



Pollution and ecological risk evaluate for the environmentally impact on Karnaphuli river, Bangladesh

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Abstract

Samples were collected low tide period from ten points in three seasons such as the pre- monsoon (November- February), monsoon (March–June) and post-monsoon (July–October), during 2015-2016. Samples were analyzed for finding of some metals concentration such as Na, K, Ca, Mg, Fe, Pb, Cu, Zn, Cd, As, Cr and Mn. The mean value was reported for each parameter. The investigated parameters were compared to national and international Standard. The concentration of some metals such as Na, K, Ca, Mg, Fe, Pb, Cu, Zn, Cd, As, Cr and Mn were found to be 327.24 ppm, 24.65 ppm, 29.42 ppm, 44.35 ppm, 15.28 ppm, 15.52 ppb, 0.018 ppm, 0.072 ppm, 0.066 ppm, <0.05 ppm, 0.62 ppm & 0.355 ppm respectively. The heavy metal pollution index (HPI) was found to be 1479.89 which was upper of the critical index limit of 100 and also indicates unsuitable for Drinking.

Keywords: evaluation, impact, heavy metal pollution index, toxic metal, detrimental

1. Introduction

Environmental problem related with urbanization and industrialization in space and time is the increased heavy metal pollution (Nriagu, 1990) ^[1]. During the last decade, awareness has grown up over environmental pollution in heavily industrialized nations. Experiencing rapid industrial developments and unplanned urban growth Bangladesh has become a developing country in recent years (Mia *et al.*, 2015) ^[2] but pollutants create huge environmental problems, primarily due to arsenic and other heavy metal pollution (Tareq *et al.*, 2003; Bhuiyan *et al.*, 2011; Islam *et al.*, 2015) ^[3, 4, 5]. Lakes, wetlands, rivers and streams have been major to the concern of civilizations throughout the human society. In all water, bodies are necessary to humans not only for drinking but also for industry, agriculture, energy production and transportation (Pathak *et al.*, 2014; Saran Ahluwalia *et al.*, 2015) ^[6, 7]. Water is important for life, it is undeniably the most valuable natural resource that exists on our earth (Matta, 2010; Matta *et al.*, 2017; Abowei and George, 2009) ^[8, 9, 10]. Originating from various natural sources and metals are gradually released into aquatic or atmospheric systems, although the anthropogenic inputs in environments have increased dramatically since the Industrial Revolution (Nriagu, 1979; Thevenon *et al.*, 2011) ^[11, 12]. Water quality available and reachable to a community has a great impact on their survival, thus global and local effort ensuring the condition of clean and safe water to rising inhabitants. Although water plays a vigorous role in sustaining human life and biodiversity, it also carried virus and diseases when impure or polluted. The existence of toxic and hazardous substances in river, estuary and marine environments not only affects the total ecosystem (Rahman *et al.*, 2014) ^[13] but also impedance of public health and blessing in Bangladesh (Alam *et al.*, 2003) ^[14]. Man can live only three or four days without water, but can go almost two months without foods. Contaminants of storehouses either

urban or agriculture sources is generally be putting in the food chain and detrimental the water quality. Estuary, a separate site, is originated at the mouths of rivers, in the narrow circumstance between the sea and the land, and interactions between physical, chemical and biological processes within an estuary can have profound influences on the transport and fate of substances discharged from the river system (Dyer, 1997; Bianchi, 2007) ^[15, 16].

Karnaphuli River, rising in the Mizo Hills of Mizoram state, northeastern India is a major water course of the Chittagong region, Bangladesh. It flows about 270 km south and southwest through the southeastern part of Bangladesh to deplete into the Bay of Bengal, 19 km below the city of Chittagong. Many industries surrounding of the karnaphuli river such as Textile mills, Soap factories, Tanneries, Pulp and paper mills, Rayon mills, Oil refineries, Paint and factories, Jute mills, Fertilizer industries, Steel and Iron mills etc. use a large amount of water for their manufacturing process and machinery requirement. After use this water with solid wastes and effluents directly or indirectly are discharged into the rivers and costal water without any treatment and finally into the Bay of Bengal. Chittagong is the commercially important and also the main port city of Bangladesh, having a population of about 4 millions, small and large industries and vast agricultural land. The city does not have modern waste treatment management facilities. International navigation routes is connected with Chittagong port, which handles annually about 5000 water craft which are about 50-60 oil tankers, 1500 ships, 1500 power driven trawler and 2000 sand boats engaged in fishing in the Bay of Bengal. As a result the Karnaphuli river estuary has become the potential for creating serious environmental problems.

Many research works have been reported the investigation report several years of physicochemical properties and heavy metal pollution in karnaphuli river but Heavy metal

pollution index (HPI) have not focused. The present study was found out to evaluate assignment and concentration of different water qualities of the Karnaphuli River. This will in turn help understanding the chronological detrimental status of the river due to the discharge of the industrial and municipal sewage causing in several pollution. The paper will help the ecologists, environmental scientists, conservationists, fishery scientists as well as the policy maker to take necessary measures for protecting the sea belt environment or ecosystem through saving the Karnaphuli from further deteriorating activities.

2. Materials and Methods

2.1 Sample Collection and analysis

On the area of the Karnaphuli river, total 30 water samples (sample K1-K10 were collected in Pre-monsoon, K11-K21 in monsoon and K21-K30 post monsoon) were collected from 10 different locations which is listed in (Table 1 and Fig. 1). Sampling location was selected at low tide of the river system. All the stations lies between 91⁰48' to 91⁰51' East longitudes and 22⁰19' to 22⁰21' North longitudes.

