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Water quality appraisal of Keti Bandar and Shah Bandar creeks of Indus delta, Sindh, Pakistan

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ABSTRACT

The present research investigation deals with the assessment of pollution status in the Indus delta creek system. This manuscript advocates the physicochemical, bacteriological characteristics and heavy metal pollution in the creek system. In the present investigation, the pH, salinity, dissolved oxygen (DO), biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), chlorophyll, cyanide, oil and grease, total phosphate, phenol, Kjeldahl nitrogen and total organic carbon (TOC) values were recorded from 36 sampling sites during 6 field surveys conducted in 2011–2013. The creek water samples were also analyzed for their heavy metal contents (As, Cd, Cr, Pb, Ni and Zn). The bacteriological parameters included in the study were total coliform count (TCC), total fecal coliform count (TFC), and total fecal streptococci (TFS). These parameters were determined as per methods described in reference [12]. Salinity of water samples ranged between 15 and 32 ‰ while pH ranged from 7.2 to 7.6. High salinity values indicated the progression of seawater into the creek system. The mean DO was low with a range of 4.2–5.7 mg/L. Low DO concentration was due to high BOD_5 (range 10–78 mg/L) while COD ranged from 320 to 1,334 mg/L. High BOD_5 load is mainly due to organic pollution coming from nearby human settlements. The mean chlorophyll-a content was 0.114 mg/L. Interestingly, higher chlorophyll-a concentration was observed near the mangroves area. The mean cyanide concentration was high, though the source of cyanide could not be traced that needs further study. Oil and grease content of water was also substantial, mainly originated from faulty boats operated in the area. Excessive concentration of oil and grease could be deleterious to marine life forms. The concentration of phosphate ranged between 2.1 and 4.6 mg/L mainly attributed to the agriculture runoff. Phenol concentration was not high (0.01–0.08 mg/L) and, therefore, could not be responsible for adverse environmental implications. The mean concentrations of total Kjeldahl nitrogen and TOC were 59.27 and 4.97 mg/L, respectively. The concentrations of heavy metals in the samples were found to be in the order Zn > Ni > Pb > As > Cr > Cd. The bacterial load was exceptionally higher in all the samples in terms of organisms of public health importance that is mainly attributed to domestic wastewater originated from nearby squatter settlements. In essence, the present study disclosed that the creeks of Indus delta are likely to be polluted mainly because of anthropogenic sources. The continuous accumulation of pollutants in the creek area may have severe ecological and health implications.

Keywords: River Indus; Pollution; Anthropogenic; Heavy metal; Public health

1. Introduction

River Indus is the lifeline of Pakistan, which provides 80% of the water consumed in the country [1]. The river originates from Tibetan Plateau, and 70% of the water is coming from glaciers melt that accounts for greatest area (>20,000 km^2) of perennial ice outside the polar regions [2]. The total drainage area of the river is 1,165,500 km^2, out of which 692,700 km^2 is in Pakistan [3]. The Indus basin is one of the largest river basins in Asia, stretches over an

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area of 1 million km^2 approximately [4]. Its annual flow is 207 billion m^3. The water normally available in the river used to irrigate about 18 million ha of land [5]. WWF [6] reported that about 170 million population of the country is directly or indirectly dependent on the Indus River System.

The main stream of River Indus has not undergone much diversion from its past alignment despite several tectonic events [7,8]. However, some of the workers suggested that the river was flowing somewhat north and toward west until it occupies its present location [9].

The complex distributary system (creeks) of River Indus toward sea created the world's second largest submarine fan in the Arabian Sea [7]. The creek system of Indus covers an area of about 5,000 km^2, which finally merges into the Indus delta [10]. The major changes of the River Indus had occurred near its mouth, and the main channels shifted significantly westward four times until it occupies the present course [11]. The wide channels of eastern delta (Khar, Wari, Kajhar, Sir and Kari creeks) penetrate deep inland leading to flood during summer monsoon particularly in lower delta plain and the Rann of Kutch [7]. Because of gradual shifting and reduced flow in the river, the tributaries of River Indus are converted into tidal creeks having high salinity values. The pollution of these creeks is also a major problem affecting the delta region.

The present research focused to determine the extent of pollution in the Indus delta creek system, which is likely to be attributed to the anthropogenic activities.

2. Materials and methods

2.1. Study area

There were altogether 18 (major and minor) creeks surveyed, which are located in the two coastal subdistricts locally called as tehsils (Shah Bandar and Keti Bundar) of district Thatta in the Sindh province. District Thatta occupies an area of 17,355 km^2 (www.pbs.gov.pk). The total area of Keti Bundar is approximately 610 km^2 [6] while that of Shah Bundar is 3,074 km^2. The sites of sample collection are presented in Table 1 and Fig. 1. Out of 18 creeks, 11 are located at Shah Bundar while 7 are present at Keti Bundar area. The largest creek is Torshan creek that is approximately 34 km long.

2.2. Sample collection

During the study 36 samples of creek water were collected during 6 field surveys in 2011–2013 with different time intervals. The samples were collected using Niskin bottles by a deterministic sampling from the pre-designated locations (Table 1 and Fig. 1). Grab samples were collected at 10 cm depth, properly labeled, stored in pre-sterilized glass bottles and kept in ice box till their transportation to the Institute of Environmental Studies, University of Karachi.

2.2.1. Physical parameters

The physical parameters of creek water were tested for pH and salinity that were determined on site using Hach sensION 156 multiparameter dissolved oxygen (DO) meter.

