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A quantitative appraisal of Lyari river effluent, Karachi, Pakistan

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ABSTRACT

This study explores the extent and possible sources of chemical contamination in Lyari River, Karachi. During the study, samples were collected from eight different locations during pre- and post-monsoon periods. The samples were analyzed for chemical parameters and heavy metals and compared with National Environmental Quality Standards (NEQS). Among all the sites, L-8 was the most polluted site as the site represents Lyari River outfall through which the river finally merges to the Arabian Sea. The concentration of all the parameters were higher (TSS, BOD, COD, cyanide, oil and grease, phenol, Pb, Ni, Cu, Cd and Cr) compared to NEQS. The concentration of metals were in the order of Ni > Cr > Cu > Cd > Pb > As. As such, no significant differences in the concentration of pollutants were observed during the pre- and post-monsoon periods. These results suggest that the Lyari River is grossly polluted with untreated domestic and industrial effluents, which presumably contribute toxicity to the marine ecosystem.

Keywords: Lyari River; Effluent; Metals; Pollution; Toxicity

1. Introduction

Unplanned urbanization, exponential population growth and unsustainable industrialization are the major causes of water pollution in Pakistan that are congruently generating higher volumes of wastewater. The wastewater of both domestic and industrial origin is being discharged without any treatment to natural drains, sewer system or water reservoirs. It has been disappointingly noticed that the public and the private sectors, are not concentrating on the wastewater treatment practices at large scale, which have rendered the masses to suffer from water-borne ailments. The situation is more alarming in the areas close to industrial sites. Even, in the mega cities the treatment facilities are only limited. In particular, industrial wastewater pollution is not manageable in the country as very little incentives are given to the industries to treat the industrial effluents [1].

Karachi is the capital of Sindh province situated at 24°51′36′N and 67°0036′E. It is the most developed and commercial hub of industrial activities. The total area of Karachi is 3,527 km^2. According to 1998 census the population was 132,352,279 but the recent estimates reported that the total population of Karachi is more than 18 million with the density of 4,115 persons/km^2. The present urban area comprising of about 3,566 km^2, which has shown 16-fold increase in the spatial expansion since 1947 [2]. According to an estimate the number of registered industrial units is more than 10,000 (and a sizeable number is in informal sector) producing food, pharmaceutical, chemical, fabric, paints, oil, steel and paper products. Apart from a few international corporations, which have established waste treatment facilities, virtually none of the industrial unit has any waste treatment facility. Most of the untreated domestic and industrial effluent is dumped into the Arabian Sea through Lyari and Malir Rivers. Karachi

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is divided into four industrial regions that are LITE (Landhi Industrial Trading Estate) in the east, HITE (Hub Industrial Trading Estate) between Karachi and Gadani in the west and SITE (Sindh Industrial Trading Estate) in the north.

Karachi city generates more than 350 MGD of domestic and industrial waste, of which only 90 MGD (less than 30% of the total waste generated) is partially treated daily at three waste water treatment plants [3]. These treatment plants are located in SITE town called TP-1 (Sher Shah) in Jamshed Town called TP-2 (Mahmoodabad) and in Mauripur called TP-3. TP-1 and TP-2 were built in 1960. TP-3 was commissioned in 1998, which is based on waste stabilization pond treatment technology. These ponds are working at about 50% of their designed capacity. The remaining untreated wastewater (70%) is dumped in the coastal area through Lyari and Malir rivers and from streams and drainages [4,5]. The coast of Karachi is now overwhelmed with pollution because of the contamination of industrial discharge, port, municipal, and transportation activities in the area [6–8]. It has been reported that 135 Km long coastline in Karachi is the most affected area along the coast of Pakistan [9]. Mashiatullah et al. [10] estimated that 1,500 ton/d BOD (Biochemical Oxygen Demand) load is added by these industries along with inorganic pollutants that is exceedingly higher in comparison with WHO standards [11].

Karachi basin is drained by two major rivers namely Malir and Lyari with catchment areas of 2,051 and 7,045 km^2, respectively [12]. As there is no more fresh water in these rivers, they are merely used for (i) dumping of garbage and industrial waste, (ii) cattle yard waste, (iii) laundry effluent, (iv) waste from unauthorized factories, (v) agriculture wastes and (vi) domestic wastewater from human settlements. Throughout the year Malir and Lyari Rivers, serve as dumping sites for the discharge of liquid and solid waste of industrial and domestic origin [13]. Lyari River is the largest watercourse flowing through urban Karachi, which was largely a seasonal river but now has become a sewer for the adjoining industrial setup and the human settlements [14]. Uncontrolled discharge of Lyari river effluent is responsible for serious environmental implications of Karachi coast. The present investigation aimed at monitoring and demonstrating the extent of pollution in Lyari River. The important causal factors of deteriorating water quality are exposed by means of multivariate analysis including principal component analysis and cluster analysis.

