Chemical Pollution Profile of Rehri Creek Area, Karachi (Sindh)

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Summary: The present investigation focuses on environmental issues along Rehri Creek area, which is an imperative creek of economic importance. During the study, a total of 30 samples of wastewater (industrial waste, Cattle colony waste and domestic waste) and seawater (infront of Rehri Goth and Lat Basti) from five sites along Rehri Creek area were collected for physical (pH and TSS), chemical (BOD_5, COD, salinity, phosphate, TKN, oil & grease and organic matter) and heavy metals (Cr, Cu, Pb, Ni, As and Zn) analysis. Results of the physicochemical analysis revealed that effluent from Cattle Colony (Site 4) is the major source of marine water pollution along Rehri Creek area as it has high levels of all parameter except pH. Other two important sources are industrial effluent (Site 1) and domestic sewer drains (Site 2). Except pH and oil and grease concentration at Site 2, the levels of all the parameters in industrial and domestic drains are not within permissible limit. Heavy metal analysis reveals that the concentration of heavy metals along the Creek is higher than previously estimated. The study showed that marine water quality of Rehri Creek is grossly contaminated with the industrial and cattle colony effluents, which are dumped into the sea without any treatment and would create an alarming situation in future. The continued accumulation of pollutant is also responsible for ecological imbalances and biodiversity losses in the area.

Introduction

Karachi is the largest city of Pakistan and a hub of industrial activity. The coastal zone of Karachi is extended up to 135 km that is exposed to heavy pollution load of both domestic and industrial origin [1]. Likewise discharges of sewage and industrial effluent 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.

Most of the coastal pollution is concentrated in Karachi harbour where an estimated 90,000 tons of oil products from vessels and port terminals are dumped every year. Extremely high levels of toxic heavy metals such as mercury have been documented, especially in the coastal waters and sea near Karachi. These are likely to have both acute and chronic toxic impacts on human beings, marine biodiversity and fish-eating birds. The impacts of these pollutants on commercial fin-fish and shrimp fisheries are unknown, but are likely to be significant [2]

Rehri Creek is one of the neighbourhoods of Bin Qasim port and supports a large community of fishermen. It is located at 24°48′ N and 64°14′ E and stretches to 21.7 km in the south east of Karachi coast, Pakistan. Its micro environment comprises of the coastal area of Bin Qasim district which includes the union council of Rehri and Ibrahim Haidery besides the two settlements of Chasma Goth and Lath Basti [3].

Rehri Creek is the heavily polluted area of Karachi coast, where the effluents from Korangi, Landhi, Karachi Export Processing Zone, Bin Qasim Industrial Area and Pakistan Steel Mill are directly discharged into the sea. In addition to these the untreated wastewater from metropolis of Karachi and domestic effluents are from smaller coastal settlements is also released into the coastal water. The consequent contamination of fisheries and other fauna poses serious and potential health hazards [4].

The Creeks 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 Rehri Creek Area reach to the mangrove areas. In addition, pollution from domestic, industrial effluents and Cattle Colony waste causes eutrophication and increases biomass in the form of algal bloom, which affects not only economically important marine fauna, but also affects mangrove seedlings. These algal blooms grow profusely and inhibit the growth of mangrove seedlings that results in mortality of mangroves on a large scale [5].

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The cumulative effect of indiscriminate disposal of domestic and industrial effluents in the creek is not only responsible for coastal degradation but also results in ecological imbalances.

The present investigation aims at the analysis of wastewater and marine water samples so as to determine the extent of pollution load entering in the creek area which is responsible for its degradation.

Results and Discussion

Table-1 and Fig. 1 show the locations of five sampling sites from which 30 samples were collected for the analysis of physical and chemical parameters such as pH, total suspended solids (TSS), Salinity, biochemical oxygen demand (BOD_5), Chemical oxygen demand (COD), organic matter, oil and grease, Total Kjeldahl Nitrogen (TKN), phosphate and and heavy metals (Cr, Cu, Pb, Ni, As and Zn). The results obtained are presented in Tables-2 and 3 and Figs. 3 and 4 and compared with National Environmental Quality Standards (NEQS) [6].

Table-1: Sampling sites along the Rehri creek.

