

ELEMENTAL DEPTH PROFILE IN SEDIMENT CORE OF KORANGI CREEK ALONG KARACHI COAST, PAKISTAN

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In the present investigation downcore variation of metals such as Al, Ca, Cr, Cu, Fe, K, Mg, Mn, Ni, V and Zn in a sediment core of 42.5 cm length from Korangi Creek, one of the pollution hit sites along Karachi coast, was studied. Proton induced X-rays emission (PIXE) was the principal analytical technique used to determine the chemical composition in sediment core. Grain size analysis and sediment composition of cored samples indicated that Korangi Creek sediments is clayey in nature. Correlation matrix revealed strong association of Ni, Cu, Cr, Zn with Fe. To infer anthropogenic input, enrichment factors (EFs) were determined. EFs showed severe enrichment in surface sediments for Ni, Cu, Cr and Zn indicating increased industrial effluents discharge in recent years. If this trend of enrichment is allowed to continue unabated, it is most likely that the local food chain in this area may be adversely affected.

Keywords: Metals, Sediment, Korangi, Enrichment, Pollution

1. Introduction

Marine pollution due to urbanization and industrial development is a major concern worldwide [1-4]. Among the components of marine environment, sediments play a critical role in distribution and circulation of toxic compounds. Marine sediments effectively sequester hydrophobic chemical pollutants entering marine environments and are sensitive indicators for monitoring contaminants in water bodies [5]. Sediments can be polluted with various kinds of hazardous and toxic substances, including metals which can accumulate in sediments. Concentration of metals in coastal estuaries can be elevated due to high inputs from natural, as well as anthropogenic sources. The favorable physico-chemical conditions of the sediments can remobilize and release the metals to the water column. It is well known that metals are cumulative as they do not decompose or migrate significantly with time.

In recent years, much attention has been paid to the chemical composition of marine sediments in

coastal regions near large industrial and urban areas because it is linked to the deterioration of oceanic ecosystems [6]. It has been reported that pollution problems in such areas lead to increased metals levels of 5 or 10 times than those characteristic of 50 to 100 years ago [7]. Sediment cores provide useful information on the chronological changes in the quality of the marine environment from a past period. Many researchers have investigated the pollution history of marine ecosystems and behavior of metals using sediment cores [8, 9]. This paper examines the spatial distribution and chemical composition of sediment cores collected from Korangi Creek, which is recipient of industrial effluents along Karachi Coast, in order to provide fundamental data for understanding the natural behavior of metals in sediment cores and their enrichment over time.

2. Study Area

Karachi is the largest city of Pakistan and a hub of industrial activity. The coastal zone of Karachi extends upto 135 km and is exposed to heavy pollution load of both domestic and industrial origin

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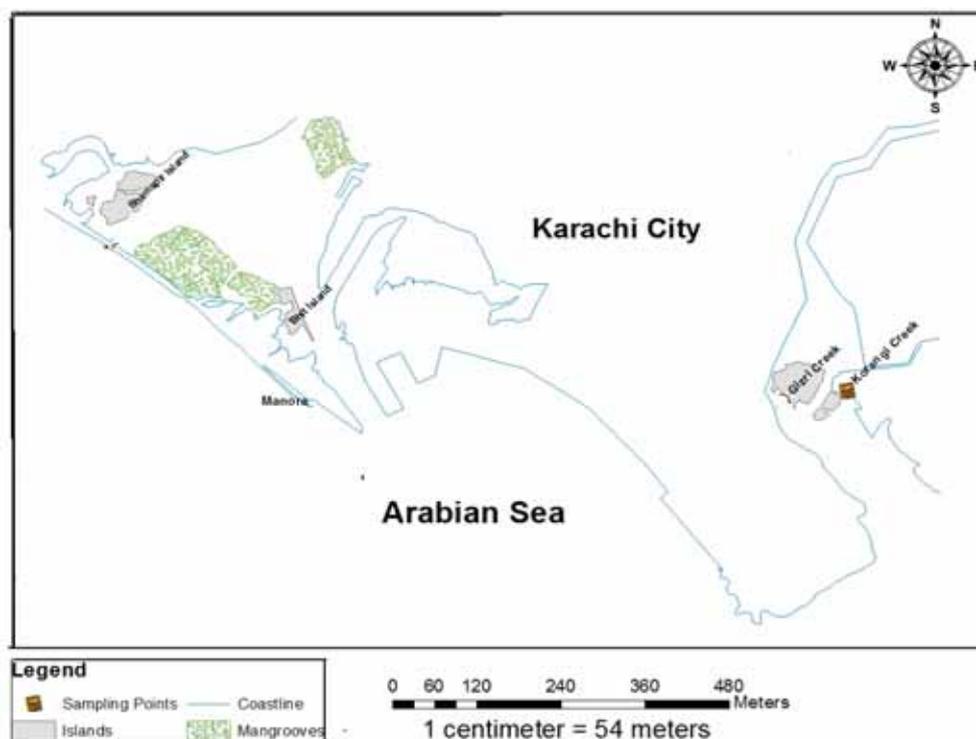


