							1.00	0.83	0.73	0.67	0.89	0.88	0.82	0.34	0.49	−0.67	−0.53	0.70

Cr	1.00	0.91	0.89	0.89	0.96	0.86	0.43	0.48	−0.79	−0.40	0.71
Mn		1.00	0.95	0.77	0.87	0.86	0.47	0.50	−0.67	−0.28	0.56
Fe			1.00	0.80	0.88	0.85	0.59	0.53	−0.66	−0.32	0.58
Ni				1.00	0.95	0.84	0.46	0.38	−0.67	−0.55	0.72
Cu					1.00	0.86	0.48	0.45	−0.76	−0.57	0.79
Zn						1.00	0.60	0.55	−0.65	−0.29	0.54
pH							1.00	0.41	−0.43	−0.20	0.37
TOC								1.00	−0.64	−0.08	0.63
									1.00	0.38	−0.83
Sand											
Silt										1.00	−0.83
Clay											1.00

>0.61 significant correlation at 0.01 level (one-tailed)

Table 4 Correlation among metals in sediment core [3]

	As	Ba	Co	Cr	Cu	Ni	Pb	Si	Zn	Fe	Mn	TOC
As	1	0.68	0.71	0.86	0.88	0.83	0.61	0.51	0.90	0.70	0.78	0.11
Ba		1	0.64	0.80	0.62	0.70	0.41	0.22	0.56	0.57	0.77	0.07
Co			1	0.71	0.81	0.67	0.75	0.56	0.78	0.80	0.76	0.34
Cr				1	0.85	0.90	0.41	0.44	0.82	0.74	0.83	-0.11
Cu					1	0.85	0.68	0.76	0.91	0.74	0.80	0.18
Ni						1	0.52	0.43	0.88	0.69	0.86	-0.08
Pb							1	0.46	0.64	0.65	0.67	0.39
Si								1	0.61	0.43	0.40	0.20
Zn									1	0.43	0.85	0.11
Fe										1	0.40	0.06
Mn											1	0.01
TOC												1

Table 5: Correlations (Pearson's linear coefficient, r) between heavy metals [4]

	Cd	Cr	Co	Cu	Pb	Mn	Ni	Zn
Cr	0.722*							
Co	0.357	0.139						
Cu	0.838*	0.722*	0.377					
Pb	0.584**	0.719*	0.451	0.704*				
Mn	0.062	-0.054	0.050	-0.123				
Ni	0.230	0.009	0.680**	0.415	0.315	0.071		
Zn	0.387	0.339	0.667**	0.495	0.704*	0.256	0.502	
% Fe	0.060	0.082	-0.052	-0.037	-0.042	-0.127	0.542**	-0.094

CONCLUSIONS:

The concentrations of metals in the surface sediments of Karachi coast are found moderate at most of the places however concentrations of some metals are found higher at some places. The concentrations of heavy metals were found much lower in Rehri creek than Korangi creek as well as most of the points along the coast. The load of heavy metal contamination is small at Rehri creek and its source is anthropogenic. Also the sediments revealed sandy nature at Rehri creek.

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