S. No.	Stations	Coordinates	Features
1	Site 1	24°49′13.53″ N 67°12′37.80″ E	Industrial effluent from Landhi Industrial area lies between Korangi fish Harbor and Rehri Goth.
2	Site 2	24°48′57.40″ N 67°13′40.08″ E	Domestic effluent Lies within Rehri Goth.
3	Site 3	24°48′50.99″ N 67°13′55.06″ E	Sea water Lies in front of Rehri Goth
4	Site 4	24°49′0.58″ N 67°15′24.61″ E	Cattle colony waste Lies between Rehri Goth and Lath Basti.
5	Site 5	24°48′28.85″ N 67°15′45.28″ E	Sea water Lies at Jetty of Lath Basti.

pH

pH of the samples ranged from 7.3 ± 0.06 to 8.9 ± 0.6 and is presented in Table-2 and Fig. 3. Lowest pH value was of domestic effluent (Site 2) that is 7.3 ± 0.06, while the sample of industrial effluent (Site 1) has the highest pH value of 8.9 ± 0.6. Prior to discharge in water body it is recommended that the waste water should have the pH ranged from 6-9 [6].

All the pH values were within the permissible limits for industrial effluents as per

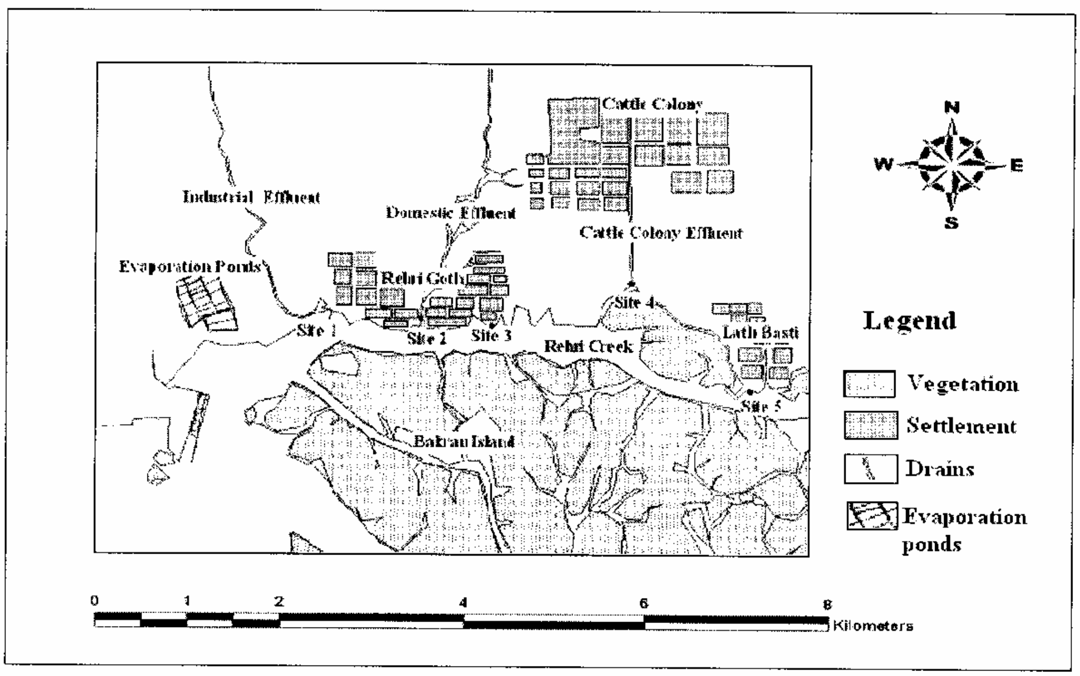

Fig. 1: Rehri creek area showing locations of sampling stations.

Table-2: Mean and variation of the physicochemical characteristics.