2.2.2. Biochemical and chemical parameters

The biochemical and chemical parameters tested were: (i) biochemical oxygen demand (BOD$_5$); (ii) chemical oxygen demand (COD); (iii) chlorophyll; (iv) cyanide; (v) DO; (vi) oil and grease (*n*-hexane extract); (vii) phenol; (viii) phosphate; (ix) total Kjeldahl nitrogen (TKN) and (x) total organic carbon (TOC).

BOD was measured using azide modification and COD was ascertained by dichromate reflux method using Hach COD reactor as described in the reference [12].

Chlorophyll content of water samples was determined by filtering the sample from membrane having pore size of 0.45 μm. The membrane was homogenized using 2–3 mL 90% acetone. The homogenized sample was transferred to a centrifuge tube, and the sediment was washed with 2–3 mL acetone. The final volume was made up to 10 mL with acetone. The sample was then kept in dark at a room temperature for 10 min and centrifuged for 10 min at 5,000 rpm. The supernatant was collected in a spectrophotometer cell, and the optical density was measured at different wavelengths (750, 663, 645 and 630 nm).

Cyanide was measured by distillation method using Drechsel gas washing bottle. DO was measured on site using Hach sensION 156 multiparameter DO meter. Gravimetric analysis was applied for the estimation of oil and grease (*n*-hexane extract). Phenol and phosphate (P) were determined by direct photometric method and ascorbic acid, respectively. The analysis of TKN was performed by the distillation method. All the abovementioned parameters were analyzed as per methods given in the reference [12].

TOC was determined by using appropriate kits of Merck NOVA 60.

2.2.3. Heavy metal analysis

The samples were also analyzed for heavy metals including As, Cd, Cr, Pb, Ni and Zn using Merck NOVA 60.

2.2.4. Statistical analysis

The data were statistically analyzed using STATISTICA ('99 Edition) software (Tulsa, Oklahoma). Descriptive statistics including mean, median, minimum and maximum value, lower and upper quartile, standard deviation, standard error and skewness were computed for each of the variables. Cluster analysis and principal component analysis (PCA) were also performed using STATISTICA ('99 Edition) software (Tulsa, Oklahoma). For cluster analysis unweighted pair group method was employed.

3. Results and discussion

3.1. Physical profile of the creeks

Table 2 represents basic statistics of physical and chemical parameters of creek water samples. pH of the water samples in all the creeks ranged from 7.2 to 7.6. In general, the pH of creek water was toward alkaline side. Bouillon et al. [13] reported pH of the Godavari estuary (India) and reported that pH was higher in freshwater zone and decreased progressively in the marine end of the estuary.

Table 1
Keti Bandar and Shah Bandar creeks of Indus delta covered in the study

S#	Name of creek	Sample code	Geographic information system (GIS) coordinates	Creek length (Km)	Creek width (Avg.) (m)	Area of creek (Km^2)
1	Sattah wah creek	C-1	24°10′52.65″N, 67°54′52.99″ E	3.8	58.57	0.2225
	(Shah Bandar)	C-2	24°11′11.83″N, 67°56′2.14″ E			
2	Pakhar creek	C-3	24°11′21.54″N, 67°56′26.85″ E	6.35	172.31	1.094
	(Shah Bandar)	C-4	24°12′8.90″N, 67°57′44.28″ E			
3	Bhai wari creek	C-5	24°7′57.00″N, 67°55′38.00″ E	7.95	66.33	0.527
	(Shah Bandar)	C-6	24°6′10.21″N, 67°54′52.49″ E			
4	Ghoray wali creek	C-7	24°6′37.79″ N, 67°54′41.64″ E	9.27	318.81	2.95
	(Shah Bandar)	C-8	24°6′36.58″ N, 67°54′34.31″ E			
5	Wari creek	C-9	24°0′8.05″ N, 67°57′7.32″ E	28.63	1,215.56	34.78
	(Shah Bandar)	C-10	23°59′3.96″ N, 67°55′2.96″ E			
6	Gahar creek	C-11	24°11′45.13″ N, 67°53′11.17″ E	9.54	41.48	0.395
	(Shah Bandar)	C-12	24°10′9.87″ N, 67°52′10.66″ E			
7	Khar creek	C-13	24°9′45.00″ N, 67°54′9.00″ E	2.24	15.67	0.0351
	(Shah Bandar)	C-14	24°8′40.29″ N, 67°53′58.23″ E			
		C-16	24°15′13.51″ N, 67°49′33.89″ E			
8	Rajan shah creek	C-15	24°15′49.89″ N, 67°49′45.45″ E	4.64	175.02	0.812
	(Shah Bandar)					
9	Khado creek	C-17	24°4′27.00″ N, 67°52′29.00″ E	14.98	843.03	12.62
	(Shah Bandar)	C-18	24°0′13.22″ N, 67°51′46.82″ E			
10	Rhorro creek	C-19	24°5′18.00″ N, 67°50′34.00″ E	27.80	313.05	8.70
	(Shah Bandar)	C-20	24°4′23.02″ N, 67°48′46.92″ E			
11	Cabin creek	C-21	24°5′54.00″ N, 67°51′11.00″ E	16.69	153.54	2.56
	(Shah Bandar)	C-22	24°8′4.55″ N, 67°51′16.10″ E			
12	Chan creek	C-23	24°11′31.00″ N, 67°25′54.00″ E	23.43	795.95	18.64
	(Keti Bandar)	C-24	24°12′1.69″ N, 67°26′26.60″ E			
13	Nari creek	C-25	24°11′15.78″ N, 67°26′2.13″ E	2.65	40.80	0.108
	(Keti Bandar)	C-26	24°11′9.67″ N, 67°26′6.28″ E			
14	Kunni creek	C-27	24°10′23.15″ N, 67°25′47.14″ E	7.33	123.86	0.91
	(Keti Bandar)	C-28	24°10′10.56″ N, 67°25′31.23″ E			
15	Phaddo creek	C-29	24°9′57.85″ N, 67°25′14.75″ E	4.33	204.94	0.89
	(Keti Bandar)	C-30	24°9′36.56″ N, 67°25′15.26″ E			
16	Hajamro creek	C-31	24°8′1.66″ N, 67°25′49.66″ E	26.36	557.88	14.71
	(Keti Bandar)	C-32	24°7′45.91″ N, 67°23′9.36″ E			
17	Torshan creek	C-33	24°7′23.95″ N, 67°25′33.25″ E	34.91	504.65	17.62
	(Keti Bandar)	C-34	24°6′48.50″ N, 67°25′43.82″ E			
18	Khobar creek	C-35	24°3′12.34″ N, 67°30′29.22″ E	6.9	278	1.918
	(Keti Bandar)	C-36	24°0′19.39″ N, 67°27′27.06″ E			