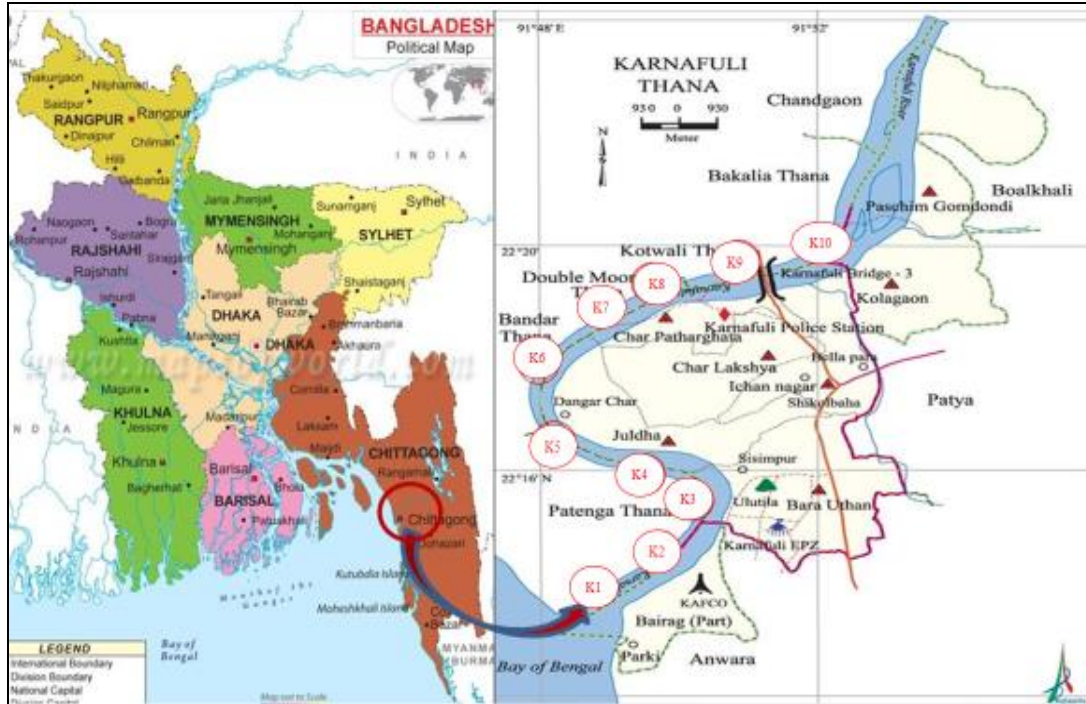


Fig. 1: Industrial Effluent discharged into the Karnaphuli

River

The sample was collected from the depth of 1-1.5 ft from

the stagnant water. About 1 L of water samples was collected each time, from every location (Figure 1).

Table 1: Sampling stations with GPS values

Sampling stations	GPS Value	Sampling stations	GPS Value
Bandor Ghat (K1, K11, K21)	22 ⁰ 19'9"N & 91 ⁰ 48'56"E	Bangla Bazar (K2, K12, K22)	22 ⁰ 19'14"N & 91 ⁰ 49'41"E
Anu mazi Ghat (K3, K13, K23)	22 ⁰ 19'21"N & 91 ⁰ 49'25"E	Mazir Ghat (K4, K14, K24)	22 ⁰ 19'22"N & 91 ⁰ 49'21"E
Custom Ghat (K5, K15, K25)	22 ⁰ 19'26"N & 91 ⁰ 49'39"E	Sador Ghat (K6, K16, K26)	22 ⁰ 19'28"N & 91 ⁰ 49'49"E
Firinghi Bazar Ghat (K7, K17, K27)	22 ⁰ 19'32"N & 91 ⁰ 50'13"E	Chaktai kha (K8, K18, K28)	22 ⁰ 19'41"N & 91 ⁰ 51'11"E
Shaaamanat Bridge (K9, K19, K29)	22 ⁰ 19'44"N & 91 ⁰ 51'22"E	Bhakoliya Khal (K10, K20, K30)	22 ⁰ 20'56"N & 91 ⁰ 51'42"E

Samples were collected in triplicate from each site, and the mean value for each parameter was reported. For accurate assessment of effluent qualities, the samples were collected carefully, from ten points (Bhandor Ghat to Bhakoliya Khal Ghat). The plastic bottles were first washed thoroughly with 10% HNO₃ and then vigorously washed by distilled water before collecting the sample to make sure that it is completely free from any undesirable materials. During sampling, the sample bottles were rinse with sample several times. After taking the sample, the bottles were labeled accurately by mentioning the name and location of the

sampling sites, date, time of collection etc. Samples were preserved in freeze on ± 4 °C for further analysis. Before heavy metal analysis, water sample (100 mL) volume, was digested after adding 2 mL of the concentrated HNO₃ (67–70%) on a hot plate and filtered through filter paper of Whatman and made up the volume to 40 mL by adding double distilled water. Individual heavy metal was analysed with the help of atomic absorption spectrophotometer (AAS) and as per the standard methods APHA 22th Edition [17]. Analytical method of water quality parameters were shown in (Table 2).

Table 2: Analytical methods of water quality parameters

Heavy Metals	Used Instruments	Model	Detection Limit (ppm)
Na and K	Flame Photometer	PFP7 Jenway	1.0 and 1.0
Ca, Mg, Fe, Zn, Cu, Cr, Pb, Cd and Mn	Atomic Absorption Spectrophotometer	AA240FS (Varian)	0.2, 0.1, 0.2, 0.05, 0.1, 0.005, 0.01, 0.001 and 0.05

2.2 Heavy metal pollution index (HPI)

Overall water quality impact on Heavy metal pollution index (HPI). Standard permissible limit for drinking water (Si) and Height desirable value (Hi) for each parameter were taken from the Indian drinking water specifications (Indian Standard 10500, 2012 and BDS Standard 1240, 2001) [18, 19]. The Standard permissible limit for drinking water (Si) refers to the maximum allowable concentration in drinking water in absence of any alternate water source. The desirable Height value (Hi) indicates the standard limits for the same parameters in drinking water.

The steps for calculation are:

- First—the weightage (W_i) calculation of i^{th} parameter;
- Second—the individual quality rating (q_i) or sub-index (Q_i) calculation for each of the heavy metal;
- Third—summing up of these sub-indices (Q_i) in the overall index.