Site	No. of Samples		pH	TSS (mg/L)	Sal %	COD (mg/L)	BOD (mg/L)	O&G (mg/L)	O.M (mg/L)	PO_4 (mg/L)	TKN (mg/L)
Site 1	6	Mean	8.9	497	1.06	1088	315	29.15	4362	2.63	4.67
		S.E	0.6	76.7	0.33	32.8	30.1	2.42	163	0.64	0.77
		Min	7.8	310	0.11	800	210	20.8	3817	1.2	2.8
		Max	10.9	740	2.26	1333	420	36	4845	5.3	7
Site 2	6	Mean	7.3	350	0.63	445	165	6.52	3635	1.75	26.78
		S.E	0.06	44.5	0.26	28.4	8.8	0.66	141	0.04	2.45
		Min	7.1	246	0.15	355	140	4.4	3066	1.6	20.7
		Max	7.5	490	1.87	533	198	9.2	3901	1.9	38.1
Site 3	6	Mean	7.4	105	4.06	162	30.3	5.23	613	0.42	1.3
		S.E	0.2	5.5	0.26	4.5	4.8	0.3	36.1	0.09	0.08
		Min	6.9	91	3.41	146	16	4.3	495	0.2	1.1
		Max	7.9	130	4.95	180	50	6.4	746	0.8	1.7
Site 4	6	Mean	7.6	1670	1.13	5218	1812	40.72	10778	78.92	69.62
		S.E	0.06	123	0.41	1835	392	3.49	1746	9.18	15.03
		Min	7.4	1224	0.31	666	350	25	6039	37.5	25.2
		Max	7.9	2100	3.06	13333	3300	49.2	18609	101.2	101.1
Site 5	6	Mean	7.3	147	4.05	265	48	2.76	573	2.22	2.65
		S.E	0.2	12.7	0.26	11.5	7.4	0.57	25.5	0.38	0.68
		Min	6.4	110	3.44	230	22	1.1	532	1.2	1.2
		Max	7.8	192	4.91	296	71	5.2	695	3.6	5.6

Sal= Salinity, TSS= Total Suspended Solid, COD= Chemical Oxygen Demand, BOD= Biochemical Oxygen Demand, O.M= Organic Matter, O&G= Oil and Grease, PO_4= Phosphate, TKN= Total Kjeldahl Nitrogen, S.E= Standard Error.

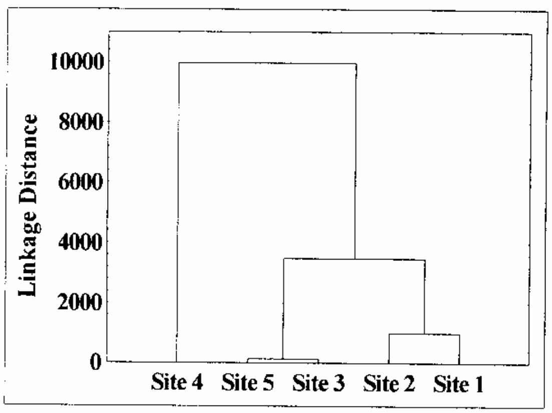

Fig. 2: Dendrogram derived from weighted pair group average between five sites, based on their effluent characteristics.

NEQS [6]. The metallic ions stability and solubility in the water is also affected by pH [7, 8]. Variation in pH of effluents may directly or indirectly affect the aquatic environment [9].

Total Suspended Solids (TSS)

The TSS values (Table-2 and Fig. 3) of the samples ranged between 105 ± 5.5 – 1670 ± 123 mg L^{-1}. The NEQS value of TSS is 200 mg L^{-1} [6]. It is evident that site 1, site 2 and site 4 have very high TSS values while site 3 and site 5 have relatively low TSS ranging from 105.5 ± 5.5 to 147 ± 12 mg L^{-1} respectively. The maximum value of TSS (1670 ± 123 mg L^{-1}) was recorded in the effluent of Cattle Colony (Site 4) which is a rich source of organic matter.

Effluents of high TSS may cause high turbidity, which prevents light from entering into the water and therefore adversely affects the process of photosynthesis. High TSS is also responsible for eutrophication in aquatic environment [10].

Salinity

The salinity of the samples ranged between 0.63 % ± 0.26 and 4.06 % ± 0.26 is presented in Table-2 and Fig. 3. Lowest salinity value (0.63 % ± 0.26) was of sample of domestic effluent of Rehri Goth (Site 2), while the sample of sea water infront of Rehri Goth (Site 3) and Lath Basti (Site 5) had the highest salinity values (4.06 ± 0.26 % and 4.05 ± 0.26 %).