2. Materials and methods

2.1. Study area

Lyari River is about 50 km long, which up to 1950's had clean water [15]. The river has very mild slope in the outfall reaches touching almost zero level at the downstream of Mauripur road bridge. The flow in the river is very much influenced by the diurnal rise and fall of the tides. It carries highly contaminated wastewater from the north and west of the city and industrial effluents from SITE and the industrial area of North Karachi and Federal B Area and finally dumps it into the Arabian Sea at Manora channel where it remain stationary during low tide [14]. At present more than 50 squatter settlements are located along both the banks of Lyari river accommodating approximately 0.8 million people. These unauthorized encroachments create obstruction in the flow of river water. Ultimately, the water level increases and storm water drains discharge into Lyari River that overflows.

2.2. Sampling

During the study, 16 samples of wastewater were collected from 08 pre-designated sites. The samples were collected during pre-monsoon (January to May 2012) and post-monsoon periods (September to December 2012). Sites of sample collection are given in Table 1.

Table 1
Sampling sites of Lyari River

Sampling site	Coordinates	Site adjacent to	Salient features of the site
L-1	25°1′34.42″N 67°5′2.62″E	Lyari Basti bridge	Start of Lyari river Domestic wastewater
L-2	24°56′43.92″N 67°5′15.23″E	Sohrab goth bridge	Waste water from north Karachi and Federal B area industrial estate
L-3	24°55′43.69″N 67°5′17.38″E	Rashid Minhas Road bridge	Waste water of both domestic and industrial origin
L-4	24°54′20.33″N 67°3′49.29″E	Sir Shah Muhammad Suleman Road bridge Near Hasan square	Waste water of both domestic and industrial origin with high flow rate
L-5	24°53′56.98″N 67°3′34.12″E	Syed Altaf Ali Road bridge	Domestic waste from Liauqatabad
L-6	24°53′33.38″N 67°2′35.44″E	Teen hati bridge	Cottage industries and industrial waste
L-7	24°53′23.76″N 67°1′52.98″E	Lasbella bridge	Cottage industries and industrial waste
L-8	24°52′18.23″N 66°58′33.03″E	Mauripur road bridge	Cottage industries and industrial waste

Effluent samples of Lyari river were collected using Niskin bottle from the surface (approximately 10 cm) at the area approachable by walk. For the collection of samples for physical and chemical parameters white plastic containers of 2 L capacity were used. The samples were collected in a way to avoid floating materials. A portion of each sample was appropriately preserved for examination according to the procedures outlined in Standard Methods for the Examination of Water and Wastewater [16]. These samples were grab collection, taken from the pre-designated locations as mentioned in Fig. 1.

2.2.1. Physicochemical parameters

The physical parameters of Lyari River tested were, pH and Dissolved Oxygen (DO). pH of the samples was determined using HACH sensation 156 multi parameter dissolved oxygen meter. Dissolved oxygen was determined using Jenway 630i dissolved oxygen meter. The DO probe was immersed in the sample stream to an adequate depth and in a manner to ensure sufficient sample movement across the probe-sensing element. The above mentioned parameters were determined onsite.

The biochemical and chemical parameters tested were (i) BOD_5 (biochemical oxygen demand) (ii) COD (chemical oxygen demand) (iii) TSS (total suspended solids) (iv) cyanide (v) oil and grease (n-hexane extract), (vii) phenol (viii) phosphate and (ix) TKN (total Kjeldahl nitrogen).

BOD was measured using azide modification and COD was ascertained by dichromate reflux method using HACH COD reactor. Cyanide was measured by distillation method described in using Drechsel gas washing bottle. Gravimetric analysis was applied for the estimation of oil and grease (n-Hexane extract) and TSS. Phenol was determined by the direct photometric method while nutrient parameters such as TKN and Phosphate were estimated by Kjeldhal method and ascorbic acid method, respectively. All the parameters mentioned above were analyzed by the methods in accordance with Standard Methods for the Examination of Water and Wastewater [16].

2.3. Statistical analysis

Statistical analysis was performed with the objective of summarizing the univariate data by descriptive statistics and the multivariate data to unravel the important dimensions of pollution inherent in the data structure, while cluster analysis was employed to seek the underlying group structure associated with the data matrix. This analysis was performed through STATISTICA (99 edition) software. Descriptive statistics were computed for each of the variables. PCA (Principal component analysis) and cluster analysis were also applied on the normalized data sets of above mentioned variables of different sites using the above mentioned software. For cluster analysis Wards method was employed with Euclidean distance as the resemblance function.

