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# ASSESSMENT OF HEAVY METAL CONTENTS AT REHRI CREEK AREA, KARACHI, SINDH

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## ABSTRACT

This study focuses on the heavy metal contamination along Rehri Creek area. Water and sediment samples were systematically collected from industrial and domestic discharges which is responsible for pollution st the area. Wastewater samples were collected from lower section of the drains at three different stations while seawater and sediments samples were collected close to these drains. Heavy metal contents were analyzed using Atomic Absorption Spectrometer. Hierarchical cluster analysis (CA) is used for statistical grouping of sites that have similar characteristics. Strong positive correlations were obtained for the heavy metals which seem to be attributable to their common origin. In addition, mineralization in the area is thought to cause variation in metal contents. Results of the heavy metal analysis in the effluent drains showed elevated concentrations of all metals except Zn at site 1 and site 2 and As at site 1 as compared to National Environmental Quality Standards. The heavy metal accumulation in the area is responsible for creating ecological disturbances which results in biodiversity losses. It is recommended that protection zones should be defined and the necessary measures be taken so as to cease the degradation of this economically and ecologically important creek.

**Key Words:** Marine pollution, Heavy metals, Rehri Creek Area

## INTRODUCTION

Pakistan has a long coastline of about 970 km divided into two parts: the coast of Sindh and the coast of Makran. The length of Sindh coast is about 270 km (Munshi *et al*., 2004). To the southeast of Karachi there is a chain of Indus river tributaries, having a vast expanse of mudflats, sand, mangroves and swamps. This system merges into the delta and the gradual shifting of the Indus river course to the east consequently converted these tributaries into tidal creeks.

Korangi/Rehri is an area of about 64,000 hectares which is over one-tenth of the tidal area of Indus River Delta (IUCN, 2003). Korangi/Rehri Creek area of Karachi coast receives untreated industrial and domestic effluents from Korangi, Landhi, Karachi Export Processing Zone, Bin Qasim industrial Area, and Pakistan Steel Mills. Moreover, effluents from small coastal settlements are also released into the Rehri Creek

The toxicity in water and sediments of southeast coast of Karachi including Rehri Creek is attributed to several factors that include untreated effluents of domestic and industrial origin, accumulation of heavy metals in sediments and the tidal regime due to monsoon (Mashiatullah *et al.*, 2004).

It has been reported that heavy metal concentrations are higher in sediment samples along Karachi coast including Rehri Creek area. Mangrove habitats in the surrounding area of Karachi serve as a sink for heavy metals. The sediments are major trap for metals followed by mangrove plants (Saifullah *et al.*, 2002 and Mumtaz, 2002).

Indiscriminate disposal of the untreated industrial and domestic waste in to the Rehri Creek has resulted in gross reduction in economically important living marine resources. Monawwar *et al.* (1999) reported high concentration of heavy metals in fishes along Karachi coast (Ashraf and Jaffar, 1988; Monawwar *et al.*, 1999; Monawwar, 2002).

The purpose of the present study was to investigate the concentration and distribution of heavy metals in waste water, marine water and sediments along Rehri Creek area and to disclose the pattern of co-occurrence of the heavy metals using cluster analysis.

## MATERIALS AND METHODS

Metal contamination in marine environment of Rehri Creek area was detected in samples of wastewater, marine water and sediments collected from six different sites (Fig 1).The samples were collected bimonthly in 2008. During the study, 45 samples were collected from pre-designated sites. The sampling sites are mentioned in Table 1 and 2. The samples were brought to Institute of Environmental Studies, University of Karachi for physical and heavy metal analysis. The Standard methods for the examination of water and wastewater were used for the analysis (APHA, 1992).