Anthropogenic factors, such as freshwater diversions, large volume of industrial and municipal effluent discharges and barriers to existing flow patterns, can change the salinity regimes of estuaries and other coastal water bodies and affect the biota [11, 12].

The salinity of coastal waters affects several important physical and chemical properties of water, such as the freezing point, specific gravity and

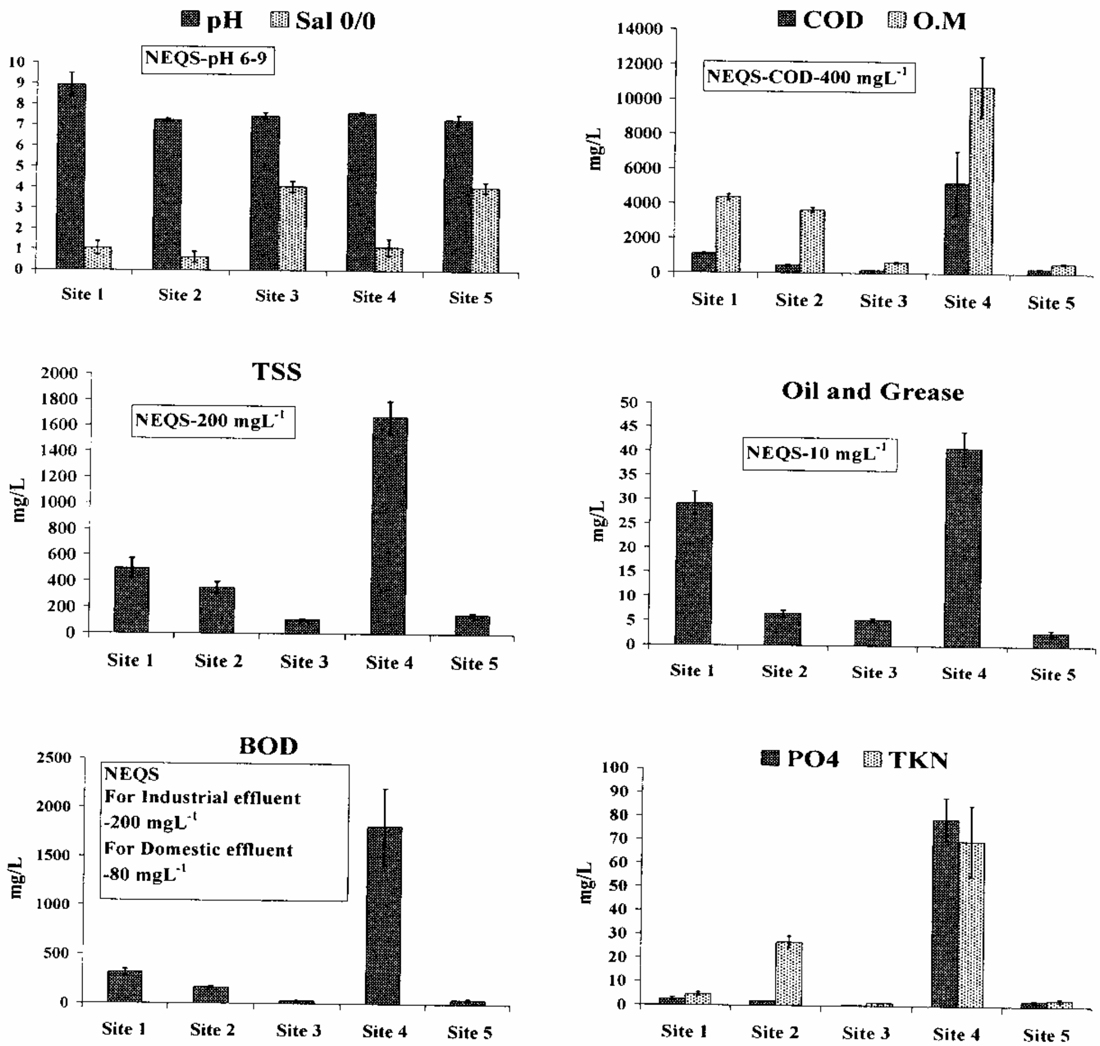

Fig. 3: Physiochemical profile of Rehri creek area.

osmotic pressure; this can have biological implications [13]. A decrease in the surrounding salinity could result in diatoms sinking to levels that impede efficient photosynthesis.