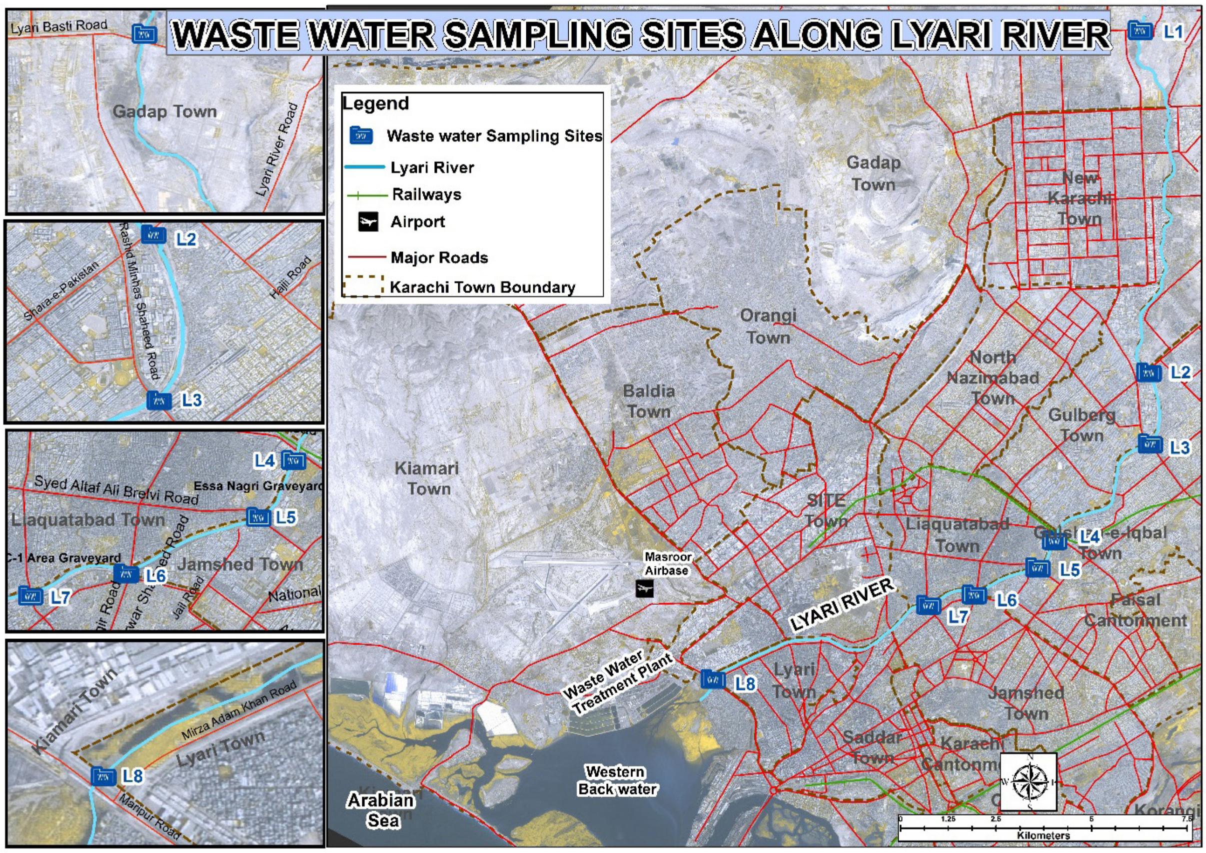

Fig. 1. Sites of samples collection.

3. Results and discussion

3.1. Physicochemical analysis

The results of pre- and post-monsoon are presented in Tables 2 and 3. The mean pH of the samples during pre- and post-monsoon were 7.61 and 7.5, respectively. The minimum pH values during both the periods were at L-1 (pH 7.2) while the maximum values were for L-2 and L-3 (7.8 and 7.9). L-1 represents the site from where the Lyari river originates whereas L-2 and L-3 are the sites through which the wastewater from North Karachi and Federal B Area industrial zone is dumped into the river. These are the two industrial areas where most of the textile and hosiery industries are located. Textile industries effluents generally have alkaline pH values.

The mean concentration of DO in Lyari river wastewater samples during the two phases were 1.28 and 2.20 mg/l, respectively. This means that DO after monsoon increased slightly. The minimum DO value at pre-monsoon was found at L-3 (0.8 mg/l) while in post monsoon it was 1.8 mg/l at L-5. In fact, these sites seem to be heavily polluted from untreated wastewater of domestic origin and that of North Karachi industrial area. Interestingly, the maximum DO value recorded was at L-1 and L-8 (Pre- and post-monsoon). L-1 is the site, which is receiving wastewater only of

Table 2
Descriptive statistics of physicochemical and metals characteristics of Lyari river during pre-monsoon period

Parameters mg/l	Mean	Med.	Min.	Max.	Std. dev.	Std. error	NEQS Into Sea
pH	7.61	7.65	7.20	7.90	0.24	0.08	6–9
DO	1.28	1.20	0.80	2.20	0.42	0.15	NA
TSS	888	915	546	1,064	169	60.03	200
BOD_5	277	267	229	356	44	15.75	80
COD	2,215	2,120	1,654	3,216	486	171	400
Phosphate	4.51	4.84	1.32	5.82	1.38	0.49	NA
TKN	51	50	38	62	7.96	2.82	NA
CN	1.46	1.28	1.13	1.98	0.35	0.12	1.0
Oil and grease	82.13	84	54	104	16.28	5.76	10
Phenol	2.65	2.66	1.27	3.86	0.80	0.28	0.3
As	0.46	0.48	0.22	0.63	0.13	0.04	1.0
Pb	5.13	5.18	3.49	6.47	0.88	0.31	0.5
Ni	16.91	16.84	14.76	20.36	1.76	0.62	1.0
Cu	8.07	8.65	3.30	10.63	2.30	0.81	1.0
Cd	5.46	5.79	4.03	7.11	1.18	0.42	0.1
Cr	16.52	16.78	11.33	19.32	2.47	0.87	1.0