1. Temperature was noted on site using portable calibrated mercury thermometer (EPA, 1998).

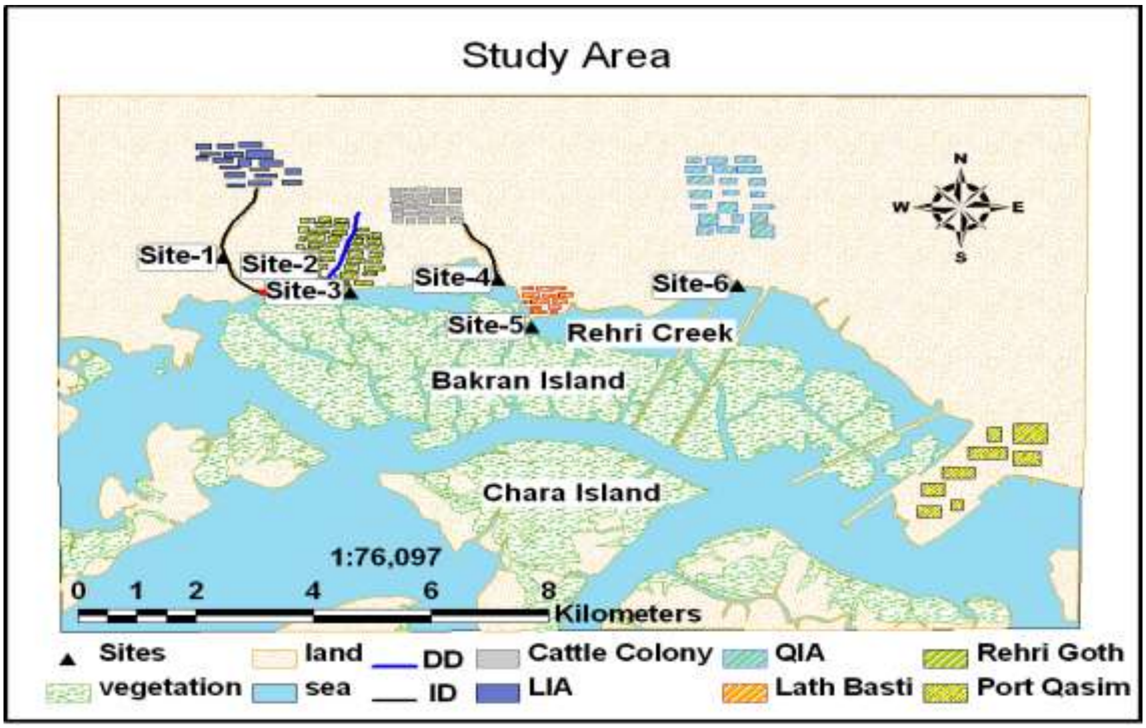
2. pH of the samples were measured on site just after the collection by JENWAY 3505 pH meter.
3. Heavy metals (Cr, Cu, Pb, Zn and Ni) were determined by digesting water and sediment in nitric acid and then analysed spectrophotometrically using atomic absorption spectrophotometer (Perkin- Elmer Analyst 700) (APHA, 1992; FAO, 1975).
4. Arsenic content was ascertained spectrophotometrically by Gutzeit Arsenic determination apparatus (APHA, 1992).
5. Data were analyzed using cluster analysis. Ward's method of minimum variance clustering was used with Euclidean distance as the resemblance function (Orloci and Kenkel, 1985).

## RESULT AND DISCUSSION

**Physical parameter:**

**pH:**

The mean pH of the samples ranged from 7.136±0.209 to 9.748±0.052 as depicted in Fig. 2 Marine water in front of Lath Basti (Site 5) shows the lowest pH value of 7.136±0.209 while the Industrial Effluent from Landhi Industrial area (Site 1) shows the highest pH value of 9.748±0.052. The pH values of industrial effluents were within the permissible limits (NEQS, 1999). There are no standards available for marine water in NEQS hence the results of marine water were not compared with any standard value.




ID: Industrial Effluent, DD: Domestic Drain, QIA: Port Qasim Industrial Area, LIA: Landhi Industrial Area

**Fig. 1. Rehri creek area showing locations of sampling stations**

pH of wastewater is considered to be an important parameter as it affects all physical, chemical and microbiological environments. Extremely acidic pH causes heavy metals to accumulate at sub soil; whereas high pH is detrimental for microorganisms. pH has been regarded as an important variable regulating the mobility of metals (Teik-Thye Lim, *et al*. 2002). In general, pH of the samples was towards alkaline side.