Chemical Oxygen Demand (COD)

The value for Chemical Oxygen Demand (COD) varies from 162 ± 4.5 – 5218 ± 1835mg L^{-1} as shown in Table-2 and Fig-3. This is well above the permissible limit [6]. The highest value (5218 ± 1835mg L^{-1}) of COD was at site 4 and lowest value (162 ± 4.5 mg L^{-1}) was at site 3. In general the COD values of all the sampling sites were quite high, which mostly represent the effluent of industrial origin.

Biochemical Oxygen Demand (BOD)

BOD_5 of the effluents is the quantity of dissolved oxygen required for the stabilization of decomposable organic matter by aerobic biochemical action [14]. The value of BOD_5 of effluents and sea water varies from 30.3 ± 4.8 (Site 3) to 1812 ± 392 mg L^{-1} (Site 4) as shown in Table-2 and Fig. 3.

The permissible range for BOD_5 according to NEQS is 200 mg L^{-1} for industrial effluent and 80 mg L^{-1} for domestic effluent. Both industrial and domestic effluents have high BOD_5 values as compared to NEQS [6]. Highest value (1812 ± 392mg L^{-1}) of BOD_5 was noted in effluent of cattle Colony (Site 4), which can cause asphyxiation resulting in loss of biodiversity [15].

Oil and Grease

The amount of oil and grease of the effluent and sea water is in the range of 2.76 ± 0.57 – 40.72 ± 3.49 mg L^{-1} (Table-2 and Fig. 3). The lowest oil and grease value (2.76 ± 0.57 mg L^{-1}) was observed for the sea water sample infront of Lath Basti (Site 5) and the highest value (40.72 ± 3.49 mg L^{-1}) was of effluent from Cattle Colony (Site 4). The NEQS value for oil and grease is 10 mg L^{-1} [16].

The addition of significant quantities of petroleum products such as oil and grease to any water body causes an immediate rise in the BOD_5 due to the activities of hydrocarbon degraders and the blockage of oxygen dissolution [16].

Oil film on the water surface reduces the amount of dissolved oxygen (DO) which affects both aquatic life forms and microbial activities which would adversely affect the aquatic biodiversity [17].

Organic Matter

The concentration of organic matter (Table-2 and Fig. 3) in water samples varies from 573 ± 25.5 to 10778 ± 1746mg L^{-1}. Highest concentration (10778 ± 1746mg L^{-1}) of organic matter was at Site 4 and lowest (573 ± 25.5 mg L^{-1}) was at Site 3.

No standard value is recommended for organic matter in NEQS [6]. Organic matter is mainly responsible for the depletion of dissolved oxygen and causes eutrophication (as it is rich source of nutrients like phosphate and nitrogen), which eventually turns the water body into swamps and marshes.

Total Kjeldahl Nitrogen (TKN)

Total Kjeldahl Nitrogen (TKN) is the sum of both ammonia and organic nitrogen. The combination of the organic nitrogen and all forms of inorganic nitrogen (NH_4, NO_3 and NO_2) make up the total nitrogen.

There is no standard value for TKN in NEQS [6]. Natural levels of TKN in water bodies are typically less than 2.0 mg/L. However, concentrations above 3 mg/L are considered excessive in natural waters [18].

The TKN concentrations (Table-2 and Fig. 3) observed in the sampling sites ranged from 1.3 ± 0.08 to 69.62 ± 15.03 mg L^{-1}. Effluent from Cattle Colony (Site 4) has the highest value (69.62 ± 15.03 mg L^{-1}) of TKN as it contains natural manure in it, which is a rich source of nitrogen. Seawater infront of Rehri creek (Site 3) has lowest concentration of TKN 1.3 ± 0.08 mg L^{-1}.