Where, (W_i) is the unit weightage of i^{th} parameter, k is the constant of proportionality and n is the number of parameters considered. Table IV shows weightage (W_i) of each metals used for HPI determination.

$$HPI = \frac{\sum_{i=1}^n W_i q_i}{\sum_{i=1}^n W_i} \tag{1}$$

Where, (Q_i) is the sub index of the i^{th} parameter and (q_i) is the quality rating. The parameter of sub index (Q_i) is calculated by

$$Q_i = W_i \times q_i \tag{2}$$

Where (C_i) is the observed value of heavy metal of i^{th} parameter, (H_i) is the Height desirable value of i^{th} parameter, and (S_i) is the standard Permissible value of the i^{th} parameter in ppb. Particularly, the critical pollution index value is 100. Table V shows HPI index and status of water quality.

$$q_i = \sum_{i=1}^n \frac{|C_i - H_i|}{|S_i - H_i|} \times 100 \tag{3}$$

Table 3: The weight (W_i) of each of Metals used for HPI determination

Heavy Metals (ppb)	Mean Value (C_i)	Std. Permissible Limit (S_i)	Highest desirable Value (H_i)	Weightage ($W_i=1/S_i$)	Quality Rating(q_i)	Sub-Index $Q_i= W_i \times q_i$
Na	327240	200000	-	0.000005	163.62	0.000181
K	24650	12000	-	0.083	205.42	17.05
Ca	29420	200000	75000	0.000133	36.5	0.00485
Mg	44420	100000	30000	0.00001	20.6	0.000206
Fe	15280	300	-	0.0033	5093	16.81
Mn	350	300	100	0.0033	125	0.4125
Pb	15.5	10	-	0.1	155	15.5
Zn	72	15000	500	0.000067	2.95	0.0000198
Cu	18.9	1500	50	0.00067	2.145	0.00144
Cd	66	3	-	0.33	2200	726
Cr	602	50	-	0.02	1204	24.08
HPI = 1479.89				$\sum W_i = 0.5405$		$\sum Q_i = 799.86$

Table 4: Heavy Metal Pollution Index and status of water quality [20]

Heavy Metal Pollution Index Level	Water Quality Status
0-25	Excellent Water Quality
26-50	Good Water Quality
51-75	Poor Water Quality
76-100	Very Poor Water Quality
>100	Unsuitable for Drinking

2.3 Statistical Analysis

Lab origin-9 pro software was used to measure the Max, Min, Sum, mean and standard deviation (SD) of the data which was shown in (Table 5).

Table 5: Statistical value of Metals in the study area

Parameter	N	Mean	SD	Sum	Min	Max
Na	30	327.2404	312.66	9817.212	7.29	915.49
K	30	24.652	20.03471	739.56	3.76	115.47
Mg	30	44.3452	36.0234	1330.356	5.47	133.53
Ca	30	29.424	16.60779	882.72	9.55	71.35
Mn	30	0.35483	0.30579	10.645	0.004	1.743
Fe	30	15.28117	20.4775	458.435	0.035	117.9
Cr	30	0.62	0.22268	18.6	0.23	0.98
Cd	30	0.06633	0.04568	1.99	0.014	0.19
Cu	30	0.0189	0.02531	0.567	1E-3	0.146
Zn	30	0.07213	0.06768	2.1638	0.01	0.384
Pb	30	15.51733	14.88124	465.52	0.22	71.91

N→Number of Sampling Stations, Std. →Standard deviation (k=95%), Min→ Minimum value, Max→ Maximum value

2.4 Multivariate statistical analysis

The main purpose of this study is to develop portable multi statistical methods which determine the water quality of river water samples in the Karnaphuli river of Chittagong, Bangladesh. Decision makers will take proper step for river water quality management system and removals technology of purification of water. To evaluate the analytical data for finding source of pollutants, multivariate statistical techniques, e.g. principal component analysis (PCA) and cluster analysis (CA) are generally used in

Environmental studies (Mendiguchi'ia *et al.*, 2004; Yongning *et al.*, 2006) [21, 22]. In the observation, multivariate analysis was executed by using Lab origin

software 9.

Principal component analysis (PCA) was executed on the river water quality data using Multivariate Analysis technique, which was used to expand the observed relationship of cluster variables in simple ways, expressed in the pattern of variance and covariance between the variable and similarities between observations. The scree plot Figure 2. Showed four PCs of Eigen values loaded 85.37% of total variance in the study areas points. The computed factor loadings, together with cumulative percentage, and percentages of variance explained by each factor are shows in (Table 6).

Table 6: Principal component analysis for river water samples.

Parameters	PC1	PC2	PC3	PC4
Na	0.02185	0.47942	-0.16186	-0.32779
K	0.01929	0.257	0.72258	0.46624
Mg	0.04373	0.47198	0.02789	-0.23053
Ca	0.01077	0.44808	0.37825	-0.2835
Mn	0.45466	-0.01189	-0.02824	-0.1271
Fe	0.47685	0.05374	-0.0787	-0.02471
Cr	0.05347	0.34742	-0.36095	0.51051
Cd	0.00722	0.36849	-0.38669	0.36969
Cu	0.47177	-0.02937	0.03383	-0.09393
Zn	0.45182	-0.04183	-0.02225	-0.06315
Pb	0.36526	-0.1358	0.13925	0.33881
Eigenvalues	4.15787	3.29508	1.02111	0.91658
% of Variance	37.80%	29.96%	9.28%	8.33%
Cumulative %	37.80%	67.75%	77.04%	85.37%
Sites				
K1	-0.42994	2.48478	1.93363	-1.54993
K2	-0.22981	2.57775	0.98949	-1.54241
K3	-0.63288	1.82431	-0.09941	-0.50617
K4	0.60802	0.61645	0.68327	-1.67948
K5	0.4224	1.40228	-0.93059	-0.00894
K6	0.90287	1.30047	-1.21234	-0.06017
K7	10.35081	-0.19124	0.06291	0.13178
K8	-1.65013	-0.09959	-0.99478	0.24361
K9	-1.07594	-1.03395	-0.57352	0.32308
K10	0.54279	-1.55141	-0.34976	0.33853
K11	-0.16889	1.21858	0.33693	-0.68252
K12	-0.36063	1.90824	-0.69414	0.12367
K13	-0.46257	1.14521	-0.18621	-0.0738
K14	-0.97629	0.76164	-0.01102	-0.73047
K15	-0.96345	2.02361	-1.08445	0.40049
K16	-0.35667	2.62691	-0.25811	0.34018
K17	0.25658	1.89277	-1.16917	0.70492
K18	-0.20194	-0.22637	-0.84767	2.04836
K19	-0.49774	0.56112	-1.42477	0.9455
K20	-0.83061	2.00127	3.30049	2.7994
K21	0.46363	-1.91256	-0.05921	-0.46207
K22	-0.57111	-1.95393	-0.26874	0.14092
K23	-0.57454	-2.44139	0.00793	-0.4644
K24	0.34555	-2.28692	1.79338	1.32124
K25	-0.82267	-1.80607	0.37989	-0.54355
K26	-0.48431	-2.32021	-0.01394	0.08939
K27	-0.28891	-2.55151	0.40312	-0.83968
K28	-0.65929	-2.16754	-0.17578	0.01627
K29	-0.98236	-1.64363	0.13527	-0.12828
K30	-0.67198	-2.15909	0.32732	-0.69546