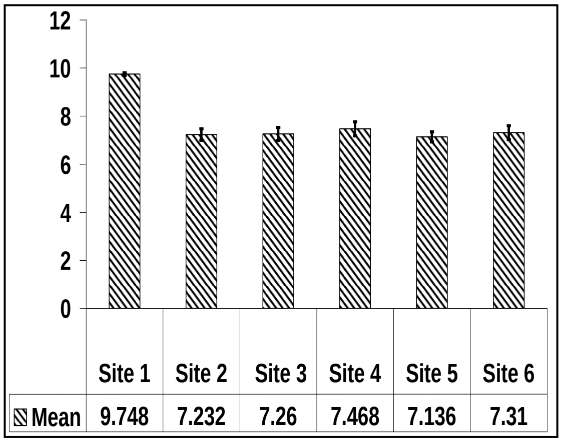



**Fig. 2. Mean of pH ± standard error**

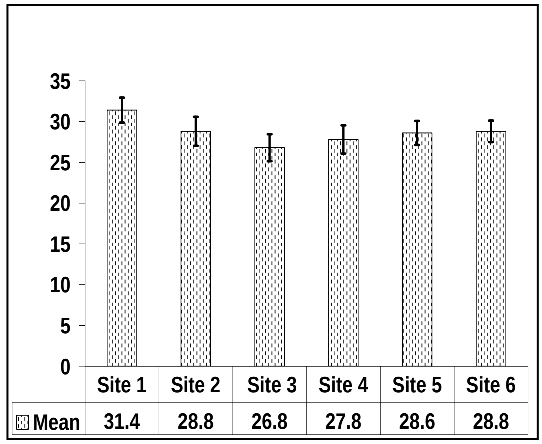



**Fig. 3. Mean of temperature ± standard error**

**Temperature:**

Mean temperature values for various samples are presented in Fig.3 which shows that temperature ranges from 23 to 36$^0$C. The highest value was found in the sample of industrial effluent from Landhi Industrial area (Site 1), while the lowest value of temperature was in the sample of marine water in front of Rehri Goth (Site 3). The temperature values of industrial effluents are within the permissible limits that is 40 $^0$C (NEQS, 1999).

**Heavy metals:**

**Seawater:**

The present investigation aims at the analysis of heavy metals (Iron, lead; zinc, chromium and arsenic) in the wastewater and marine water samples so as to determine the extent of metal pollution load entering in the Creek area that is responsible for its degradation. The results obtained are presented in Table 4 & Fig. 4 and are compared with National Environmental Quality Standards (NEQS, 1999). Results disclosed high concentration of heavy metals in marine water of Rehri Creek area. The present results were consistent with the previous reports (Saifullah *et al*., 2002; Saifullah *et al*., 2004; Mumtaz, 2002).

**Iron:**

The mean concentration of $Fe^{+2}$ presented in Fig 4, ranged from 0.35±0.0158 ppm to 15.582±1.0199 ppm. The maximum $Fe^{+2}$ concentration was recorded at site 1 whereas minimum concentration was recorded at site 4. All industrial and domestic wastes (site 1, site 2 and site 4) contain $Fe^{+2}$ above the maximum permissible limit of National Environmental Quality Standards (NEQS, 1999) and marine water at site 3 and site 5 showed high concentration (0.35 ppm at site 3 and 5.568 ppm at site 5) comparable to previously reported studies (0.06 ppm at site 3 and 0.115 ppm at site 5) by Saifullah *et al.*, (2004).

Untreated industrial and domestic drains near the coastal area are the sources of iron in the marine environment. Iron in the marine environment can be found as soluble (free; $Fe^{+2}$ and $Fe^{+3}$) and insoluble inorganic forms, dissolved organic complexes, colloidal forms, mineral particles and in living cells (Hutchins, 1995). The mobility of $Fe^{+2}$ is moderate and $Fe^{+3}$ is low, limited co precipitation as limonite, but under some conditions colloidal suspensions of undissociated hydrous iron bearing organic complexes may be stable. In the present research, only $Fe^{+2}$ was ascertained.

**Lead:**

Mean concentrations of Pb are presented in Fig 4 which ranged from 7.118±0.4117 ppm to 13.721±1.9683 ppm. The maximum Pb concentration was recorded at site 5 whereas minimum concentration was recorded at site 1. Marine water in front of Rehri Goth and Lath Basti showed high concentration of Pb as they are receiving most of industrial and domestic effluent. Effluent from Landhi Industrial Area, Cattle Colony and Rehri and Landhi town had Pb concentrations much higher than the NEQS value (NEQS, 1999). Marine water in front of Rehri Goth (site 3), Lath Basti (site 5) and Port Qasim Industrial Area (site 6) showed high concentrations (9.43 ppm at site 3, 13.721 ppm at site 5 and 10.155 ppm at site 6). These results are consistent with the finding of previous study (Mumtaz, 2002).