Phosphate

Phosphate concentration of the industrial effluents was noted in the range 0.42 ± 0.09 - 78.92 ± 9.18 mg L^{-1} as can be seen from Table-2 and Fig. 3. Cattle Colony effluent (Site 4) shows highest phosphate concentration (78.92 ± 9.18 mg L^{-1}) while sea water sample infront of Rehri Goth (Site 3) shows the lowest concentration (0.42 ± 0.09 mg L^{-1}). No standard value is recommended for phosphate in NEQS [6].

Phosphorus is an essential macronutrient that is a limiting factor to plant growth [19]. In excess, phosphorus triggers eutrophic conditions which involve the prolific growth of algal and other aquatic plants. Algal growth can have lethal impacts on aquatic life and, at high concentrations, can be toxic.

Algal blooms can also contain toxic strains of bluegreen algae which may kill birds, domestic animals, aquatic macro invertebrates thereby causing reduction in biodiversity [19, 20]. The eutrophication at Rehri Creek is attributed to high concentration of PO_4-P in the effluent of both domestic and industrial origin.

Heavy Metals

Metal concentrations at five sites are summarized in Table-3 and Fig. 4 and indicate that the sediments were highly contaminated. However, the concentration of all metals showed spatial and temporal variation, between sites and with time. Arsenic (As) ranged from 0.02 ± 0.001 – 0.04 ± 0.006 mg g^{-1}, chromium (Cr) 0.02 ± 0.002 to 0.04 ± 0.008 mg g^{-1}, copper (Cu) 0.12 ± 0.004 to 0.87 ±