Figure 1. Location map of study area.

[10, 11]. Over time, urbanization, discharge of sewage and industrial effluents into aquatic and marine ecosystems is also on the rise. The organic load of sewage depletes oxygen levels in water and indirectly reduces the diversity of animal and plant life.

Korangi Creek is situated on south east coast of Karachi and is an environment which is subject to anthropogenic emissions (Figure 1). It receives industrial effluents from Korangi and Landhi Industrial State. In addition to these effluents, the untreated wastewater from the metropolis of Karachi and domestic effluents from smaller coastal settlements are also released into the creek. The Korangi Creek area is dominated by mangroves that serve as a spawning and nursery ground for a number of commercially important marine fauna. The toxic pollutants from the Korangi Creek reach the mangrove areas [12] which may pose serious and potential health hazards to fisheries and other fauna in the area [13]. The impact of these pollutants on commercial fin-fish and shrimp fisheries are unknown, but are likely to be significant [14].

3. Materials and Methods

3.1 Core Collections

A sediment core was collected from Korangi Creek (24°46'30"N and 67°13'18"E). The sampling location was determined by GARMIN III global positioning system (GPS). The core was collected from a boat with the help of gravity corer (KC Kojak Demanmark A/S) having acrylic coring pipe (2 m long and 7 cm diameter). Acid washed coring pipe was driven into the sediment until it reached 43 meters depth. The core was slowly retrieved back, capped with its cover immediately and marked as to indicate the upward direction. The core was transported in a vertical position and frozen for 2 days in the vertical position after which it was sliced at 2.5 cm increments; the sliced samples were stored in clean, labeled polythene bags. Prior to analysis, all the sediment samples were dried at 70-80 °C until constant weight. The shells in the sediments were handpicked. Raw samples were used to determine grain size and sediment composition. Sediment composition was determined following Krumbein and Pettijohn method [15]. Grain size analysis was done using a set of 5 sieves ranging from 2000 μm

Table 1. PIXE analysis of soil-7 IAEA reference material.

Elements	IAEA Values			Lab. Results	
	Range (ppm)	Mean	SD	Mean (ppm)	SD
Al	44000-51000	47500	3500	51600	2830
Ca	157000-174000	165500	8500	211260	11408
Cr	49-74	60	9	81	8
Cu	9-13	11	1	15	5
Fe	25300-26300	25800	500	27400	1510
K	11300-12700	12000	700	12300	713
Mg	11000-11800	11400	400	5060	330
Mn	604-650	627	23	740	140
V	59-73	66	7	52	8
Zn	100-108	104	4	114	7

to 70 μ for 15 minutes using Rotop sieve shaker [16]. Nature of the sediments was found using GRADISTAT software. Enrichment factor (EFs) were calculated as described by Mashiattullah et al. [17].

3.2 Sample Preparation for Metal Analysis by PIXE

Principal analytical technique used to determine the chemical composition in sediment core was proton induced X-rays emission (PIXE). Five milligram of each sediment sample was mixed with 10 microlitre of $Y(NO_3)_3$ solution in double distilled water containing 1.16 mg of Yttrium as internal standard and mounted on a small piece of 20 micrometer thick Mylar. The area covered by the sample on the Mylar was about 1.5 cm^2 . The samples were placed inside a desiccator and dried under a lamp. The samples were mounted on a wheel controlled by a stepper motor and placed inside the analytical work station for analysis [18].