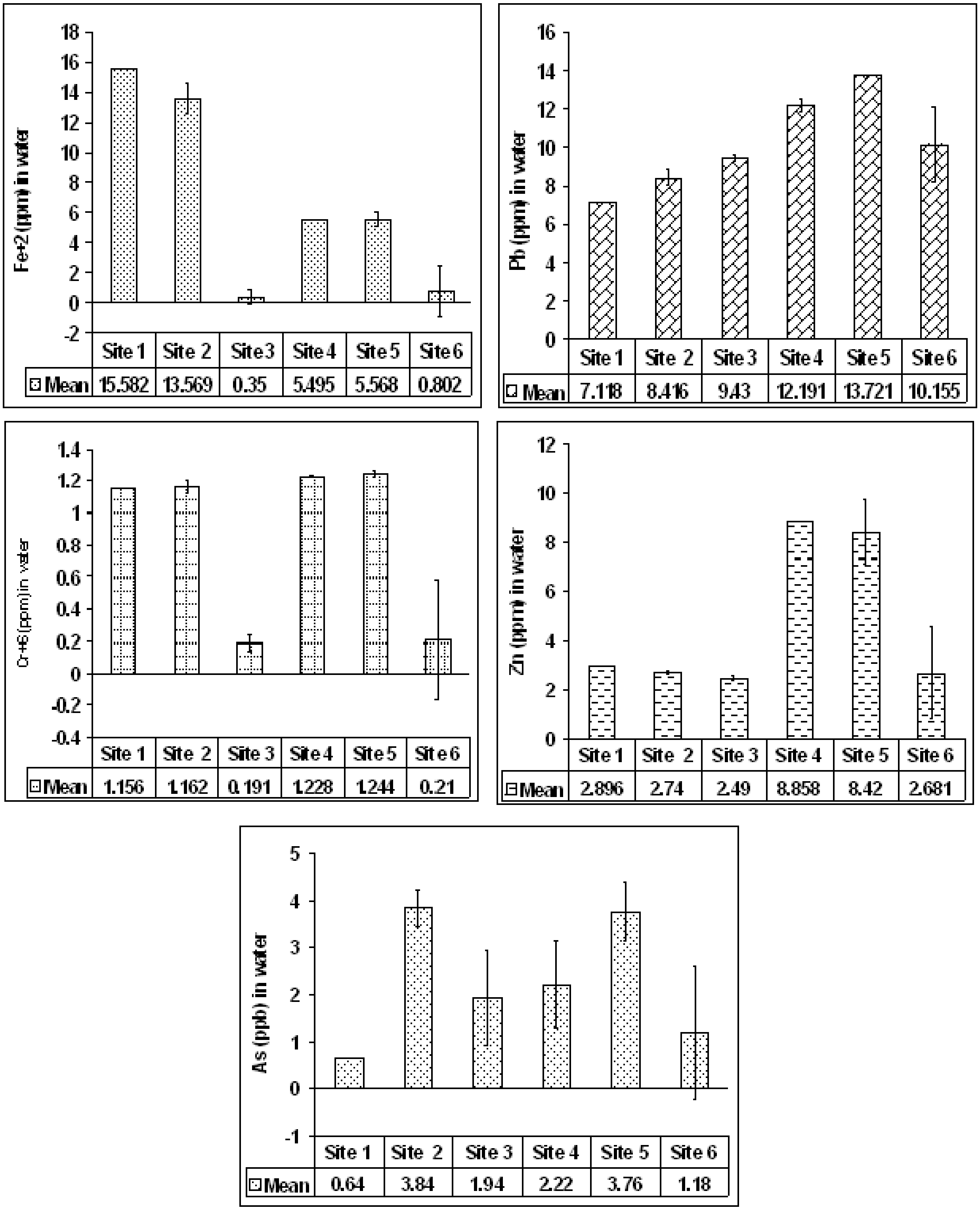



**Fig. 4. Heavy metal profile of wastewater and marine water of Rehri creek area.**

The pH of marine environment has a pronounced effect on the solubility of lead (Pb). In the present study the pH of samples was towards alkaline side which increases the Pb availability thereby causing toxicity to aquatic biota (Misra and Dinesh, 1992).