Table 3
Descriptive statistics of physicochemical and metals characteristics of Lyari river during post-monsoon period

Parameters mg/l	Mean	Med.	Min.	Max.	Std. dev.	Std. error	NEQS
pH	7.50	7.45	7.20	7.80	0.21	0.07	6–9
DO	2.20	2.05	1.80	2.90	0.42	0.15	NA
TSS	613.50	596	459	785	93.98	33.23	200
BOD	236.63	244	145	278	43.11	15.24	80
COD	1,495	1,489	1,241	1,834	200.33	70.83	400
Phosphate	2.14	2.30	0.98	2.56	0.49	0.17	NA
TKN	33.63	32.00	21.00	54.00	11.12	3.93	NA
CN	0.92	1.05	0.35	1.22	0.30	0.10	1.0
Oil and grease	62.75	56.50	46.00	98.00	16.25	5.75	10
Phenol	0.57	0.57	0.36	0.95	0.18	0.06	0.3
As	0.36	0.37	0.16	0.52	0.14	0.05	1.0
Pb	4.48	4.71	2.85	6.12	1.16	0.41	0.5
Ni	15.58	14.94	13.31	19.61	2.10	0.74	1.0
Cu	11.00	10.95	8.35	13.54	1.72	0.61	1.0
Cd	4.79	4.95	3.21	6.12	1.04	0.37	0.1
Cr	14.34	14.34	12.58	15.96	1.29	0.46	1.0

domestic origin. While L-8 represents the site where the maximum flow could be seen which is responsible for dissolution of atmospheric oxygen. The typical sewage like smell all along the Lyari River indicates high organic load, which is responsible for creating anoxic conditions. No significant variation pertaining to DO concentration was recorded during the two periods. Low DO concentrations could be due to high BOD values which indicate heavy stress on the ecosystem [17]. Allan et al. [18] reported that reduced DO levels significantly increased the acute toxicity of ammonia to *Penaeus monodon* (leader prawns). In general, DO at all sampling stations during the two study periods remained less than 3.0 mg/l. It can be argued that the river is facing hypoxic condition which normally occurs when DO concentration is <2.0 mg/l [19]. Lower DO (<4.0 mg/l) occurred mainly in summer in coastal waters and estuaries [20]. Khan et al. [21] also reported similar values of DO of Lyari river effluent.

All water bodies carry some suspended solids (SS) under normal conditions [22]. Nevertheless, increased SS concentration may cause variation in physical, chemical and biological properties of the water body. Variation in temperature, filling of water reservoirs through the accumulation of solids and reduced penetration of light are associated with physical change which depreciates aesthetic quality of water [23]. Chemical variations may cause the release of nutrients, heavy metals and pesticides [24,25] in to the aquatic system. Moreover, having high organic content these SS (decaying plant and animal matter) can reduce the levels of DO in water, producing hypoxic conditions detrimental to fishes and other aquatic life forms. The mean value of SS was relatively high during pre-monsoon season (888 mg/l) compared to post monsoon (613.5 mg/). SS of biological origin have a propensity to increase the BOD. High concentration of SS prevents the entry of light into the water, which may damage submerged vegetation because of limited photosynthesis owing to reduced light intensity reaching the deeper water. The dead vegetation will be biodegraded by the microorganisms that will consume more oxygen thus producing suffocation detrimental to aquatic fauna. High SS absorbed more heat and thus intensify surface water temperature [26]. During high hydraulic load the SS concentration is relatively higher [27]. However, in the present study TSS concentration was low during high hydraulic flow after post monsoon.

The major indices mostly used to govern the organic pollution in an aqueous system are BOD_5 (biochemical oxygen demand), COD (chemical oxygen demand), and TOC (total organic carbon). BOD represents organic pollution while COD characterizes both organic and inorganic pollution load, respectively in the wastewater discharges [28].