The samples were irradiated by a proton beam of 3.8 MeV energy from the National Electrostatic Corporation tandem pelletron accelerator model 6SDH-2 installed at the Accelerator Laboratory, Centre For Advanced Studies in Physics, Government College University, Lahore. The characteristic X-rays emitted by the target were detected by an energy dispersive Si(Li) detector placed at right angle to the direction of the proton beam at a distance of approximately 15cm. The detector has an area of 30 mm^2 and energy resolution of 138 eV. The detector has 0.34

micrometer thick aluminum coated NORVAR window. The semiconductor detector was cooled to liquid nitrogen temperature for optimum results. Beam current used in the experiment was ten nano-amperes and each sample was irradiated for 900 seconds. The beam current was measured by a Faraday cup. The signal from the detector was processed by the usual PIXE electronics and displayed by multi channel analyzer as channel (elements) versus peak height (concentration) spectrum. The spectrum for each sample was recorded and stored in the computer. The detector was energy calibrated by the characteristic L, X-ray emission from a gold target.

The system was calibrated for concentration measurements by K X-rays using known salt mixture containing 12 elements $Z = 11$ to $Z = 38$ with $Y(NO_3)_3$ as internal standard and by L X-rays. To check the accuracy of calibration, target was prepared from the International Atomic Energy Agency (IAEA) reference material SOIL-7 in a manner described above using $Y(NO_3)_2$ as the internal standard. The results obtained for IAEA SOIL-7 reference material are presented in Table 1.

Error for the elements Al, K, Ca and Fe is less than 7% and for Mg 19%. The measured value of Mg differs from the IAEA value by a factor of two, this could perhaps be due to self absorption of low energy X-rays of Mg. Concentration of all other elements are within or close to the range specified by IAEA.

Table 2. Description of the sediment (surface) .

	μm	ϕ	Grain Size Distribution			
Mode 1:	2400.0	-1.243	Gravel:	20.1%	Coarse Sand	2.0%
			Sand:	20.0%	Medium Sand	1.0%
			Mud:	0.0%	Fine Sand	0.0%
D ₁₀ :	1403.8	-1.423	Clay:	57.0%	V Fine Sand	0.9%
Median or D ₅₀ :	2257.3	-1.175	V Coarse Gravel:	0.0%	V Coarse Silt	0.0%
D ₉₀ :	2681.9	-0.489	Coarse Gravel:	0.0%	Coarse Silt	0.0%
(D ₉₀ / D ₁₀):	1.9	0.344	Medium Gravel:	0.0%	Medium Silt	0.0%
(D ₉₀ - D ₁₀):	1278.1	0.934	Fine Gravel:	0.0%	Fine Silt	0.0%
(D ₇₅ / D ₂₅):	1.2	0.766				
(D ₇₅ - D ₂₅):	487.3	0.311				

4. Result and Discussion

4.1 Grain Size and Sediment Composition

Grain size distribution is one of the most important characteristics of sediments. It is the most fundamental property of sediment particles, affecting their entrainment, transport and deposition. Grain size analysis, therefore, provides important clues to the sediment provenance, transport history and depositional conditions. Grain size analysis was carried out only for the surface sediment of the core. GRADSTAT was applied for the determination of grain size statistic. This software gives a range of cumulative percentile values (the grain size at which a specified percentage of the grains are coarser), namely D₁₀, D₅₀, D₉₀, D₉₀/D₁₀, D₉₀ - D₁₀, D₇₅/D₂₅ and D₇₅ - D₂₅. Grain size analysis of the Korangi Creek sediment samples reveal that the sediment is clayey in nature. Table 2 gives the detailed description of the sediment. The D₅₀ value was 2257.3 μm . Fig. 2 shows the variations in statistics of grain size.

Sediment composition was determined for all sub samples and the results are shown in Figure 3. Clay was dominating particle in all core slices. Top 10 cm is around 60% clayey, 20% sand and 20 % silt while the remaining section comprise of around 50% clay and 50% silt + sand. Metals concentrations and grain size are, in general, inversely related i.e., metal concentration increases with decreasing grain size of sediments. Large amounts of metals are bound in the fine-grained fraction of the sediment, mainly because of its high

surface area-to-grain size ratio and humic substance content [19, 20].