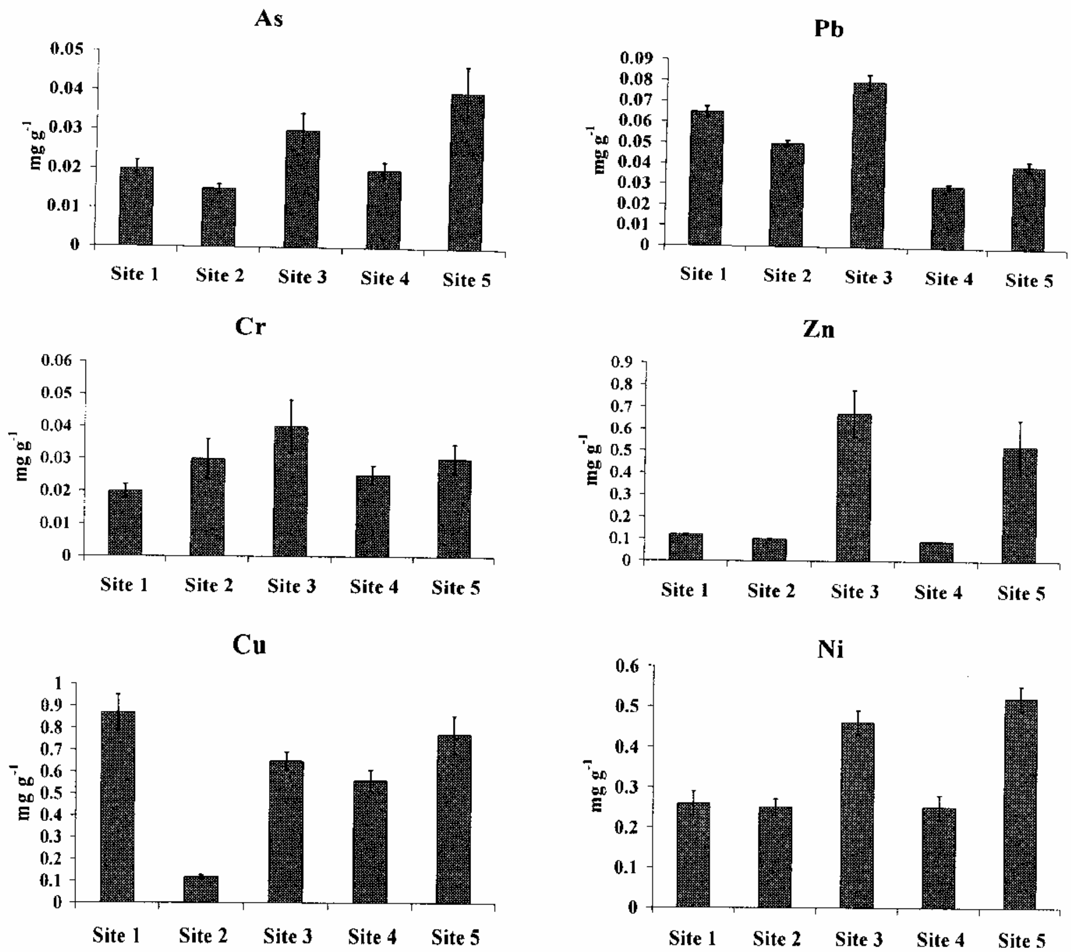

Fig. 4: Heavy metal profile of Rehri creek area

Table-3: Mean and variation of the heavy metal characteristics.

Site	No. of Samples		As ($mg\ g^{-1}$)	Cr ($mg\ g^{-1}$)	Cu ($mg\ g^{-1}$)	Pb ($mg\ g^{-1}$)	Ni ($mg\ g^{-1}$)	Zn ($mg\ g^{-1}$)
Site 1	6	Mean	0.02	0.02	0.87	0.065	0.26	0.12
		S.E	0.002	0.002	0.081	0.002	0.03	0.002
		Min	0.014	0.011	0.69	0.057	0.18	0.112
		Max	0.026	0.024	1.24	0.072	0.36	0.13
Site 2	6	Mean	0.015	0.03	0.12	0.05	0.25	0.1
		S.E	0.001	0.006	0.004	0.001	0.02	0.006
		Min	0.011	0.012	0.11	0.047	0.18	0.085
		Max	0.018	0.054	0.14	0.057	0.31	0.12
Site 3	6	Mean	0.03	0.04	0.65	0.08	0.46	0.67
		S.E	0.004	0.008	0.040	0.003	0.03	0.106
		Min	0.021	0.012	0.55	0.066	0.33	0.39
		Max	0.05	0.064	0.78	0.089	0.51	0.97
Site 4	6	Mean	0.02	0.025	0.56	0.03	0.25	0.09
		S.E	0.002	0.002	0.048	0.001	0.03	0.001
		Min	0.017	0.014	0.44	0.024	0.18	0.084
		Max	0.03	0.033	0.71	0.039	0.41	0.095
Site 5	6	Mean	0.04	0.03	0.77	0.04	0.52	0.52
		S.E	0.006	0.004	0.085	0.002	0.03	0.122
		Min	0.019	0.019	0.45	0.029	0.44	0.14
		Max	0.064	0.046	1	0.046	0.61	0.87

As= Arsenic, Cr= Chromium, Cu= Copper, Pb= Lead, Ni= Nickel, Zn= Zinc.

0.081 $mg\ g^{-1}$, nickel (Ni) 0.25 ± 0.03 to 0.52 ± 0.03 $mg\ g^{-1}$, lead (Pb) 0.03 ± 0.001 to 0.08 ± 0.003 $mg\ g^{-1}$ and zinc (Zn) 0.09 ± 0.001 to 0.67 ± 0.106 $mg\ g^{-1}$. The heavy metal concentrations are higher compared to previous studies undertaken along the Pakistan coast. Rizvi et al. [21], in their study of Bakran and Gharo creeks, Karachi, observed comparatively low concentrations, showing Cu concentrations ranging from 0.013 to 0.017 $mg\ g^{-1}$ and Zn 0.032 to 0.051 $mg\ g^{-1}$. Studies from Karachi harbor showed that Cu ranged from 0.029 $mg\ g^{-1}$, Ni from 0.029 to 0.051 $mg\ g^{-1}$, Zn from 0.071 to 0.170 $mg\ g^{-1}$, Cr from 0.028 to 0.336 $mg\ g^{-1}$ and Pb from 0.016 to 0.055 $mg\ g^{-1}$[22]. Studies from other regions have shown elevated levels of heavy metals in aquatic systems and sediments in the area, which are at the receiving end of effluents discharges from the urban area [23-25].

Species of marine birds as well as human beings consume fish from this creek. Because of high concentration of heavy metals in the seawater the fish presumably have accumulated concentrations of heavy metals as has been demonstrated earlier [26]. Thus the health of birds and human beings is likely to be affected indirectly by the high concentration of heavy metals in seawater.