**Chromium:**

In the current study the mean level of $Cr^{+6}$ ranged between 0.191±0.0033 ppm to 1.244±0.3744 ppm (Fig. 4). The values of site1, site 2 and site 4 are slightly higher than the NEQS limit that is 1mg/L (NEQS, 1999). Site 5 and site 6 showed slightly higher levels of $Cr^{+6}$ compared to other sites reported (Mumtaz, 2002).

Compounds of chromium are on the National Pollutant Inventory (NPI) reporting list 2000-2001, $Cr^{+6}$ and $Cr^{+3}$. The environmental effects of $Cr^{+6}$ compounds are quite different from that of $Cr^{+3}$ compounds. $Cr^{+6}$ can have a high to moderate toxic effect on plants, birds or land animals. $Cr^{+6}$ does not change its oxidation state easily and there is a high potential for accumulation of $Cr^{+6}$ in fish life. In the present study $Cr^{+6}$ is ascertained which is infact harmful for marine organism (Environmental Defense Fund, 1998).

**Zinc:**

Presence of zinc (Zn) in marine environment is mainly attributed to anthropogenic activities. Zinc is added mostly due to industrial activities, mining, coal and waste combustion and steel processing. Some soils are heavily contaminated with zinc where zinc is mined or refined, or where sewage sludge from industrial areas is used as fertilizer.

Zn was found in a range between 2.49±0.0151-8.858±1.2880 ppm as shown in Fig.4, which was higher than estimated in previous studies (Monawwar, 2002). In industrial and domestic effluents Zn was within permissible limits (NEQS, 1999) except effluent from Landhi Cattle Colony which showed high level of Zn.

**Arsenic:**

Mean As ranged from 0.64±0.3919 ppb to 3.84±1.0087 ppb (Fig 4). Site 2 has maximum As concentration (3.84±1.0087 ppb) as compare to site 1 and site 4 whilst maximum concentration (3.76±1.4190ppb) in marine water was found at site 5. Site 2 and site 4 show elevated levels of As whereas site 1 has As concentration under the permissible limit (NEQS, 1999).

Arsenic is found as a free element as well as a common component of the sulphide ores of many metals. Arsenic is mainly emitted by the copper producing industries, but also during lead and zinc production and in agriculture. It cannot be destroyed once it has entered the environment and cause toxic health effects to humans and animals.

Arsenic alters basic cellular fuction linked with energy production in terrestrial biota (Ghosh et. al., 2004). Arsenic is toxic because of its resemblance with phosphorus (P) in As(V) form and its ability to form covalent bonds with S in the As(III) form. Most organisms take arsenate (an analogue of anions of phosphate) via their phosphate transport system. It has been hypothesized that arsenate replaces phosphate in energy-transfer phosphorylation reactions. This mechanism reveals that arsenic can directly affect the soil biota and microbial populations (Ghosh et. al., 2004; Maliszewska-Kordybach and Smreczak, 2004).

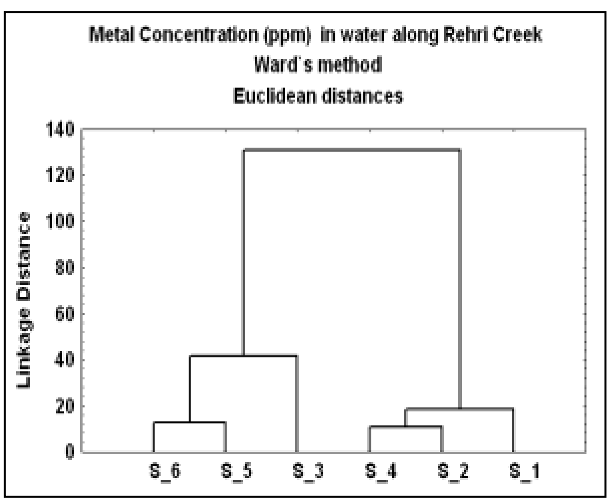



**Fig 5. Dendrogram derived from average metal concentration in water between six sites. The linkage distance defined by Euclidean distance and the combination of cluster is based on Ward's method**