4.2. pH

The accumulation of certain trace metals in sediments is directly or indirectly controlled by redox conditions through either a change in redox state and/or speciation [21]. Variations in pH with depth in sediment core are shown in Figure 4. pH in the Korangi Creek core samples was acidic (around 6.1-6.5) starting from a depth of 42.5 cm to subsurface. On closer observation it appears that the top 10 cm slices have pH values closer to neutral whereas for the bottom sediments from a depth of 10 cm till 42.5 cm the pH values are in the range of 6.3-6.0. This indicates that only the recent sediment deposits have a pH value of about 6.5 and if this trend continues, sediments at top will become neutral in nature with time.

4.3 Down Core Profiles of Metals

Sediments represent one of the ultimate sinks for metals discharged into the environment. A variety of processes lead to the association of metals with solid phases, such as direct adsorption by fine grained inorganic particles of clays, adsorption of hydrous ferric and manganese oxides which may in turn be associated with clays, adsorption on, or complexation with natural organic substances which may also be associated with inorganic particles, and direct precipitation as new solid phases [22]. Elemental ranges with means of the metal studied in this work are given in Table 3.

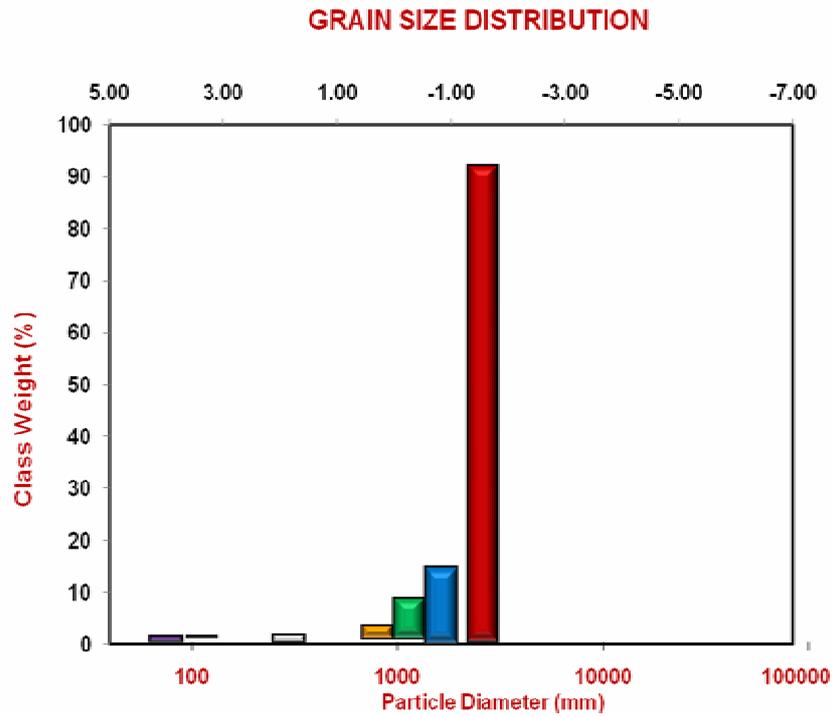


Figure 2. Grain size of Korangi Creek sediment.