The mean BOD_5 value of Lyari river samples during pre-monsoon was 277 mg/l while that of post monsoon was 236.6 mg/l. The maximum BOD value was recorded at L-4 (pre-monsoon) and L-6 (post-monsoon). L-4 represents the site near Hassan square bridge. This is the site, which receive purely domestic wastewater. From L-4 the flow of river considerably increases due to steep gradient. L-6 receives wastewater mainly from cottage industries. These industries comprise of plastic recycling, hosiery manufacturing, paint industry, battery smelting industries. These industries are located at the informal sector, as their industrial units do not pay taxes. Moreover, the industrial operations are so polluting that there is a constant conflict between the industry owners and local residents. Khan et al. [29] reported the maximum BOD value of 229 mg/l of Lyari River. The results of Khan et al. [29] are corroborated with the present findings. High BOD level is an indication of organic pollution. The BOD concentration of Lyari River samples were relatively higher from the viewpoint of NEQS (National Environmental Quality Standards of Government of Pakistan; 80 mg/l). Another factor which could contribute to high BOD levels is the indiscriminate dumping of municipal solid waste, which undergoes microbial decomposition and thus increase organic load. A high BOD level decrease DO concentration as oxygen is utilized by the microorganisms producing anoxic condition harmful to marine life.

Jin et al. [30] are of the opinion that there is no obvious linear relationship exists between BOD and COD. However, in estuary having sewage contamination, a linear correlation is likely to occur between BOD and COD. In the present study, there are multiple sources of untreated domestic and industrial wastewater that ultimately finds its way into the Lyari River. Elevated COD values in the River can largely be attributed to continuous accumulation of toxic chemicals. Comparison of the results of COD for pre-and post-monsoon clearly reveled that COD of Lyari river samples was relatively higher during pre-monsoon. Low COD results after monsoon may be due to the dilution factor because of high hydraulic load. The highest COD value was recorded at L-8 (3,216 mg/l). This is the site where Lyari River forms an estuary and finally merges into the Arabian Sea. The minimum value nonetheless was recorded at L-1 from where the river starts. In general, the COD values are higher than NEQS (150 mg/L). However, according to NEQS (2000) the standard is 400 mg/l if the effluent is discharged into the sea. The present results are consistent with the findings of Khan et al. [29].

The environment of coastal lagoon is characterized by high inputs of nutrients responsible for high rates of primary productivity [31]. After weathering of clays or detritus particles, phosphate ions are rapidly absorbed, and produce insoluble forms of Al, Ca or Fe phosphates that can be solubilized by bacteria and Fungi [32]. Boto [33] reported that the concentration of 31 µg/l is considered as low. The concentration of phosphate in Lyari river wastewater samples during pre-monsoon ranged between 1.32 (L-1) and 5.82 (L-4) mg/l. The concentration of phosphate was relatively lower during post monsoon (0.98–2.56 mg/l). The presence of phosphates is mainly attributed to the use of detergents. In fact, phosphate is the main contributor of eutrophication in water bodies. The mechanism of flow of phosphorus, between water and sediments is an intricate phenomenon which is influenced by physical, chemical and biological mechanisms and depends on temperature, pH and redox potential [34]. Mesnage and Picot [35] reported that in the Mediterranean coastal lagoons eutrophication in summer is mainly due to the excessive inputs of nutrients (i.e., N and P) where the sediments serve as a reservoir of phosphate. In the present study heavy algal blooms were observed at Lyari river outfall (L-8) that represents eutrophic condition mainly due to ample input of phosphates and nitrates from untreated effluent.

European Environmental Agency (EEA) stated that nutrients (phosphorus and nitrogen), chlorophyll-a and oxygen concentrations are eutrophication variables [36]. It may be noticed that Lyari River forms a lagoon before entering into the Arabian sea. The enrichment of coastal lagoons however, varies with the nature of the nutrients [37]. In Rhode Island lagoons, the augmentation involves elevated inputs mainly of dissolved inorganic nitrogen (DIN) [38]. Most of the DIN enters as nitrate In Buttermilk Bay [39] while sometimes as ammonium or in the form of urea. Caraco et al. [40] and Howarth [41] reported that N is the nutrient that possibly impedes phytoplankton production in temperate marine systems. In shallow coastal lagoons as in the present case the predominant form of inorganic nitrogen is ammonium [42]. In the sediments there is lesser diffusion of oxygen that primarily reduces rates of nitrification that exhibits low concentrations of nitrates in the sediments. In the present study, the focus was on the available nitrogen in the form of total Kjedahl nitrogen (TKN). The mean value of TKN during pre-monsoon was 51 mg/l while that of post monsoon it was 33.63 mg/l. The highest TKN value was recorded at L-3 during pre-monsoon (62 mg/L). High TKN values could also be attributed due to flushing of organic matter originated from anthropogenic sources.

Cyanide is widely used in electroplating, metal refining, organic chemical production and many other processes [43]. Cyanide is toxic to human when inhaled, ingested or absorbed by the skin. It has been reported that acute toxicity to cyanide may cause death within 96 hours at a concentration of 0.1–0.3 mg/l [44]. The mean cyanide concentration of Lyari river effluent during pre-monsoon was found to be 1.46 mg/l while that of post monsoon the mean value was relatively low (0.92 mg/l). According to NEQS the maximum allowable limit is 1.0 mg/l. The lower cyanide values may be attributed to the dilution factor after the rain. Highest concentration of Cynaide was found at L-7 which is located at Lasbella Bridge. Most of the cottage industries are located in the vicinity of this site. This site also receives untreated effluent form Sher Shah industrial area. These industries are located both formal and informal sectors. The concentration of cyanide ranging between 0.005 and 0.01 mg/l has adverse effect on fish in the form of growth retardation, decreased metabolic rate, reduced swimming performance, reproduction impairment and elevated respiratory rates [45]. This could be mainly because cyanide restricts oxygen metabolism by obstructing cytochrome oxidase. Continuous accumulation of cyanide in to the sea through Lyari river effluent is alarming as it would be responsible for causing detrimental effect to the marine fisheries.