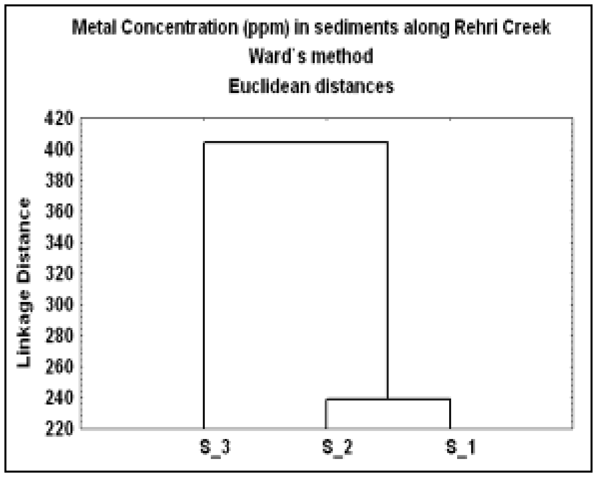



**Fig 6. Dendrogram derived from average metal concentration in sediments between three sites. The linkage distance defined by Euclidean distance and the combination of cluster is based on Ward's method**

**Table 1. Sampling sites for water sample along the Rehri creek**

| S.No | Sites | Coordinates | Features |
|---|---|---|---|
| 1 | Site 1 | $24^{0}49^{/}13.53^{//}$N $67^{0}12^{/}37.80^{//}$ E | Industrial Effluent from Landhi Industrial area |
| 2 | Site 2 | $24^{0}48^{/}57.40^{//}$N $67^{0}13^{/}40.08^{//}$ E | Domestic Effluent from Landhi town and Rehri Goth |
| 3 | Site 3 | $24^{0}48^{/}50.99^{//}$N $67^{0}13^{/}55.06^{//}$ E | Marine water in front of Rehri Goth |
| 4 | Site 4 | $24^{0}49^{/}0.58^{//}$ N $67^{0}15^{/}24.61^{//}$ E | Effluent from Landhi Cattle Colony |
| 5 | Site 5 | $24^{0}48^{/}28.85^{//}$N $67^{0}15^{/}45.28^{//}$ E | Marine water in front of Lath Basti |
| 6 | Site 6 | $24^{0}48^{/}58.44^{//}$N $67^{0}17^{/}49.13^{//}$ E | Marine water in front of Port Qasim Industrial area |

**Table 2. Sampling sites for sediment along the Rehri creek**

| S.No | Sites | Coordinates | Features |
|---|---|---|---|
| 1 | Site 1 | $24^{0}48^{/}50.99^{//}$N $67^{0}13^{/}55.06^{//}$ E | Sediments in front of Rehri Goth |
| 2 | Site 2 | $24^{0}48^{/}28.85^{//}$N $67^{0}15^{/}45.28^{//}$ E | Sediments in front of Lath Basti. |
| 3 | Site 3 | $24^{0}48^{/}58.44^{//}$N $67^{0}17^{/}49.13^{//}$ E | Sediments in front of Port Qasim Industrial area |

**Sediments:**

Metal concentrations at three sites are summarized in Table 4 that indicate the sediments were highly contaminated with heavy metals. However, the concentration of all metals studied showed spatial and temporal variation, between sites and with time. As ranged from 2.26±0.9162 to 2.54±0.8292 ppb, Cr 6.478±0.0910 to 47.18±2.7275 ppm, $Fe^{+2}$ 13.724±1.4768 to 44.63±3.4098 ppm, Pb 44.514±5.7697 to 251.41±11.9765 ppm, Zn 51.632±1.0933 to 135.82±3.8889 ppm and Ba 433.366±1.465 to 828.63±25.3617 ppm.

The heavy metal concentrations were higher except As and $Fe^{+2}$ compared to previous studies undertaken along the Pakistan coast (Mumtaz, 2002), showing As concentration 1.074 ppm, Cr concentration 11.43 ppm, Fe concentrations 387.1 ppm, Pb concentration 13.02 ppm and Zn concentration 53.74 ppm.