Cluster Analysis

In order to classify the samples and to draw their similarities, cluster analysis was performed. The result of cluster analysis is a dendrogram (Fig. 2). The dendrogram exhibits close similarity (linkage) of industrial waste (Site 1) samples with that of domestic waste (Site 2). These two types of effluents have many characteristics in common, including medium levels of TSS, salinity, BOD_5, PO_4, TKN, Pb and low level of Ni and Zn. The two seawater samples Rehri Creek (Site 3) and Lath Basti (Site 5) together form a small group, characterized by medium pH, high As, Cr and high to medium Ni and Zn. Cattle colony waste (Site 4) samples differs considerably from the rest of the samples. It differs from others in high levels of TSS, COD, BOD_5, Organic matter, PO_4, TKN and As and low levels of Pb, Ni and Zn.

Experimental

During the study, altogether 30 samples were collected from pre-designated sites (Table-1) once in two month through out the year, 2007. Wastewater samples were collected at their outfall into the sea whereas seawater samples were collected at a distance of 3m from the shore at low tide.

At the time of collection, pH was determined and subsequently samples were brought to Institute of Environmental Studies, University of Karachi for physical and chemical analysis. BOD was determined on the day of collection of samples and for the rest of the analysis the samples were kept at 4^0C after adding 2 ml conc. H_2SO_4/L. The methods used for the analysis are as mentioned in Standard Methods for Examination of Water and Wastewater, American Public Health Association [27].

1. pH of the samples was measured immediately after collection by JENWAY 3505 pH meter.
2. TSS was determined by gravimetric analysis in which known amount of sample was filtered through the pre weighed filter paper. Filter paper was then dried at 103-105°C and then weighed. Difference in weight show TSS level in the sample [27].
3. Salinity was determined by using Inolab WTW series Cond 720 salinity meter.
4. BOD_5 was determined using 300-ml Winkler bottles. The dissolved oxygen was determined before and after incubating the sample, after appropriate dilution, at 20°C for 5 days. Alkali-azide modification method was used to ascertain BOD_5 [27].
5. COD was determined by dichromate reflux method using Hach COD reactor [27].
6. Oil and grease were determined by first extracting in n-Hexane inside a separating funnel, the extract is then evaporated at 72°C in pre weighed beaker and after evaporation the beaker was reweighed, difference in weight gives oil and grease content in water sample [27].
7. For organic matter determination 100 ml sample was first evaporated using a china dish, after evaporation the dish was dried at 103-105°C and weighed. Then dried sample was heated to 550 °C in a furnace and then cooled. The dish was then weighed and difference in weight revealed organic matter in the water sample.
8. Heavy metals (Cr, Cu, Pb, Zn and Ni) were determined by first digesting 100 ml evaporated sample in nitric acid and then analysed spectrophotometrically using atomic absorption spectrophotometer (Perkin- Elmer Analyst 700) [27].
9. Arsenic content was ascertained spectrophotometrically by Gutzeit Arsenic determination apparatus [27].
10. TKN was determined by first digesting a sample of 50 ml in Kjeldahl flask and then distilled using kjeldahl apparatus. The distillate was collected in a nesler tube having 5 ml boric acid finally TKN was ascertained colorimetrically as per method described in standard methods [27].
11. Total phosphate was determined spectrophotometrically by ascorbic acid method [27].
12. Data were analyzed using cluster analysis. Weighted pair average clustering strategy was employed using Euclidean distance as the resemblance function [28].

Conclusion

It is concluded that the entire physicochemical parameters of industrial and domestic wastewater except pH and oil and grease levels at site 2, show marked divergence from the NEQS [6]. Moreover, heavy metals found in the sediments of five sites along Rehri Creek are higher than formerly ascertained [21].

Physicochemical analyses discovered that the major source of pollution at Rehri Creek is the waste from Cattle Colony which contains a high organic content. Other major source of pollution at Rehri Creek is the effluent from injudicious discharge of untreated industrial effluents directly into the sea. This includes waste form Landhi industrial area (LIA) and Port Qasim industrial area.

It is suggested that the effluents should be treated prior to discharge and may be processed for recovery of waste materials before releasing into the sea so as to save this ecologically and economically important creek.

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