The salinity values of all the samples fluctuated between 15 and 32 ‰. The lowest salinity value was of C-35 and C-36 (Khobar creek) whereas the highest salinity value was of C-28 (Kunni creek). These sampling sites were located at Keti Bundar. High salinity values indicated that seawater is extensively progressing toward the creek system of Indus delta. Wang et al. [14] reported high salinity values in the northern Arabian Sea after the event of Cyclone Gonu in 2007. Bhutta and Smedema [15] reported that the salts of marine origin present at shallow depth of the Indus delta. In addition, the Indus irrigation water has also introduced salts but this water was mostly of low salinity (200–300 ppm). Thus, the high salinity value in the creek water is mostly of marine origin. Harrison et al. [16] also reported salinity ranges from 38 to 40 ‰ during the dry season, which decreased to 32–35 ‰ during the rainy season (July and August) in creeks of Indus delta.

In general, river water in arid and semi-arid regions of the world suffer from increased salinity that is mainly due

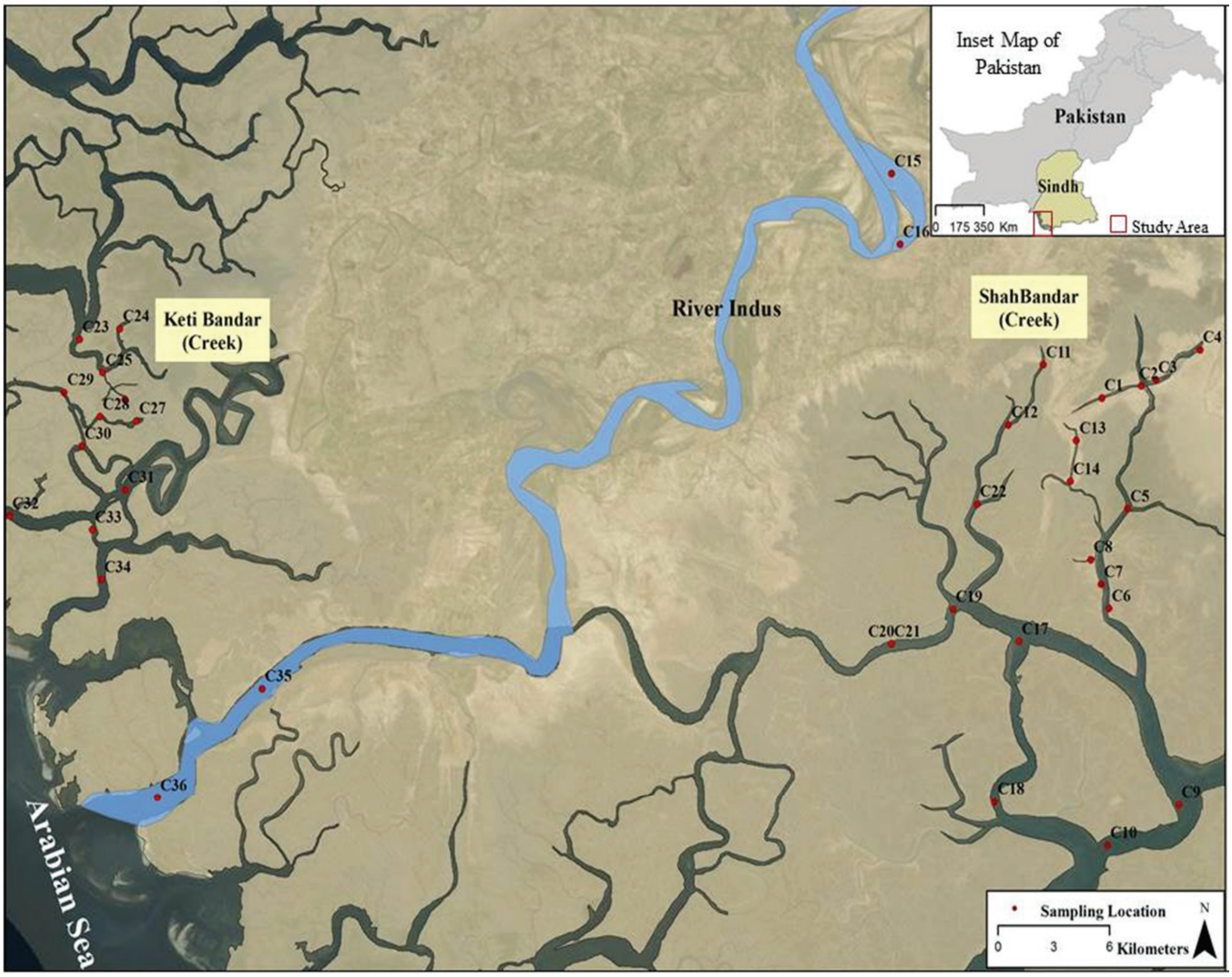

Fig. 1. Sites of sample collection.

to the fact that the drainage water from the agricultural land is returned to the river downstream. As a result, the downstream irrigated agricultural lands were affected by soil salinity [17]. This phenomenon is well known in the Indus river basin.