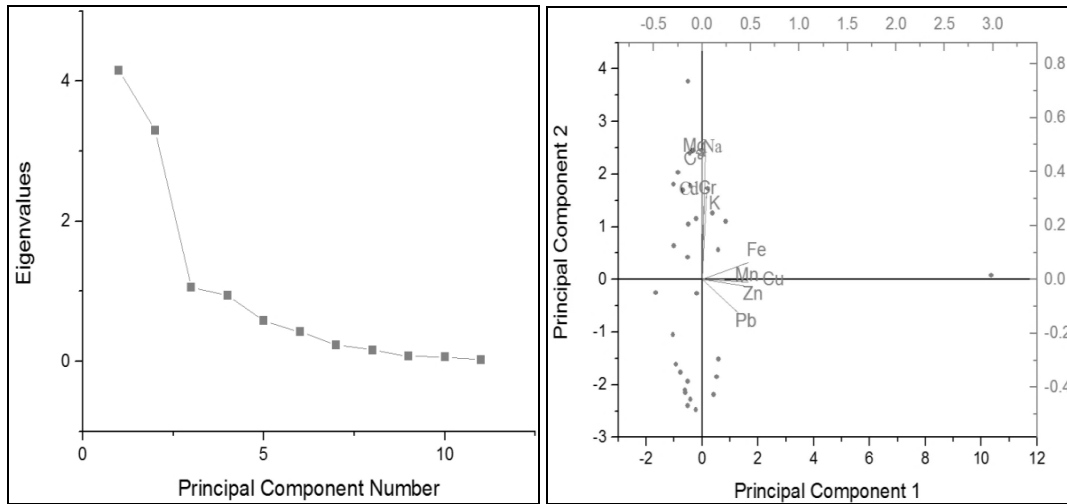


Fig. 2: Principal component analysis by (a) scree plot of the properties roots (eigenvalues), and (b) biplot in PC2 and PC1

The PC1, PC2, PC3 and PC4 for river water quality data were elucidated the total variance of 37.80%, 29.36%, 9.28% and 8.33% respectively. The PC1 in the data sets explained 37.80%, of total variance, and it was positive loaded with Mn, Fe, Cu and Zn which were significantly distributed in K4, K6, K7 and K10. The PC1 was also derived from several industries such as tannery, battery and steel mill industries are located in the study area, which are responsible for Heavy metals pollution. The PC2 in the data sets explained 29.36%, of total variance, and it was positive loaded with Na and Mg which were significantly distributed in K1 to K6, K11 to K17, K19 and K20. The PC3, accounting for 9.28% of total variance, was positively loaded on Potassium which was widely distributed in K1, K2, K4, K20 and K24. The PC4, accounting for 8.33% of total variance, was positively loaded on Potassium which was widely distributed in K17 to K20, K22 and K24.

Intuitive similarity relationships between any one sample and the entire data set were help to Hierarchical Agglomerative Clustering (HAC) which is generally illustrated by a dendrogram (McKenna, 2003) [23]. Some dramatic status gives dendrogram which is help data analysis such as actual summary of the clustering system, expose a picture of the groups and their intimacy, with an amazing fall on dimensionality of the original data. Hierarchical CA has been executed to observe and predict of

associated to the same cluster were likely to be found from a same source of minerals in the surface water. It is hold two main clusters which were led to forecast metals groupings in the ground water datasets and the results are shown in Fig. 3a. Cluster 1 included Na, Mg, Ca, Cr, Cd and K which might be explained by the sources of domestic, sewage, tannery, electrical, agricultural and leaching of fertilizers. Cluster 2 consists of Mn, Cu, Fe, Zn and Pb it lighted the influence of metals pollution of river water by the source of battery and steel industry.

Dendrogram using Average Linkage (Between groups)
Re scaled Distance Cluster Combine

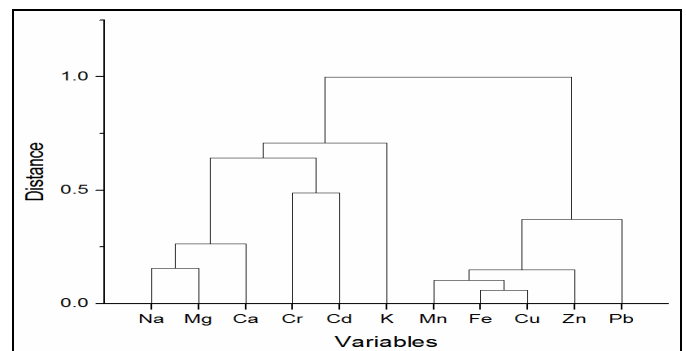
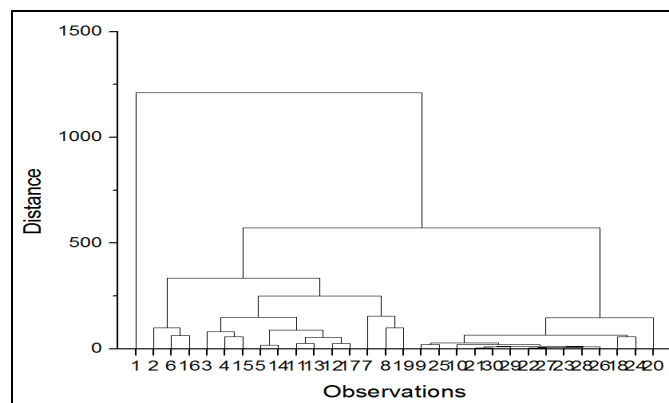


Fig. 3a: Dendrogram showing the hierarchical clusters of analyzed heavy metal



K1 K2 K6 K16 K3 K4 K15 K5 K14 K11 K13 K12 K17 K7 K8 K19
K9 K25 K10 K21 K30 K29 K22 K27 K23 K28 K26 K18 K24 K20

Fig. 3b: Dendrogram showing the hierarchical clusters of analyzed samples site.