Oil and grease are known to hinder the dissolution of atmospheric oxygen in the water thereby creating anoxious conditions. Oil film on the water surface reduces the amount of dissolved oxygen (DO) which affects both aquatic life forms and microbial activities. The chemical components that are present in different types of oil are more toxic rather than oil itself. Out of these components, the most important are petroleum hydrocarbons that occur worldwide both in liquid and gaseous phase in the form of organic compounds. The addition of significant quantities of petroleum products 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. Oil and grease also tend to sink to the bottom and continue to deposit there where they undergo relatively slow microbial degradation due to anoxic environment. The average oil and grease concentration during the two phases were 82.13 and 62.75 mg/l, respectively. Maximum allowable limit as per NEQS (2000) is 10 mg/l. Highest concentration was found at Lyari river outfall (L-8). This would mean that the natural system of removal of oil through the process of photo-oxidation, sedimentation and biodegradation is not working efficiently because of anoxic condition. Biodegradation rate of oil is hard to foresee due to the intricacy of the environment, while biodegradation rates are also dependent on the components of oil and petroleum products [46]. Distribution of oil in marine environment may cause an increased toxicity to marine life forms that could be lethal [47,48].

Phenol is often considered as one of the major component of industrial wastewater particularly chemical industry. In addition to this it is also present in appreciable quantity in the discharges of metal, pharmaceutical, paint, varnish and textile industries [49]. The information about the phenol toxicity at ecosystem level is limited [50]. It has been reported that photolysis is the primary transformation process of the polychlorinated phenols [51]. They also reported that summer photolysis and microbial degradation rates are higher than those of winter. According to NEQS (2000) the maximum desirable limit for phenol is 0.1 mg/l. whereas, the mean phenol values of pre- and post-monsoon periods were 2.65 and 0.57 mg/l. that are toxic to marine life forms. Relatively lower concentration of phenol after post monsoon may be attributed to heavy influx of water after rain. The highest concentration of phenol was observed at L-8 (Lyari river outfall at Mauripur road bridge). Phenol is detrimental to marine life forms even at concentration as low as 5 μg/l [49]. Phenols once enter in fish body mainly affect the metabolism, survival, growth and reproductive system [52–54].

Arsenic concentration in aquatic system varies greatly. Arsenic is commonly used as a pesticide, rodenticide, fungicide, and wood preservative [55]. Microorganisms have the tendency to convert methylate inorganic arsenic to methane-arsenic acid and dimethyl arsenic acid (cacodlylic acid); having much less toxicity the latter is converted in to volatile methylarsines in soil. The results of As concentration in Lyari river effluent is given in Table 2. The concentration of As is as low as 0.22 mg/l to as high as 0.63 mg/l during pre-monsoon period. While in post monsoon season the concentration fluctuated between 0.16 and 0.52 mg/l. The highest concentration of As was recorded at L-8 (Lyari river out fall). Still the As values are with in the permissible limit as per NEQS (1.0 mg/l). The origin of arsenic is from the effluent generated from the industries located both in formal and informal sectors. Mansoor and Mirza [56] reported maximum concentration of 0.252 mg/l of As in Lyari river effluent. Khan et al. [21] also reported similar values of As from the Lyari river effluent.

Lead in wastewater originated from electro-plating, lead smelting and metal- finishing industries, etc and responsible for severe toxicity to the human beings [57,58]. Some of these industries are located in SITE and Federal B Area industrial estate. The average concentration of Pb during pre- monsoon was 5.13 mg/l and 4.48 mg/l during post monsoon period. Maximum concentration was reported at L-8. Pb concentration was extremely higher as compared to

NEQS (0.5 mg/l). The principle source of Pb is the industrial discharges originated from different industrial estate of which paint industries effluent has much high level of Pb. Khan et al. [21] also reported elevated values of Pb from Lyari river effluent.

Cadmium and Nickel are toxic metals mainly originated from electro plating, battery smelting, phosphate fertilizers, pigments, alloys and stabilizers [59]. Out of these industries, only plating and cadmium–nickel battery industries are located at some places in the study area. Madoni [60] reported that nickel is present approximately 3.8×10^6 kg/ y concentrations from industrial and municipal discharges mainly from electroplating wastes and steel mill. Nickel and its compounds are carcinogenic [61], but its toxicity to marine life forms is not well recorded. The average concentration of Ni during pre- and post-monsoon period was 16.91 and 15.58 mg/l, respectively found at L-8. The mean Cd concentration varies from 5.46 to 4.79 mg/l during the both periods, respectively. According to NEQS the maximum allowable limit for Cd and Ni is 0.1 and 1.0 mg/l, respectively. This would means that the concentration of Ni and Cd is extremely higher as compared to NEQS. Their continuous accumulation in to the sea is detrimental to marine biota.