3.2. Chemical profile of the creeks

The mean DO concentration of creek water samples ranged between 4.2 and 5.7 mg/L. The lowest DO concentration was observed at C-17 and C-20 (Khado and Rhorro creek; 4.2 mg/L) while highest was observed at C-1 (Sattah Wah creek; 5.7 mg/L). Low DO concentrations could be due to high BOD_5 values, which indicate the stress of creek ecosystem [18]. The primary mechanism of global oxygen formation is through plant production in the sea [19]. Aerobic and anaerobic mineralization processes at water and sediment interface depletes oxygen and regenerates nutrients [20]. The circulation of nutrients can promote phytoplankton blooms and can also sustain macroalgal growth [21]. Wildish et al. [22] suggested that the upwelling and downwelling phenomena control the levels of oxygen in seawater that supplies oxygen-saturated water and removes DO deficit water. Allan et al. [23] reported that reduced DO levels significantly increased the acute toxicity of ammonia to leader prawns (*Penaeus monodon*). Out of 36 sampling sites only 26 have DO concentration less than 5.0 mg/L (C-8, C-9, C-11, C-12, C-16–C-22, C-25 and C-27–C-36). It can be argued that the creeks of Indus delta are still not facing hypoxic condition, which normally occurs when DO concentration is <2.0 mg/L [24]. Relatively higher temperature after post-monsoon also attributed in low DO concentration [18]. This was also observed in the present study. Lower DO concentrations (<4.0 mg/L) occurred largely during summer in both the estuary and adjacent coastal water [25].

The main indexes generally used to determine the organic pollution load in an aqueous system are BOD_5, COD and TOC. BOD_5 represents the biodegradable portion of the organic pollutants while COD represents the pollution load of most wastewater discharges [26].

The BOD_5 values of creek water samples ranged between 10 and 78 mg/L with a mean value of 36 mg/L. The highest BOD_5 level was recorded at C-23, which was collected from Chan creek. High BOD_5 level is an indication of organic

Table 2
Descriptive statistics of physical, chemical and bacteriological parameters of Keti Bandar and Shah Bandar creeks of Indus delta

Parameters (mg/L)	Mean	Median	Min.	Max.	Lower quartile	Upper quartile	Standard deviation	Standard error	Skewness
pH	7.286	7.3	7.2	7.6	7.2	7.3	0.1018	0.0169	1.32362
Salinity (‰)	23.361	23	15	32	18	29.5	6.0149	1.0024	0.103629
DO	4.780	4.65	4.2	5.7	4.4	5.2	0.4559	0.0759	0.590962
BOD_5	36.00	30	10	78	25.5	44	16.668	2.7780	0.778902
COD	582.08	545.5	320	1,334	424	667	221.78	36.963	1.237514
Chlorophyll	0.114	0.045	0.022	0.422	0.0405	0.096	0.1415	0.0235	1.76278
Cyanide	1.214	0.32	0.11	8.32	0.2	0.7	2.4223	0.4037	2.55539
Oil and grease	132.72	95	65	575	79	136.5	110.93	18.488	3.339172
Total phosphate	2.986	2.8	2.1	4.6	2.6	3.25	0.6071	0.1011	1.106713
Phenol	0.046	0.045	0.01	0.08	0.036	0.0545	0.0153	0.0025	0.115651
TKN	59.277	60.35	31.9	79.2	50.8	67.95	12.609	2.1016	–0.40867
TOC	4.970	5.195	2.27	6.75	4.25	5.525	1.0506	0.1751	–0.26292
As	0.035	0.033	0.01	0.08	0.021	0.0515	0.0189	0.0031	0.629259
Cd	0.013	0.0135	0.001	0.031	0.002	0.025	0.0116	0.0019	0.152103
Cr	0.027	0.028	0.011	0.046	0.0215	0.034	0.0096	0.0016	0.018241
Pb	0.577	0.5875	0.316	0.891	0.5155	0.6435	0.1194	0.01991	0.21386
Ni	0.628	0.63	0.45	0.82	0.61	0.7	16.560	2.7600	5.999723
Zn	0.863	0.815	0.37	1.67	0.675	0.91	0.3122	0.0520	1.029472
TCC MPN/100 mL	1,704.61	2,400	2	2,400	1,100	2,400	939.07	156.51	–0.83
TFC MPN/100 mL	1,104.7	460.00	2	2,400	210	2,400	1,031.0	171.84	0.38
TFS MPN/100 mL	4.72	3.50	2	11	2	7	3.14	0.52	0.79

pollution that could mainly be due to high suspended solids concentrations of biological origin. However, in the present case it was mainly due to indiscriminate disposal of organic waste in the area. Suspended solids may include a wide variety of materials, such as silt, decaying plant and animal matter that can increase the turbidity of water. The sites showing relatively higher BOD_5 levels are close to human settlements (C-10, C-22 and C-23). This suggests that the organic load is mainly of anthropogenic origin. Similar results were also reported by other authors [27–29] indicating that the oxidation of organic matter results in the reduction of DO concentration. This may lead to increase in BOD_5. Another factor, which could contribute to high BOD_5 levels, is the dumping of discarded fishes by the local fishermen, which undergo microbial decomposition and thus increase organic load. A high BOD_5 level tends to reduce DO concentration because oxygen is consumed by microorganisms creating anoxic condition detrimental to marine life [30,31].