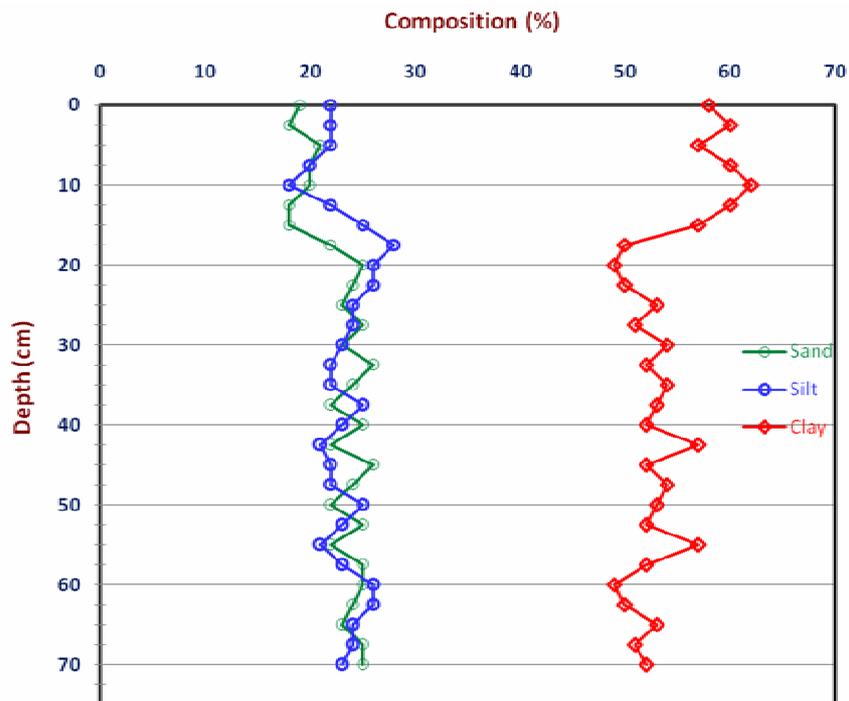


Figure 3. Percent composition of sand, silt and clay in the core.

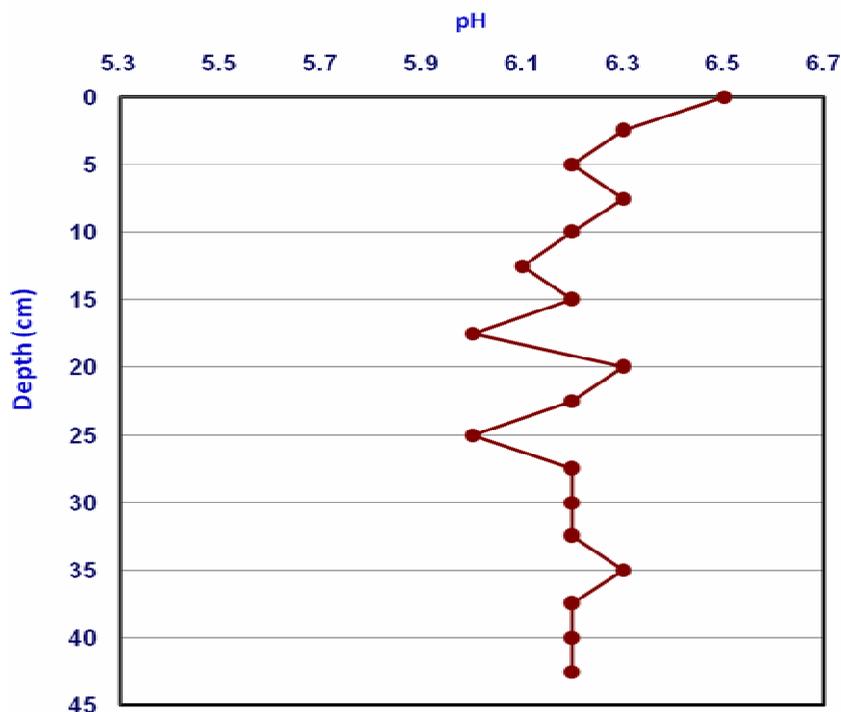


Figure 4. Downward profile of pH in core.

Table 3. Ranges and mean values of metals.

Element	Range (ppm)	Mean (ppm)	Uncertainty/Error	LOD (ppm)
Al	3890-5002	4377	628	10
Ca	3190—3987	3446	30	10
Cr	34-72	53	578	10
Cu	16-56	30.4	15.2	10
Fe	2459-4321	3494	13	10
K	7567-9486	8477	20	10
Mg	2659-4238	3085	244	10
Mn	76-187	139.5	12.1	10
Ni	18.9—66.0	38.9	15.5	5
V	42.0—84.0	54.9	31.3	5
Zn	78.0—224.0	124.9	41.0	5

The standard uncertainty was calculated at 95% level of confidence level using formula .

$$= s/\sqrt{n}$$

Where s = standard deviation, and n is the number of measurements.