Copper in the waste discharges may originated from mining operations, electronic industries, tanneries, electroplating and petrochemical and textile industries [62,63]. Copper (Cu) is an vital trace element for human health and present in highest concentrations in the liver, nuts and legume [64,65]. Cu causes liver cirrhosis and damage to kidney, brain and other organs [66]. The mean Cu concentration during, pre- and post-monsoon periods are 8.07 and 11.0 mg/l. The highest concentration was found at L-8. The concentration of Cu was remarkably higher as compared to NEQS limits (1.0 mg/l).

Chromium is widely used in the leather tanning, fungicides, ceramic industry, glass industry, photography, chrome plating, and corrosion control. The natural Cr concentration of surface waters is about 0.5–2 μg/l. The results of Cr analysis of Lyari River are presented in Table 2. The average Cr concentration during pre- and post-monsoon periods were 16.52 and 14.34 mg/l, respectively. According to NEQS the maximum allowable concentration is 1.0 mg/l. The highest concentration was observed at L-7. Exceptionally high concentration in the Lyari river effluent is mainly from ceramic, glass industry and tanneries located at SITE area. These industries are discharging their effluent without any treatment. The continuous accumulation of Cr in the sea through Lyari river is potentially hazardous to the marine life forms. Cr can also be accumulated in fishes through bioaccumulation from where it enters into the food chain and induces toxicity in humans.

3.2. Statistical analysis

The dendogram derived from pre- and post-monsoon data of the water quality of Lyari river are shown in Figs. 2 and 3, respectively.

The dendogram obtained for pre-monsoon data (Fig. 2) shows three distinct groups of which group A and C each comprise of solitary sample, while the large group B consists of 6 samples. Sample L-8 (group A) represents the outfall of

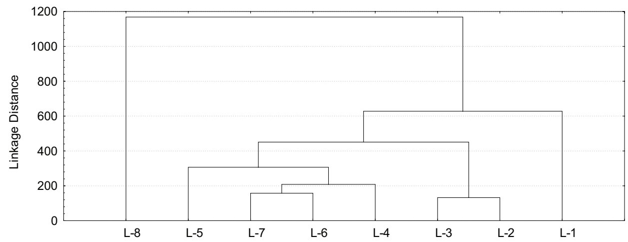

Fig. 2. Dendogram derived from Ward's method of eight sites based on physical, chemical and metal analysis of water samples of Lyari River during Pre-monsoon.

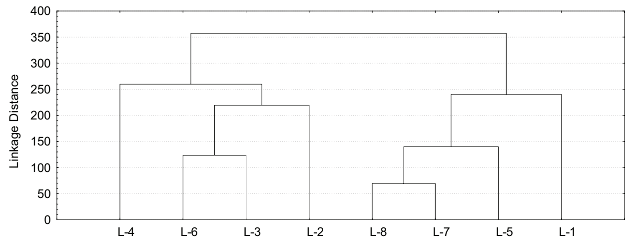

Fig. 3. Dendogram derived from Ward's method of eight sites based on physical, chemical and metal analysis of water samples of Lyari River during Post-monsoon.

Lyari river with high values of BOD, COD, Oil and grease, TSS, Phenol, Pb, Ni and As while low value for DO. On the other hand group B comprises of samples which have high pH and phenol, medium DO, BOD, COD, Oil and grease, Pb and Ni but low DO. Whilst group C represents a relatively better quality as compared to groups A and B. It has neutral pH, relative higher DO and less BOD, COD and Pb.

The dendogram pertaining to post-monsoon data (Fig. 3) discloses two distinct groups A and B. group A that comprises of 4 samples represent relatively greater BOD, COD, phenol, As and oil and grease. Group B is characterized by relatively lower levels of BOD, COD and pH. While the values for TKN, CN, oil and grease and all the heavy metals are at a higher level.

Principal component analysis (PCA) ordination results for pre- and post- monsoon are reported in Tables 4 and 5 and Figs. 4 and 5, respectively. Table 4 shows that first 3 components together explained 84.67% of the total variance inherent in the data matrix. The first component that accounted for 49.46% of the total variance is mainly a function of CN, pH, Ni, Cd and TKN while the second PCA component that explained 24.05% of the total variance was chiefly regulated by BOD, COD, Oil and grease, As and Pb. Third component with 11.15% explained variance is largely controlled by CN, TSS, Cu, PO_4 and phenol. To some extent the first component represents water chemistry while second largely depicts the controlling influence of pollution. Third component is apparently a mixture of the first two components. The three-dimensional ordination diagram shows the grouping obtained in cluster analysis.