Mean COD of all the samples of creeks of Indus delta was 582.08 mg/L. The highest COD value was found at C-4 (1,334 mg/L) while lowest was estimated at C-10 (320 mg/L). Jin et al. [32] are of the opinion that there is no apparent linear relationship exists between BOD and COD in relatively clean seawater samples away from the shore. A linear correlation does exist between BOD and COD in estuary having relatively high concentration of sewage contamination. In the present case, there is no apparent and significant source of industrial waste at the vicinity of sample collection sites. However, untreated domestic wastewater from the nearby settlements may find its way to these sites mainly because of non-existence of sewerage system. The quantity of untreated discharges is not as high that could significantly affect the seawater quality. The high COD values in the creek area are mainly attributed to continuous accumulation of toxic chemicals mainly of anthropogenic origin, which depreciates the water quality [27,33].

Among three types of chlorophyll (chlorophyll-a, chlorophyll-b and chlorophyll-c), type "a" is an important determinant in the assessment of biological activity pertaining to floral component of an ecosystem especially algae for which it is used as an algal biomass indicator. Hence, chlorophyll-a is under discussion (Table 2). The mean chlorophyll of all the sites was 0.114 mg/L. Higher chlorophyll concentrations were observed at the sites close to the mangroves (C-8, C-9, C-23, C-28 and C-29; 0.422 mg/L). The higher values of chlorophyll could be mainly due to higher temperature and higher wind velocity. The movement of nutrients can stimulate phytoplankton and can also withstand macroalgal growth, which are responsible for increase in chlorophyll concentration [21].

Cyanide is used for fish collection in many parts of the world. According to Rubec and Pratt [34] very little scientific research has been published on the effects of cyanide on marine fish. Fish exposed to a sublethal dose of cyanide showed no adverse effect after 1 or 2 weeks after collection [35]. Doudoroff [36] suggested that acute toxicity to cyanide may cause death within 96 h at a concentration of 0.1–0.3 mg/L. Leduc [37] reported that concentration of cyanide ranging between 0.005 and 0.01 mg/L may exhibit adverse effects on fish in the form of reduced growth, decreased swimming performance, increased metabolism, inhibition of reproduction and increased respiratory rates. This could be mainly due to the fact that cyanide interferes with oxygen metabolism by blocking cytochrome oxidase. Alazemi et al. [38] reported that cyanide caused desquamation of filamental epithelium at 0.05 mg/L in freshwater fish (*Gnathonemus petersii*). The mean cyanide value of creeks of Indus delta is 1.214 mg/L. The highest concentration (0.67 mg/L) was recorded at C-2 and C-24. It is important to note that the concentration of cyanide is quite alarming as there is no apparent source, which is available in the vicinity. Moreover, cyanide is also not used for the collection of fish in the study area. It may be due to the fact that cyanide in the creek system may come from nearby catches. In fact more detailed study is required to find out the ultimate source of cyanide in the creeks of Indus delta.

Oil and grease in any concentration in water is unacceptable. Oil pollution is a major contributor to deteriorate marine water quality [39]. Dispersed oil causes an increased toxicity to marine life, which is detrimental to marine biota [40,41]. 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 in any amount hampers the dissolution of atmospheric oxygen in the water thereby creating anxious condition detrimental to marine life form. Oil film on the water surface reduces the amount of DO, which affects both aquatic life forms and microbial activities [42]. Routine fishing and navigation operations in marine environment also constitute a significant source of oil and grease that is subjected to rapid degradation by marine bacteria especially in oxygenated environment. However, they also tend to sink in the bottom and continue to deposit there where they undergo relatively slow microbial degradation due to anoxic environment. The oil and grease concentration of creek water samples ranged between 65 and 575 mg/L. Khan and Shaukat [43] and Khan et al. [44] reported relatively higher values of oil and grease in creek water of Indus delta. It can be seen from Table 2 that the creek water is grossly polluted with oil. This would mean that the natural system of removal of oil through the process of photo-oxidation and biodegradation is not working efficiently because of lesser availability of oxygen. Oil biodegradation rates were, however, difficult to predict due to the complexity of the environment while rate of biodegradation was also dependent on the components of oil and petroleum products [45]. The major source of oil and grease in the creek system is faulty due to defective boats commonly used for fishing.

Orthophosphoric acid is the principal form of dissolved inorganic phosphate that exists in the seawater. Phosphate ions are quickly absorbed after weathering of clays or detritus particles, forming insoluble forms of aluminum, calcium, or iron phosphates owing to their negative charge [46]. Fungi and bacteria have the ability to solubilize these compounds [47]. According to Martin [48] the average concentration of dissolved orthophosphate in seawater is 0.073 mg/L. Boto [49] reported that the concentration of 0.031 mg/L is considered as low. The concentration of total phosphate in all the samples ranged between 2.1 and 4.6 mg/L with an average of 2.98 mg/L. These values are higher as compared with the values reported above. The input of phosphate in creek waters is from nearby anthropogenic sources through the use of inorganic fertilizers. Izonfuo and Bariweni [50] reported that the higher values of nutrients in the Epie creek (Niger delta) are mainly due to the runoff. The highest concentration of phosphates was observed at C-32 (4.6 mg/L), which represents the main tributary of River Indus through which it enters into the sea. This is the area that represents extensive agriculture on both the sides. Vazquez et al. [51] reported that 18 μg/L of phosphates from mangrove area is quite low as compared with those reported in the present study. The mechanism of flow of nutrients, including phosphorus, between sediments and water is a complex phenomenon, which is influenced by biological, physical, and chemical processes and depends on pH, temperature, and redox potential [52]. Mesnage and Picot [53] reported that in the Mediterranean coastal lagoons the major problem is an excessive input of nutrients (i.e., N and P) causing eutrophication in summer. The similar phenomenon is also observed in some of the creeks closed to human settlements.