Figures 5 to 7 show the down core variations in the concentrations of metals in creek sediments. Mg, K and Ca behavior in the core was more or less uniform with their concentration varying from the bottom to the top (Figure 5). Mg and Ca

followed more or less similar pattern. Their concentrations were almost constant from bottom to 10 cm from the top where their concentrations increased. However after 5 cm their concentration shot beyond 4000 ppm at the surface. K concentration showed a gradual increase. Increased variation in K concentration is observed from 7.5 cm to surface. A detailed study is needed to explain the recent but uniform increase in the concentrations of K over the years.

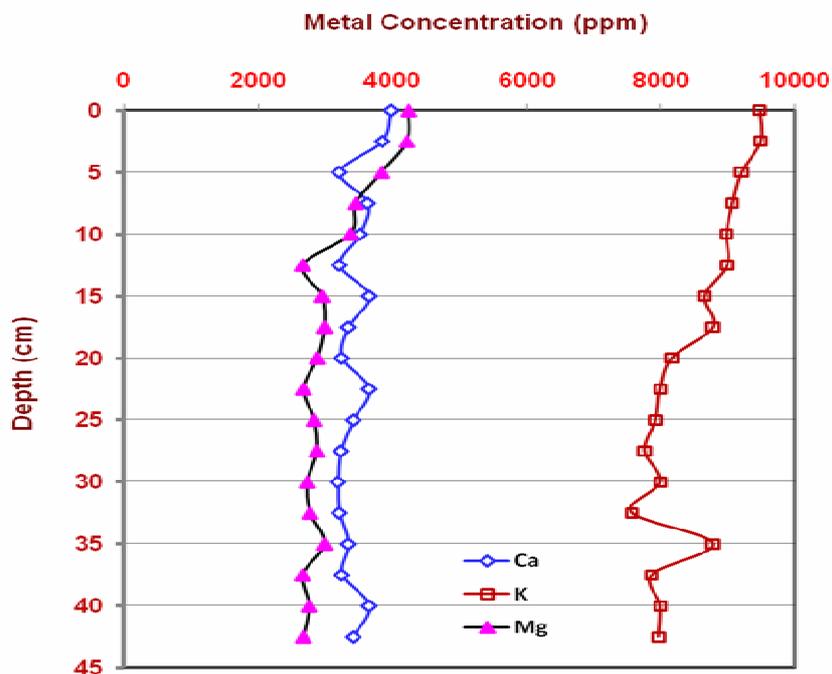


Figure 5. Down core variations in the concentrations of Mg, K and Ca.

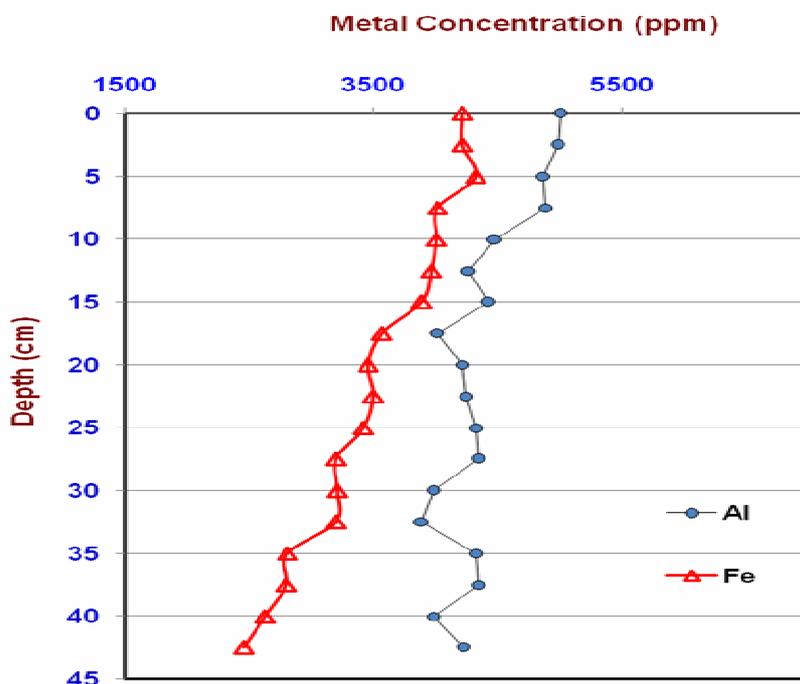


Figure 6. Down core variations in the concentrations of Al and Fe.