CA was applied to characterize the spatial similarities and site grouping among the sampling points. Particular group or class shows similar properties according to their sources, distribution and chemical behavior with respect to the analyzed parameters in a samples cluster. The 30 sampling points denoted by 10 sampling sites for river water fall into three clusters (Fig. 3b). Cluster 1 consists of 15 sampling points which were K2, K6, K16, K3, K4, K15, K5, K14, K11, K13, K12, K17, K7, K8 and K19. This sampling point closely contaminated through industrial effluents discharged in the river directly or indirectly. K2 and K19 lies at the distant part of the study area and sampling stations K5, K14, K11, K13, K12 and K17 is the mostly polluted region. Cluster 2 included to 14 sampling points like K9, K25, K10, K21, K30, K29, K22, K27, K23, K28, K26, K18, K24 and K20. Cluster 2 shows most of the industry situated in the

sampling points K9, K25, K10, K21, K30, K29, K22, K27, K23, K28 and K26 whereas cluster 3 stand-alone which was K1. This site less contaminated of river water due to leaching of parent material and agricultural runoff.

3.0 Result and Discussion

The concentrations of Heavy metal in the water of the river varied with temperature and location (Bhuyan and Islam, 2017) [24]. During the sampling period I observed on the surface of the Karnaphuli river water have a lot of floating materials and water hyacinth. The observation emphasizes on the Metals concentration and eutrophication in the Karnaphuli River which is directly and indirectly hamper environmental ecosystem of river water. Agricultural runoff, anthropogenic and municipal wastes are main sources of over concentrated pollutant.

Table 7: Observed value of Heavy Metals in Karnaphuli river water in three seasons

para→ S Site↓	Na ppm	K ppm	Mg ppm	Ca ppm	Mn ppm	Fe ppm	Cr ppm	Cd ppm	Cu ppm	Zn ppm	Pb ppb	As Ppm
K1	526.81	44.52	124.916	71.35	0.233	9.02	0.50	0.048	0.02	0.068	6.46	<0.05
K2	915.49	34.65	95.52	64.6	0.386	12.97	0.55	0.065	0.013	0.052	11.58	<0.05
K3	664.15	32.14	133.53	24.2	0.272	8.58	0.87	0.029	0.011	0.047	6.21	<0.05
K4	717.17	22.9	58.17	45.35	0.491	20.99	0.43	0.032	0.036	0.07	14.15	<0.05
K5	598.85	20.01	58.96	35	0.453	23.36	0.76	0.12	0.024	0.077	10.74	<0.05
K6	802.69	22.75	45.28	26.5	0.428	20.24	0.67	0.14	0.015	0.198	9.68	<0.05
K7	307.93	28.26	58.25	31.35	1.743	117.9	0.80	0.056	0.146	0.384	71.91	<0.05
K8	421.39	13.37	29.05	18.6	0.004	0.035	0.90	0.042	0.018	0.01	0.22	<0.05
K9	33.22	3.76	16.95	29.8	0.121	4.84	0.64	0.068	0.005	0.036	18.93	<0.05
K10	15.31	18.79	13.22	12.81	0.395	25.71	0.54	0.063	0.028	0.1024	14.06	<0.05
K11	499.9	25.29	63	50.8	0.324	18.79	0.63	0.071	0.023	0.0408	10.45	<0.05
K12	527.6	24.06	90.51	37.5	0.254	14.74	0.80	0.12	0.016	0.0537	9.51	<0.05
K13	476.15	21.99	59.08	43.75	0.262	21.59	0.98	0.029	0.006	0.0437	9.13	<0.05
K14	594.89	20.91	61.68	37.05	0.19	6.21	0.55	0.068	0.001	0.0616	9.79	<0.05
K15	662.18	22.89	68.89	36.15	0.224	9.17	0.88	0.13	0.002	0.0389	6.63	<0.05
K16	856.12	41.22	65.69	44.4	0.323	14.1	0.55	0.19	0.008	0.0492	14.83	<0.05
K17	542.94	26.99	71.99	30.8	0.53	24.08	0.91	0.14	0.016	0.0503	9.73	<0.05
K18	47.6	20.72	60.81	12.16	0.21	8.79	0.97	0.085	0.004	0.0388	39.65	<0.05
K19	324.14	13.25	32.99	26.45	0.295	12.39	0.91	0.12	0.015	0.0386	11.6	<0.05
K20	115.47	115.47	33.43	53.45	0.197	5.74	0.87	0.092	0.009	0.0421	10.31	<0.05
K21	11.102	12.16	7.14	19.34	0.859	7.57	0.46	0.036	0.029	0.0594	12.23	<0.05
K22	15.31	13.16	8.02	11.64	0.24	10.93	0.48	0.045	0.015	0.063	13.89	<0.05
K23	15.39	10.89	5.47	10.82	0.17	6.91	0.35	0.021	0.012	0.1199	10.27	<0.05
K24	45.78	47.59	14.52	9.55	0.213	4.79	0.33	0.019	0.014	0.0752	56.07	<0.05
K25	30.38	17.41	11.19	21.96	0.349	8.21	0.38	0.025	0.012	0.0471	6.69	<0.05
K26	11.34	11.89	6.46	10.6	0.202	8.27	0.43	0.028	0.019	0.0552	22.1	<0.05
K27	11.99	14.26	8.06	12.6	0.455	10.71	0.23	0.014	0.012	0.0871	10.88	<0.05
K28	9.88	12.44	7.3	10.24	0.331	6.95	0.45	0.034	0.008	0.0613	14.82	<0.05
K29	8.75	12.83	12.37	24.5	0.135	6.02	0.44	0.043	0.012	0.0479	14.42	<0.05
K30	7.29	12.99	7.91	19.4	0.356	8.83	0.34	0.017	0.018	0.0456	8.58	<0.05