**Cluster Analysis:**

***Metal Concentration in water:*** The dendrogram resulting from Ward's minimum variance clustering shows two main groups (Fig.5). Each of the group contains three sites. Group 1 which includes sites 3, site 5 and site 6, is characterized by generally lower concentrations of $Fe^{+2}$ , Zn and $Cr^{+6}$ and high concentrations of As and Pb. On the other hand, group 2 which contains site1, site2 and site 4 exhibits low levels of As and Pb and greater concentration of $Fe^{+2}$, Zn, and $Cr^{+6}$.

***Metal Concentration in sediments:*** The result of cluster analysis is a dendrogram (Fig 6). The dendrogram exhibits close similarity (linkage) of sediments in front of Rehri Goth with that of Lath Basti. These two types of sediments have many characteristics in common, including low levels of $Fe^{+2}$, $Cr^{+6}$, Zn, and Pb and high level of As. Sediments in front of Port Qasim Industrial Area (site 3) is distinct from the other two sites having higher concentrations of $Fe^{+2}$, $Cr^{+6}$, Zn and Pb and lower concentration of As.

**Table 3. Heavy Metal content in water samples along Rehri creek.**

| **Sites** | **Year 2008 Months** | **Heavy Metals $Fe^{+2}$ (ppm)** | **Pb (ppm)** | **$Cr^{+6}$ (ppm)** | **Zn (ppm)** | **As (ppb)** |
|---|---|---|---|---|---|---|
| **Site 1** | Mean | 15.582 | 7.118 | 1.156 | 2.896 | 0.64 |
| | S.E | 1.0199 | 0.4117 | 0.0372 | 0.0569 | 0.3919 |
| **Site 2** | Mean | 13.569 | 8.416 | 1.162 | 2.74 | 3.84 |
| | S.E | 0.4637 | 0.1795 | 0.0517 | 0.0678 | 1.0087 |
| **Site 3** | Mean | 0.35 | 9.43 | 0.191 | 2.49 | 1.94 |
| | S.E | 0.0158 | 0.3430 | 0.0033 | 0.0151 | 0.9249 |
| **Site 4** | Mean | 5.495 | 12.191 | 1.228 | 8.858 | 2.22 |
| | S.E | 0.4377 | 0.0424 | 0.0424 | 1.2880 | 0.6183 |
| **Site 5** | Mean | 5.568 | 13.721 | 1.244 | 8.42 | 3.76 |
| | S.E | 1.6940 | 1.9683 | 0.3744 | 1.8853 | 1.4190 |
| **Site 6** | Mean | 0.802 | 10.155 | 0.21 | 2.681 | 1.18 |
| | S.E | 0.0222 | 0.5728 | 0.0054 | 0.0895 | 0.4758 |
| | Min | 0.305 | 5.698 | 0.18 | 2.41 | 0.2 |
| | Max | 55.284 | 89.352 | 40.29 | 76.96 | 7.6 |
| | NEQS (ppm) | 2.0 | 0.5 | 1.0 | 5.0 | 1.0 |

**Table 4. Heavy Metal content in sediment along Rehri creek.**

| **Sites** | **Year 2008 Months** | **Heavy Metals $Fe^{+2}$ (ppm)** | **Pb (ppm)** | **$Cr^{+6}$ (ppm)** | **Zn (ppm)** | **As (ppb)** |
|---|---|---|---|---|---|---|
| **Site 1** | Mean | 13.724 | 44.514 | 6.913 | 51.632 | 2.26 |
| | SE | 1.4768 | 5.7697 | 0.1212 | 1.0933 | 0.9162 |
| **Site 2** | Mean | 17.796 | 50.814 | 6.478 | 64.88 | 2.54 |
| | SE | 3.0811 | 8.7586 | 0.0910 | 0.9070 | 0.8292 |
| **Site 3** | Mean | 44.63 | 251.41 | 47.18 | 135.82 | 1.06 |
| | SE | 3.4098 | 11.9765 | 2.7275 | 3.8889 | 0.2749 |
| | Min | 9.3 | 27.92 | 6.25 | 48.5 | 0.2 |
| | Max | 54.2 | 281.75 | 55.5 | 146.5 | 4.8 |

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