Downward profile of Al and Fe is shown in Figure 6. Fe content gradually increased from bottom to surface. Al contents followed an uneven pattern, its concentration remained less than 4500 ppm upto a depth of 12.5cm. However, above this

depth to the surface its concentration rises to 5000 ppm which may be attributed to increased industrial activities using Al such as: boat making and paint industries.

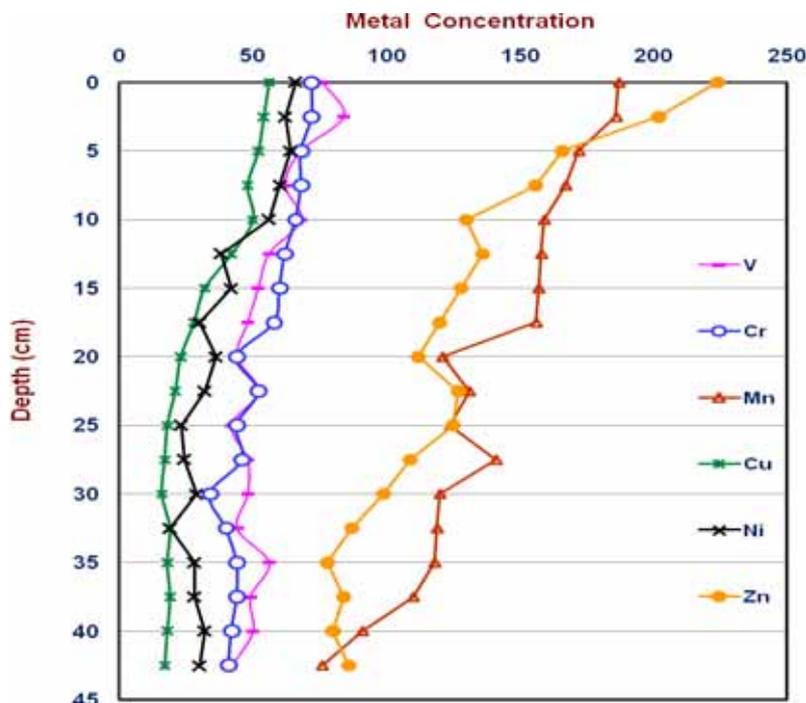


Figure 7. Down core variations in the concentrations of V, Cr, Mn, Cu, Ni and Zn.

Depth wise variations in the concentrations of V, Cr, Mn, Cu, Ni and Zn are shown in Figure 7. Concentration of Zn and Mn found in sediment at high levels varied in the examined samples over a broad range. The most significant differences were in Zn, from 76 in the bottom most layers to 224 in the surface layer. Mn concentration increased from 76 ppm at the bottom to 187 ppm at the surface. V, Cr, Cu, and Ni also showed increasing pattern. The difference in concentration of Cr, Cu, Ni and V, were similar from top to bottom, Cr 34 – 72, Ni 19-66, Cu 16- 56 and V 42.00 -84.00. Mn and Zn were found to be the highest occurring metals in the core as compared to V, Cr, Cu and Ni and their contents were elevated significantly in upper layers. Mn and Zn values in the bottom most layer are higher than V, Cr, Cu and Ni which indicate that backgrounds values of Mn and Zn are higher than for other elements studied.

The increasing trends of metals concentration in the surface samples shows increased deposition of these metals due to industrial effluents. Metals are released from specific local sources such as discharge from smelters (Cu, Ni), metal based industries (Zn, and Cr from electroplating), paint and dye formulators (Cr, Cu, and Zn), petroleum refineries (Mn, Pb), as well as effluents from

chemical manufacturing plants [3]. Once accumulated into the sediments, metals can be mobilized and find their way into overlying water column. Although these metals are essential for aquatic life but at elevated levels they may become toxic to some species [23].