Many studies reported that the contamination level of heavy metals in water along the Karnaphuli estuary and its nearby coastal area (Hossain, 2010) [25]. ADB reported that the tannery Industry at Kalurghat, Chittagong though the effluent 150,000 litres per day and Karnaphuli Paper Mills (KPM) at Chittagong discharge about 0.35 tons of China clay per day (MoEF, 2005) [26] that Pollutes river water. The fiscal year of 1994-1995 government reported that 2528 metric tonnes of wastes were dumped from shrimp processing units into the Bay of Bengal via the Karnaphuli River (Hassan, 2006) [27]. Moreover, 05 major canals (Rajakhali Canal and Chaktai canal etc) carry domestic,

industrial waste and sewages effluents to the River Karnaphuli (Islam *et al.*, 2015) [28]. Karnaphuli river received wastewater discharged into surface drains that is ultimately carry from Nasirabad industrial area’s mainly chemical, leather, textile and steel re-rolling industries (Dey *et al.*, 2015) [29]. Presence of heavy metals in the river water causes dangerous impact on the aquatic ecosystem.

Observed value of heavy metals in Karnaphuli river water in three season’s shows in (Table 7) and (Table 8) showed Environmental risk factor and ecological risk index for heavy metals in the Karnaphuli River.

Table 8: Ecological risk index for heavy metals in the Karnaphuli River

Metals (ppm)	Exceeded Samples	EU (1986) [30]	ECR (1997) [31, 32]	IS 10500: (2012, 1998) [18, 33]	USEPA (2018) [34]	WHO (2011, 2008) [35, 36]
Na	K1-K8, K11-K17 and K19	-	200	-	-	200
K	K1-K8, K10-K22, K24- K25 and K27-K30	-	12	-	-	-
Ca	-	-	75	75	-	-
Mg	K1-K5, K7 and K11-K18	-	30-35	30	-	-
Mn	K1-K7 and K9-K30	0.05	0.1	0.1	0.05 (SMCL)	0.05
Fe	K1-K30	0.2	0.3-1.0	0.3	0.3 (SMCL)	0.1
As	-	0.01	0.05	0.05	0.01	0.02
Cr	K1-K30	0.05	0.05	0.05	0.1 (MCL)	0.05
Zn	-	-	5	5	5 (SMCL)	-
Pb	K1-K7 and K9-K30	0.01	0.05	0.01	0.015 (AL)	0.01
Cd	K1-K30	0.003	0.005	0.003	0.005(MCL)	0.003
Cu	-	2.0	1.0	0.05	1.3 (AL)	2.0

Para→ Parameters, MCL→ Maximum Contamination Level, SMCL→ Secondary Maximum Contamination Level, Std. →Standard, AL→ Action Level

The observed average Sodium (Na) concentration was found to be 327.24 ppm while the maximum and minimum Na concentration was found 915.49 ppm in pre-monsoon and 7.29 ppm in post-monsoon respectively. According to the different guideline (BDS-1240, 2001) [19] and (WHO, 2011) [38] the permissible limit of Na concentration is 200 ppm which is indicates observed value exceeded the recommended value. (Table 8) showed that the observed values exceeded the acceptable limit in these sites (K1-K8, K11-K17, and K19) in pre-monsoon and monsoon. Main source of Na in the river water and in sediment may be the untreated or partially treated industrial effluent which is dumped into the river. Different types of sodium salt are used by industries (mainly tannery, dying) for their process run. If sodium concentration is higher as combined with chlorine and sulfate then the water would not be suitable for irrigational use (Azizullah *et al.*, 2011) [37]. Sodium polluted irrigated water makes the soil pudding and therefore, decrease the water intake capability and becomes hard in which makes seed germination difficulties. Higher concentration of sodium may impose osmotic stress on the aquatic biota (Raza *et al.*, 2007) [38]. Therefore, the population of biota may be decreased which makes a lame ecosystem.

Potassium (K) average concentration was found to be 24.65 ppm while the maximum and minimum K concentration was found 115.47 ppm in monsoon and 3.76 ppm in pre-monsoon respectively. According to the different guideline listed in (Table 8) the permissible limit of K concentration is 12 ppm which is indicates observed value exceeded the recommended value. (Table 8) showed that the observed values exceeded the acceptable limit in these sites (K1-K8, K10-K22, K24- K25 and K27-K30) in three seasons. Water contaminated by K could not be used for drinking, cooking and household purpose (Islam *et al.*, 2018) [39].

The presence of metal concentration is harmful to aquatic life but iron compound in water may be the degree of toxicity nature. Investigation showed that the average concentration of Iron (Fe) was found to be 15.28 ppm while the maximum and minimum Fe concentration was found 117.9 ppm and 0.035 ppm in pre-monsoon. According to the different guideline listed in (Table 8) the permissible limit of Fe concentration is 0.3 ppm which is indicates observed value exceeded the recommended value. In the three seasons, the observed values exceeded the acceptable limit in these sites (K1-K30) which is listed in (Table 8). The concentrations of Fe in the Karnaphuli River estuary were

observed higher than the recommended value (Das *et al.*, 2002) [40]. Terrestrial input and untreated waste water from metallurgy, paint and pigments, alloy industries are related to the higher values of Fe (Sarkar *et al.*, 2016) [41]. Domestic sewages, land washout, river run off and shipping activities are responsible for the higher concentration of Pb, Cu, Fe, Ni and Cr and lower concentration of Mn and Cd than that of the recommended values in karnaphuli river (Das *et al.*, 2002) [40].

Calcium (Ca) average concentration was found to be 29.42 ppm while the maximum and minimum Ca concentration was found 71.35 ppm in pre-monsoon and 9.55 ppm in post-monsoon respectively. According to the different guideline listed in (Table 8) the permissible limit of Ca concentration is 75 ppm which is indicates observed value pleasant tolerable limit. (Table 8) showed that the observed values not exceeded the acceptable limit of the observed areas in three seasons. Long time ingestion of excess Ca may cause hyperkalemia, urinary tract calculi, calcification in soft tissues like kidneys and in arterial walls and suppression of bone remodeling (Heaney *et al.*, 1982) [42].