Phenol and its compounds in any water body mostly originate from industrial sources [54]. Phenol once entered in fish body mainly affects the metabolism, survival, growth and reproductive system [55–57]. However, the information about the phenol toxicity at ecosystem level is limited. Hwang et al. [58] studied the rates of photolysis and microbial degradation of phenol and other associated compounds in estuarine water. They reported that photolysis is the primary transformation process for the polychlorinated phenols. They also reported that winter photolysis and microbial degradation rates were lower than the summer values. Eklund and Kautsky [59] in their review article reported that many macroalgae are more sensitive to phenol than other aquatic organisms. The mean phenol value of all the samples was 0.046 mg/L that fluctuated in a narrow range between 0.01 and 0.08 mg/L. Apparently, there is no source of phenol in the vicinity of the study area. It may be due to the limited use of janitorial agents by the nearby fishing communities.

The eutrophication phenomena for coastal waters is recently recognized, and its scientific understanding is still in progress [60]. European Environmental Agency described that N and P nutrients, chlorophyll-a and oxygen concentrations are the eutrophication variables [61].

Caraco et al. [62] and Howarth [63] reported that N potentially retards phytoplankton production in temperate marine systems. Harrison et al. [16] reported NO_3 for N ranged from l to 8 μM, NH_4 from 2 to 15 μM, and P from 0.2 to 2 μM in some of the creeks of Indus delta. In the present study the focus was on the available nitrogen in the form of Kjeldahl nitrogen. The average TKN of all the sites ranged between 31.9 (C-7) and 79.2 mg/L (C-12) with an average of 59.27 mg/L. The high concentration of TKN is mainly due to the flushing of organic matter originated from anthropogenic sources. It has been reported that dissolved organic nitrogen is seeped from anthropogenic sources, vegetation and overlying soils [64]. The elevated concentration of Kjeldahl nitrogen could also be correlated to the use of fertilizer. These results corroborate the findings of Leod and Hegg [65] who described that the surface water quality is affected by the pasture runoff after the application of commercial fertilizers followed by rain. Another possible source of Kjeldahl nitrogen could be the disposal of dead fishes in the area from the fishing communities. In general, both N and P are responsible for increased primary productivity of these sites.

Organic form of carbon is important for heterotrophic microbial activity while inorganic carbon including carbon dioxide is essential for autotrophic as well as photosynthetic metabolism. Their presence in excessive quantity indicates organic pollution, which may be due to domestic wastewater as well as industrial wastewater especially from food and dairy industries. Table 2 summarizes the TOC content of all the sampling sites. It was found to be as low as 2.27 mg/L and as high as 5.19 mg/L.

3.3. Heavy metal profile of the creeks

The mean metal (As, Cd, Cr, Pb, Ni and Zn) concentration is reported in Table 2. The concentration of Ni and Zn were exceptionally higher as compared with other metals. Other metal concentration is in the following order: Pb (0.577 mg/L) > As (0.035 mg/L) > Cr (0.027 mg/L) > Cd (0.013 mg/L). The mean concentration of As was 0.035 mg/L. Ahmed et al. [66] reported that approximately 16%–36% population in Sindh is consuming water containing As with the concentration ranging between 10 and 50 μg/L that exhibited exposure to high arsenic levels. Baig et al. [67] reported As values (13–106 μg/L) in the groundwater of Jamshoro district (Sindh) that were well within the limits. The As concentration in the creek water samples ranging between 0.01 and 0.08 mg/L that is much higher than the WHO permissible limit (0.01 mg/L). High concentration of As was observed in the surface water and groundwater of India and Bangladesh whereas in some parts of Bangladesh the As concentration is as high as 1,000 μg/L [68,69]. The consumption of As contaminated water is responsible for chronic ailments [67]. It may elucidated that the sources of As in the study area are natural rather than anthropogenic but at the same time it cannot be overruled that natural occurrence of As varied due to the geological and climatic changes [70]. Arsenic can be freely mobilized and transported by warm or hot water in the geothermal areas, like the study area [71].The extensive usage of arsenic-containing pesticides could also be the possible source that may contaminate creek water. Alamgir et al. [72] reported elevated levels of As in surface water of the study area.

The concentration of Cd ranged between 0.001 and 0.031 mg/L. The highest Cd concentration (0.031 mg/L) was recorded at C-5 (Bhai wari creek), C-19 (Rhorro creek) and C-25 (Nari creek). Cd in the water bodies usually comes from battery manufacture and electroplating. As such these industries are not available in the vicinity of the sampling sites. The source of Cd seems to be natural rather than anthropogenic. Bruland et al. [73] reported that the concentration of Cd in seawater varies between 0.02 and 0.12 μg/L but the values of Cd were relatively higher as compared with WHO guidelines value (0.003 mg/L) in the study area. According to Ouseph [74] similar values (1.8–4.2 μg/L) were obtained from Cochin estuary, India.

The mean concentration of Cr in all the creek samples was 0.027 mg/L (0.011–0.046 mg/L). The highest concentration (0.046 mg/L) was found at C-6 and C-17 (Bhai wari and Khado creeks). Jabeen and Chaudhry [75] reported that concentration of heavy metals was highest at the downstream of River Indus than the upstream. The river receives untreated wastewater from different sources including both domestic and industrial discharges. Water pollution intensifies particularly due to reduced flow, which has tremendously reduced the river natural assimilative capability.