Results from regression analysis (Table 4) shows significant correlation between metals concentrations. K significantly correlates with Mg, V, Fe and Cu. Ca and Mg are also positively correlated. Significant positive correlation is also found between Cr, Ni, Cu, Zn and Fe. Ni, Cu and Zn show high correlation indicating common anthropogenic sources which are municipal, domestic, and discharges of industrial effluents, mainly steel, dying and leather industries.

4.4 Enrichment Factor (EF)

Enrichment factors were calculated to assess the degree of contamination and to understand the distribution of the elements of anthropogenic origin from sites by individual elements in sediments. Al, Fe and Mn are commonly chosen as the normalizing elements while determining EF values, as these usually occur in soil and do not vary much [24, 25]. In the present study Al was used as

Table 4. Correlation among metals in sediment core.

	Al	Ca	Cr	Cu	Fe	K	Mg	Mn	Ni	V	Zn
Al	1	0.60	0.71	0.75	0.69	0.71	0.77	0.72	0.75	0.63	0.79
Ca		1.00	0.66	0.62	0.60	0.65	0.81*	0.62	0.67	0.66	0.73
Cr			1.00	0.88*	0.90*	0.67	0.75	0.88*	0.83*	0.82*	0.85*
Cu				1.00	0.82*	0.88*	0.58	0.79	0.95*	0.85*	0.90*
Fe					1.00	0.89*	0.70	0.68	0.79*	0.75	0.85*
K						1.00	0.80*	0.71	0.60	0.86*	0.94*
Mg							1.00	0.71	0.60	0.85*	0.39
Mn								1.00	0.84*	0.76	0.84*
Ni									1.00	0.87*	0.87*
V										1.00	0.82*
Zn											1

*Significant correlation at 0.01 level (1- tailed)

Table 5. Enrichment factors of elements in sediment core.

	Ca	K	Mg	Al	V	Cr	Mn	Fe	Ni	Cu	Zn
Surface	2.10	5.12	4.86	1.00	22.20	31.85	5.49	2.11	54.94	60.63	66.69
Mean	2.08	5.24	4.02	1.00	18.20	26.65	4.62	2.00	36.23	26.53	41.91

reference element because Al is chemically inactive element with respect to other elements [26]. EFs were calculated using the following equation [26].

$$\text{Enrichment Factor} = (\text{Cn/Al})_{\text{sample}} / (\text{Cn/Al})_{\text{background}}$$

where, Cn is the concentration of element "n". The background value is that of average values of element in shale [27].

EF values were interpreted as suggested by Ergin et al. [28] and Birch [29]. According to their classification where EF < 1 indicates no enrichment, < 3 is minor; 3-5 is moderate; 5-10 is moderately severe; 10- 25 is severe; 25-50 is very severe; and > 50 is extremely severe. Table 5 shows metals EFs in core sediments (EFs for surface and mean of all sub samples). EFs for surface are greater than for overall samples for all the elements studied. The order of EFs in the

sediment core for surface and overall is summarized as: Zn>Ni>Cr>Cu>K>V>Mn>Mg> and Ca (Overall) and Zn>Cu>Ni>Cr>V>K>Mg>Fe>Ca (surface).

The surface sediments showed extremely severe enrichment for Ni (54.94), Cu (60.63) and Zn (66.69), very severe for Cr (31.85), severe for V (22.2), moderate for Mn (5.49) and K (5.12) indicating increase in Ni, Cu, Zn, Cr and V concentration in the recent few years due to the close proximity of this site to industrial discharges.

5. Conclusion

The results of sediment core analysis reveal that:

- Korangi Creek sediments are clayey in nature
- The sediment pH is slightly acidic, ranging between 6.1-6.5. However recent sediment depositions indicate a neutral sediments.

- Positive correlations exist between Ni, Cu, Cr, Zn with Fe and with each other indicating common source.
- Metal concentrations show extremely severe enrichment for Ni, Cu and Zn and severe enrichment for Cr in surface samples indicating increased industrial effluent discharge in the area.
- The enrichment trend of Ni, Co, Cu and Zn is threatening the marine life of the Korangi Creek and it is most likely that the local food chain may be adversely effected.
- The concentration of metals in the bottom most layers can be used as baseline/ background values in further studies.

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