Magnesium is main parameter of chlorophylla which plays an important role in ecosystem. Higher concentration of Mg makes hard water which creates difficulties in household washing. Like Mg, Ca also creates problem in household washing. Investigation showed that the average concentration of Magnesium (Mg) was found to be 44.45 ppm while the maximum and minimum Mg concentration was found 133.53 ppm in pre-monsoon and 5.47 ppm in post-monsoon respectively. According to the different guideline listed in table10, the permissible limit of Mg concentration is 30 ppm which is indicates observed value exceeded the recommended value. (Table 8) showed that the observed values exceeded the acceptable limit in these sites (K1-K5, K7 and K11-K18) in pre-monsoon and monsoon.

Manganese (Mn) average concentration was found to be 0.35 ppm while the maximum and minimum Mn concentration was found 1.74 ppm and 0.004 ppm in pre-monsoon. According to the different guideline listed in (Table 8) the permissible limit of Mn concentration is 0.05 ppm which is indicates observed value exceeded the recommended value. (Table 8) showed that the observed values exceeded the acceptable limit in these sites (K1-K7 and K9-K30) in three seasons. Manganese (Mn) is an essential element for both animal and plant and its deficiency may cause brutal skeletal and reproductive abnormalities for animal (Sivaperumal *et al.*, 2007; NAS,

1973)^[43, 44] reported that 0.1 % of earth crust comprises of Manganese.

Cadmium (Cd) is a carcinogenic agent which is used in pigment, battery and paint industries. Cadmium (Cd) average concentration was found to be 0.066 ppm while the maximum and minimum Cd concentration was found 0.19 ppm in monsoon and 0.014 ppm in post-monsoon respectively. According to the different guideline listed in (Table 8) the permissible limit of Cd concentration is 0.005 ppm which is indicates observed value exceeded the recommended value. (Table 8) showed that the observed values exceeded the acceptable limit in these sites (K1-K30) in three seasons. Cadmium is carcinogenic and can cause acute and chronic illness for human (Nyamangara *et al.*, 2008)^[45]. Heavy metal pollution is a major problem for the Karnaphuli River estuarine and the concentrations of As, Cr, Cd and Pb were higher than the acceptable values which is indicate that the river of Karnaphuli is polluted by heavy metals and may be create vulnerable effect on this riverine ecosystem (Ali *et al.*, 2016)^[46].

Chromium (Cr) is hazardous trace element for public health if the daily intake is exceeded by permissible limit 0.05 mg/L but the deficiency of Cr can cause glucose, protein and lipid metabolism disturbance (Calabrese *et al.*, 1985)^[47]. Chromium (Cr) average concentration was found to be 0.62 ppm while the maximum and minimum Cr concentration was found 0.98 ppm in monsoon and 0.23 ppm in post-monsoon respectively which is indicates the sewage and effluents from the port area are responsible (Islam *et al.*, 2014)^[48]. According to the different guideline listed in (Table 8) the permissible limit of Cr concentration is 0.05 ppm which is indicates observed value exceeded the recommended value. (Table 8) showed that the observed values exceeded the acceptable limit in these sites (K1-K30) in three seasons. This high value of Cr can be the source of industrial sewage, tannery, plating, pigment and dying industries (Sarkar *et al.*, 2015)^[49].

Copper (Cu) is an essential element for enzyme, but the high consumption of Cu can cause severe health problems (Goreel *et al.*, 1997)^[50]. Copper (Cu) average concentration was found to be 0.62 ppm while the maximum and minimum Cu concentration was found 0.15 ppm in pre-monsoon and 0.001 ppm in monsoon respectively. According to the different guideline listed in (Table 8) the permissible limit of Cu concentration is 1.0-2.0 ppm which is indicates observed value pleasant tolerable limit. (Table 8) showed that the observed values not exceeded the acceptable limit of the observed areas in three seasons. (Aksu and Isoglu, 2005)^[51] Reported that cleaning and plating industries can be the potential source of copper. Lower concentration of Cu detected in water may be the result of forming complex with organic compound (Zhu and Alva, 1993)^[52].

Zinc (Zn) average concentration was found to be 0.072 ppm while the maximum and minimum Zn concentration was

found 0.38 ppm and 0.01 ppm in pre-monsoon. According to the different guideline listed in (Table 8) the permissible limit of Zn concentration is 5 ppm which is indicates observed value exceeded the recommended value. (Table 8) showed that the observed values pleasant tolerable limit. (Table 8) showed that the observed values not exceeded the acceptable limit of the observed areas in three seasons. These higher concentrations of Zn are related to the industrial discharge and natural sources. According to (Hamed *et al.*, 2009; Naymangara *et al.*, 2008)^[53, 54] at alkaline pH, Zn can be precipitated as ZnCO₃ which is suspected for lower concentration of Zn in surface water and higher concentration in sediment.

Lead (Pb) is used in battery and paint industries. Lead (Pb) average concentration was found to be 15.52 ppb while the maximum and minimum Pb concentration was found 19.91 ppb and 0.22 ppb in pre-monsoon. According to the different guideline listed in (Table 8) the permissible limit of Pb concentration is 0.01 ppm which is indicates observed value exceeded the recommended value. (Table 8) showed that the observed values exceeded the acceptable limit in these sites (K1-K7 and K9-K30) in pre-monsoon and post-monsoon. Urea Fertilizer Factory discharges untreated effluents directly into the River Karnaphuli. Karnaphuli river polluted by Hg, Pb, Cr, Cd and As from 144 industries, degradable and persistent organic and inorganic compounds from 297 industries and oil, lubricants from (40-50) tankers (Rahman, 2013)^[55].

Arsenic (As) is a hazardous element for human. The consumption of As is exceeded by the permissible level cause arsenicosis. Arsenic produce mostly from Chittagong hill tracts or the upland Himalayan catchments which are linked with the karnaphuli river (Mitamura *et al.*, 2008)^[56]. Arsenic concentration is varied from 0.001 to 0.005 mg/L in surface water. The observed As concentration were found to be less than 0.005 ppm which is indicate that karnaphuli river is free from As contamination. According to the different guideline listed in (Table 8) the permissible limit of As concentration is 0.005 ppm.