The concentration of Pb ranged between 0.316 and 0.891 mg/L (mean = 0.577 mg/L). The highest concentration was at C-17 (0.891 mg/L; Khado creek) while lowest at C-1 (0.316 mg/L Sattah Wah creek). The possible sources of Pb could be mainly due to the fuel used for operating the fishing vessels [76]. The fishing vessels in the area are mostly operated through petrol or diesel. Mostly the engines of the fishing vessels are defective, and spillage of the fuel is a common problem. The concentration of Ni varied between 0.45 and 0.82 mg/L that might be introduced from natural sources. Nickel compounds can cause a number of ailments, such as dermatitis, lung fibrosis, cardiovascular diseases, kidney problems and cancer of the respiratory tract [77,78]. Midrar-Ul-Haq et al. [79] reported that 75% of the surface water samples in Karachi have high concentration of nickel as compared with maximum permissible limit. The nickel concentration of creek water samples ranged between 0.45 mg/L (C-24 Chan creek and C-36 Khobar creek) and 0.82 mg/L (C-6 Bhai wari creek). Nickel and its compounds have a number of industrial and commercial uses, and the advancement of industrial development has led to elevated emission of pollutants into ecosystems. Nickel may originate from both natural sources and anthropogenic activities.

Zinc concentration ranged between 0.37 and 1.67 mg/L (mean = 0.863 mg/L). Zinc is mostly used for galvanizing steel and iron products and in Zn-based alloys for die castings. Zinc is an important elements for human health [80]; its high concentration may lead to adversarial health impacts [81,82]. Rahman et al. [83] reported a higher Zn concentration (4.02 mg/L) in Karachi water supplies that could be possibly coming from the faulty water distribution network.

The concentrations of the heavy metals in the samples were found to be in the order Ni > Zn > Pb > As > Cr > Cd. Bryan [84] reported that Cu, Zn and Pb are normal constituents of marine and estuarine environments. The additional quantities are introduced from industrial wastes or sewage [85]. However, no industrial setup is available closed to the study area. Possible sources of these metals are generally of anthropogenic origin [86]. When these metals enter in the biogeochemical cycles they become potentially toxic and cause detrimental effects to marine organisms [87]. The concentration of heavy metals in seawater is mainly influenced by biological uptake [88] released from bottom sediments mixing of water masses and transport of terrestrial materials [89,90]. The results confirmed that the heavy metal pollution in creek is of great concern, moderately serious. In some sites Ni, Zn and Pb are relatively higher that may lead to serious ecological consequences in long term.

3.4. Bacteriological analysis

In Pakistan all types of water resources are gravely polluted with the organisms of public health importance [91–94]. Shar et al. [95] reported that in Khairpur district of Sindh 100% of the water samples were contaminated with total coliforms and fecal coliforms. The major source of bacteriological contamination in the study area is the domestic wastewater originated from the nearby human settlements [93,94]. As such no sewerage infrastructure is available in the study area; therefore, the untreated domestic wastewater ultimately finds its way into the creek system. Bacteriological analysis reveals that there is an increase in contamination due to organisms of public health importance after rain. This could possibly due to the runoff from the surroundings providing favorable conditions for the organisms to sustain and multiply [96]. Since the number of fecal coliforms and fecal streptococci discharged by human beings and animals are significantly different, therefore, it is suggested that the ratio of FC to FS count in a given sample can be used to detect whether the pollution is derived from the human or from animal wastes [97]. The FC/FS ratio in water in animal origin is generally considered to be less than 1.0 [97] whereas it is more than 4.0 for human beings [97]. If the ratio is within 1 to 2 the interpretation is uncertain [97]. This ratio is very helpful in determining the source of pollution [98]. The mean values of total coliforms and total fecal coliforms were 1,704.61 and 1,104.7 MPN/100 mL. The number of fecal streptococci was relatively low in all the samples. In general, during the rainfall and flood conditions the microbial load of the flowing water increases, which depreciates the creek water quality.

3.5. Statistical analysis

3.5.1. Multivariate analysis

The dendrogram resulting from unweighted pair-group averaging strategy of cluster analysis is presented in Fig. 2. Four groups can be recognized. Sample 5 forms an isolated group with a single member from Pakhar creek situated at Shah Bundar. Group 2 includes 2 members from Keti Bundar characterized by low COD high in chlorophyll and oil and grease. Group 3 comprises 17 samples that have generally high levels of Pb, Ni, TCC, TFC and lower levels of COD. The fourth group of 16 samples shows lower levels of Pb and Cr and usually high levels of Zn, salinity, COD and TKN. This seems that the sites close to the human settlements are polluted mainly with organic waste. The analysis further revels that the sources of heavy metals are mainly natural rather than anthropogenic except for Pb.

3.5.2. Principal component analysis (PCA)

The results of PCA are shown in Table 3. The first, second and third components explained 19.91%, 13.13% and 11.05% of total variance, respectively. Together, the first three components accounted for 44.10% of the total variance in the data matrix. The first component is predominantly governed by pH, DO, Zn and Ni. The second component is basically controlled by Cyanide, Cr, salinity and chloride. Whereas, the third component is largely dependent on Zn, Pb, oil and grease, and chloride concentrations. The three dimensional ordination is shown in Fig. 3.