Table 5 shows that the first three components accounted for 83.20% of the total variance contained in the data matrix.

Table 4
Results of PCA of physical, chemical and metals analysis of water samples of Lyari River during pre-monsoon

Component	Eigenvalue	Percentage variance	Cumulative percentage variance	First 5 eigenvector coefficients	Associated variables
1	7.914903	49.46814	49.46814	–0.066189	CN
				–0.044931	pH
				–0.038554	Ni
				0.031024	Cd
				–0.017948	TKN
2	3.849010	24.05631	73.52446	0.047678	COD
				0.043843	Pb
				–0.038117	BOD
				–0.036691	Oil and Grease
				0.025043	As
3	1.784480	11.15300	84.67746	–0.034066	CN
				0.032663	TSS
				0.012292	Cu
				0.011950	Phosphate
				0.000158	Phenol

Table 5
Results of PCA of physical, chemical and metals analysis of water samples of Lyari river during post-monsoon

Component	Eigenvalue	Percentage variance	Cumulative percentage variance	First 5 eigenvector coefficients	Associated variables
1	8.445510	52.78444	52.78444	0.055135	Phosphate
				0.042954	CN
				–0.012159	COD
				–0.011586	pH
				0.005833	TSS
2	3.428721	21.42951	74.21395	0.021022	Cd
				0.020555	Cu
				0.004373	TKN
				0.003542	Pb
				0.003027	Cr
3	1.438008	8.98755	83.20150	0.113406	Cu
				–0.063102	Oil and Grease
				–0.031151	Ni
				–0.028517	Phosphate
				–0.011478	COD

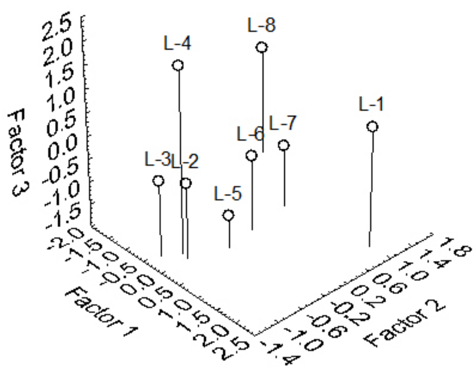

Fig. 4. Principal component analysis ordination (3D) of physical, chemical and metal analysis of water samples of Lyari River during Pre-monsoon.

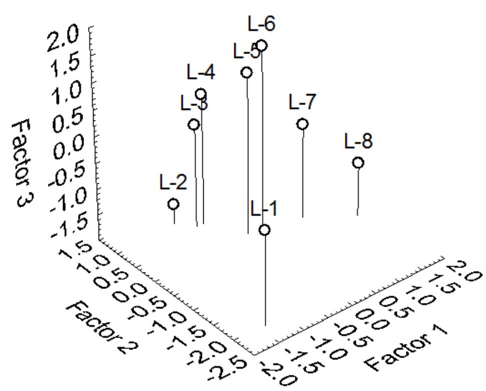

Fig. 5. Principal component analysis ordination (3D) of physical, chemical and metal analysis of water samples of Lyari River during Post-monsoon.

The first component that retains 52.78% of the total variability is basically controlled by PO_4, CN, COD, pH and TSS. The second component of PCA that accounted for 21.42% of the total variance is primarily a function of Cd, Cu, TKN, Pb and Cr. The third component with 8.98% of the total variance is governed by Cu, Oil and grease, Ni, PO_4 and COD. Again the first component represents the water chemistry while second component largely represents the influence of heavy metals. The third component represents both the properties related to chemical groups and heavy metals.

4. Conclusions

An environmental pollution survey of Lyari river disclosed that the Lyari river contains a heavy organic load which depletes the desirable DO concentration requires to sustain the riverine ecosystem. The natural system of removal of oil through the process of photo oxidation, sedimentation and biodegradation is also not working efficiently thereby creating anoxic condition. The levels of cyanide and phenols are quite alarming which are detrimental to marine flora and fauna. Heavy metal particularly Cu, Cd, Pb and Ni were also exceptionally higher in the effluent samples. The study thus concluded that Lyari river is continuously receiving untreated domestic and industrial waste water which finally empties in the Arabian sea responsible for the deterioration of valuable marine life. Degradation of marine fisheries is responsible for serious economic and social consequences.

This study further disclosed that the capacity of the municipal government of Karachi to treat the wastewater is only very limited (30%). The remaining 70% is dumped in to the coastal area therefore, the coast of Karachi is now overwhelmed with pollution because of the contamination of industrial, port, municipal, and transportation activities in the area. It is suggested that that the municipal capacity be further strengthen and new low cost wastewater treatment system be established to treat the huge amount of wastewater that is considered as economic burden. Moreover, the economic potential of the treated effluent has not been fully valued in Pakistan as the use of treated wastewater can avoid environmental problems of discarding it into adjacent water bodies. Therefore, the considerable quantities of fresh water can be saved for human consumption.

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