All the obtained data selected to statistical analysis. In statistical analysis, a Karl Pearson's correlation matrix was developed between parameters for data assessment of Karnaphuli river water to measure the variations in parameters at different parameters. A correlation matrix was calculated by the Lab origin-9 pro software. This correlation matrix (Table 9) of river water was calculated in order to ascertain the relationship among metals where Strong correlation ($p < 0.01$) and significant correlation ($p < 0.05$). High correlations between specific heavy metals in water may reflect similar levels of contamination and/or release from the same sources of pollution, mutual dependence and identical behavior during their transport in the river system (Li *et al.*, 2009; Chen *et al.*, 2012; Suresh *et al.*, 2012; Jiang *et al.*, 2014)^[57, 58, 59, 60].

Table 9: Correlation matrix among the Metals

Metals	Na	K	Mg	Ca	Mn	Fe	Cr	Cd	Cu	Zn	Pb
Na	1										
K	0.175	1									
Mg	0.781	0.291	1								
Ca	0.676	0.496	0.690	1							
Mn	0.041	-0.022	0.051	0.029	1						
Fe	0.125	0.014	0.153	0.099	0.893	1					

Cr	0.395	0.221	0.497	0.259	0.030	0.211	1				
Cd	0.565	0.218	0.357	0.334	0.005	0.087	0.512	1			
Cu	-0.007	-0.003	0.045	0.032	0.901	0.942	0.061	-0.096	1		
Zn	0.031	-0.004	0.0001	-0.065	0.818	0.881	-0.023	0.004	0.856	1	
Pb	-0.246	0.088	-0.106	-0.229	0.576	0.642	-0.013	-0.112	0.657	0.636	1

Na was positive significant correlated with Ca ($r=0.676$), Mg ($r=0.781$), and Cd ($r=0.56$) respectively and also negative insignificant correlated with Pb ($r=-0.246$) and Cu ($r=-0.01$). K was positive significant correlated with Ca ($r=0.5$) and also negative insignificant correlated with Mn ($r=-0.02$), Zn ($r=-0.004$) and Cu ($r=-0.003$). A positive significant correlation of Mn was correlated with Fe ($r=0.89$), Cu ($r=0.90$), Zn ($r=0.82$) and Pb ($r=0.58$) respectively and also negative insignificant correlation with K ($r=-0.02$). Cr was positive significant correlated with Mg ($r=0.5$) and Cd ($r=0.5$) also negative insignificant correlated with Zn ($r=-0.02$) and Pb ($r=-0.01$). Cd Showed positive significant correlation with Na ($r=0.56$) and Cr ($r=0.51$) also negative insignificant correlated with Cu ($r=-0.09$) and Pb ($r=-0.11$). A positive significant correlation of Ca was also correlated with Na ($r=0.68$), K ($r=0.5$) and Mg ($r=0.69$) respectively and also negative insignificant correlated with Pb ($r=-0.07$) and Zn ($r=-0.23$). Mg showed positive significant correlation with Na ($r=0.78$), Ca ($r=0.69$) and Cr ($r=0.5$) respectively and also negative insignificant correlated with Pb ($r=-0.11$). A significant correlation of Fe correlated with Mn ($r=0.89$), Cu ($r=0.94$), Pb ($r=0.64$) and Zn ($r=0.88$) respectively. Zn showed positive significant correlation with Fe ($r=0.88$), Cu ($r=0.86$), Pb ($r=0.64$) and Mn ($r=0.82$) respectively and also negative insignificant correlation with K ($r=-0.004$), Ca ($r=-0.07$) and Cr ($r=0.23$). A significant correlation of Pb correlated with Fe ($r=0.64$), Mn ($r=0.58$), Cu ($r=0.66$) and Zn ($r=0.65$) respectively and also negative insignificant correlated with Na ($r=-0.25$), Ca ($r=-0.11$), Mg ($r=-0.23$), Cd ($r=-0.11$) and Cr ($r=0.01$).

Conclusion

Heavy Metal index (HPI) technique used to assess the suitability of surface water. In the investigation, HPI was found 1479.89 which is indicate that the Karnaphuli river water is unsuitable for drinking. The Karnaphuli river water used for domestic, industrial and irrigation purposes and without purified its water is not safe for drinking, irrigation and industrial uses. Investigation shows that the concentration of toxic Metals such as K, Mg, Na, Fe, Mn, Cu, Cr, Cd, Zn and Pb in the Karnaphuli River water were higher than the Permissible limit and the concentration of Cu, Zn and Ca were pleasant tolerable level. As a result these toxic Metals were polluted the karnaphuli river water day by day. Because of a large amount of water is used for their manufacturing process and machinery requirement. After use this water with solid wastes and effluents are discharged into the rivers and costal water without any treatment. Empirical data also shows that the Firingi Bazar Ghat and Custom Ghat are the highest polluted stations and the Bandhar ghat, Anu Mazi Ghat and Shador Ghat are second highest polluted stations respectively. This study proved that, industrial area is severely polluted than non-industrial area. It is suggested that to protect the aquatic ecosystem by eco-friendly and planned industrial growth. Most of the dissolved heavy metals were found to be higher concentrations during pre-monsoon than that of the post-monsoon. This trend indicates that during low flow

condition of river, the accumulation of the metal concentration increases. The lower concentration of heavy metals during post-monsoon might be due to the dilution effect of water [61, 62, 63]. After the study it can be concluded that the Karnaphuli river water is being polluted gradually by haphazard and unplanned industrialization. The presence of heavy metals from dyeing industries, oil spills from ship braking industries and ongoing vessels in the aquatic environment is the major concern because of their heavy toxicity, bio-accumulating tendency in the biota. Pollution by heavy metals is a threat to human life and the entire environment as well as the wetland ecosystem (Islam and Tanaka, 2004; Igwe and Abia, 2006) [64, 65]. The availability of the heavy metal in river water directly affects the fish physiology and by the consumption ultimately affects the human health.

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