4. Conclusions

The study reveals that the major pollutants are contributed by local anthropogenic activities. The inverse relationship between DO with BOD and DO with total nitrogen implies that the organic nitrogen plays a major role in the exhaustion of DO in the creek systems. The local dumpling from the nearby human settlements is expected to be the main source of organic pollution. The level of COD was recorded at the highest value. The concentration of chlorophyll was higher at the sites closed to the mangroves area. The concentration of cyanide was relatively higher; however, no significant source was identified. The high total phosphorus and total nitrogen concentrations in comparison with inorganic forms of phosphate and nitrogen indicate the high organic matter contribution into the creek area. The presence of oil and grease concentration can be attributed mainly to faulty fishing vessels. The concentration of heavy metals was in the order Zn > Ni > Pb > As > Cr > Cd. High level of these metals

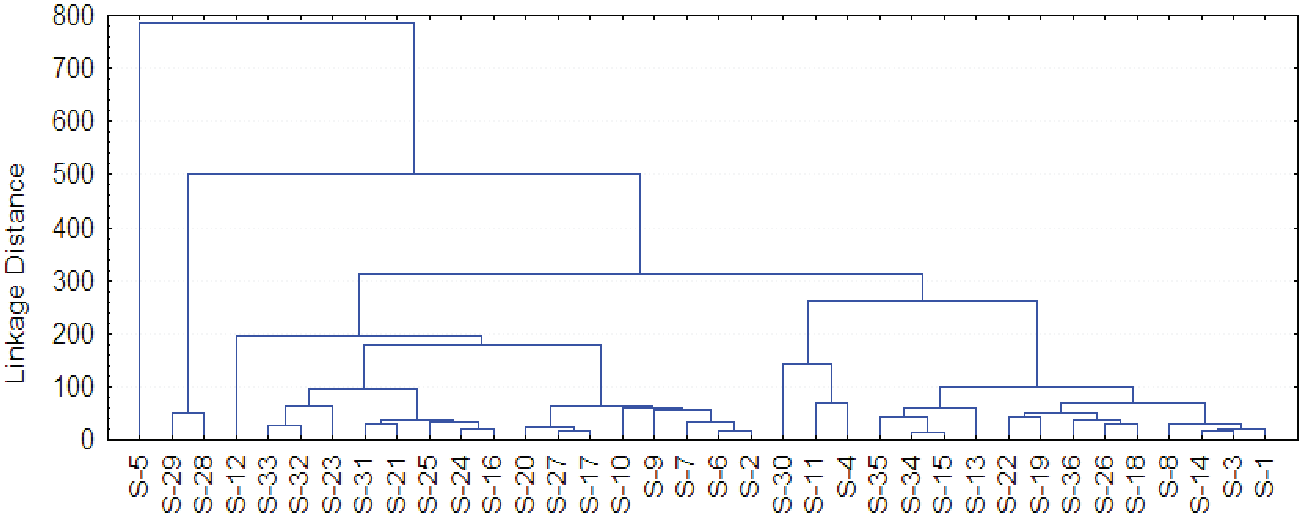

Fig. 2. Dendrogram derived from unweighted pair group method of physical, chemical and bacteriological parameters of Keti Bandar and Shah Bandar creeks of Indus delta.

Table 3
Results of principal component analysis (PCA) of physical, chemical and bacteriological parameters of Keti Bandar and Shah Bandar creeks of Indus delta

Component	Eigenvalue	Percentage variance	Cumulative percentage variance	First 3 eigenvector coefficients	Associated variables
1	3.584449	19.91361	19.91361	0.743156	pH
				0.697801	DO
				–0.598464	Zn
2	2.364850	13.13805	33.05166	–0.732445	Cyanide
				0.619894	Cr
				–0.600721	Salinity
3	1.989331	11.05184	44.10350	0.564716	Zn
				–0.564080	Pb
				0.653087	Oil and grease

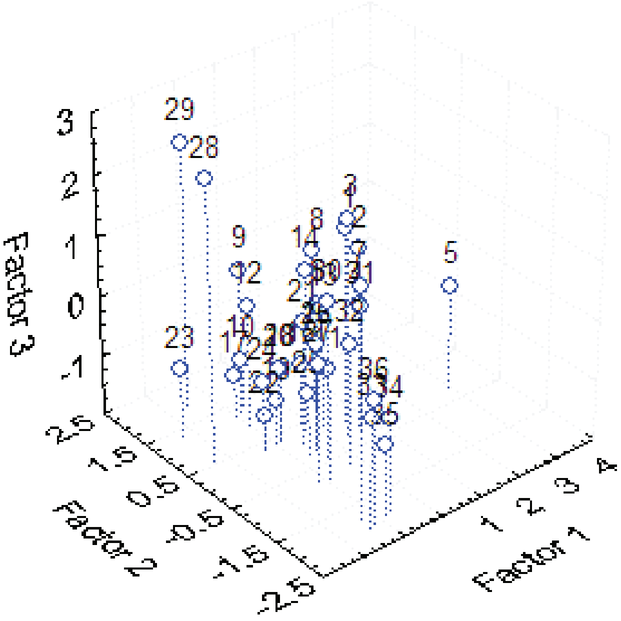

Fig. 3. Principal component analysis ordination (3D) of physical, chemical and bacteriological parameters of Keti Bandar and Shah Bandar creeks of Indus delta.

can harm creek ecosystems, plants, and animals and cause health problems in humans. In terms of bacteriological quality the creek water is gravely polluted due to the organisms of public health importance. In this case study, hierarchical cluster analysis and PCA helped to group the sampling sites having similar characteristics pertaining to creek water quality that reflects natural and anthropogenic pollution sources. The result reveals that whole of the study areas is heavily contaminated mainly because of anthropogenic sources. However, increase in heavy metal concentration largely reflects the natural sources.

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