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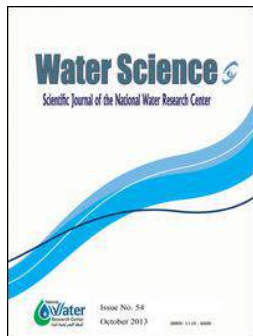8 PUBLICATIONS 18 CITATIONS

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Assessment of some physicochemical parameters and determining the corrosive characteristics of the Karnaphuli estuarine water, Chittagong, Bangladesh

Md. Ripaj Uddin [a], Md. Moazzem Hossain [b,c], Shakila Akter[a], Muhammad Edris Ali[d] and Md. Aminul Ahsan[a]

[a]Institute of National Analytical Research & Service (INARS), Bangladesh Council of Scientific and Industrial Research (BCSIR), Dhaka, Bangladesh; [b]Industrial Physics Division, Bangladesh Council of Scientific and Industrial Research (BCSIR), Dhaka, Bangladesh; [c]Atomic Energy Research Establishment, Bangladesh Atomic Energy Commission, Savar, Dhaka, Bangladesh; [d]Department of Chemistry, Chittagong College, College Road, Chittagong, Bangladesh

ABSTRACT

The comprehensive study was found out to evaluate the concentration of different water qualities of the Karnaphuli river. Samples were collected from ten points (Bhandor Ghat to Bhakoliya Khal Ghat) in three seasons (winter, rainy, and spring) during the Hydrological Year 2014–2015 for continuous monitoring. Collected samples were analyzed for finding of some physicochemical parameters Temperature, pH, Alkalinity, Acidity, Total hardness, Sulfate, Chloride, Total Dissolved Solids (TDS), and CO_2. The investigated parameters were compared to the national and international standards. The mean values of water Temperature, pH, Alkalinity, Acidity, Total hardness, Phosphorus, Sulfate, Chloride, TDS, and free CO_2 were found to be 28.36° C, 6.25, 275.63ppm, 19.75ppm, 259.29ppm, 0.904ppm, 70.74ppm, 534.63ppm, 778.83ppm & 18.03ppm, respectively. Water Quality Index (WQI), Langelier Saturation Index (LSI) and Ryznar Stability Index (RSI) values were found to be 99.92, −3.06 & 12.36, respectively, which indicate that the water quality is not good.

Introduction

The Karnaphuli river flowing through the region of Chittagong and the Chittagong hills, which is one of the most important rivers in Bangladesh. There was an overview of the concentrations of some physicochemical parameters, trace metals, pesticides, and oil along with their load in some fish and shellfish and ambient environment of the Karnaphuli river. It contains all kinds of garbage and perform urgent significant preface among the territory's scheme. The port of Chittagong is situated on the bank of the Karnaphuli. Most of the industries and prime sea port of this country are situated there. Among the Millennium Development Goals (SDGs), are reduced the population control, ensure safe drinking water to all, ensure proper domestic waste water and introduce joint water management system of global community. The United Nations Convention on the Law of the Sea (UNCLOS, 1982) defined pollution as the introduction by human, directly or indirectly, of substances or waste into the marine environment, including estuaries, which result or are likely to result in such deleterious effects as harm to living resources and marine life, hazards to human health, hindrance to marine activities, including fishing and other legitimate uses of the sea, impairment of quality for use of the sea water and reduction of amenities. Production and emissions of pollutants are usually derived from human settlements, resources used and interventions, such as infrastructural development and construction, agricultural activities, industrial developments, urbanization, tourism etc. Contaminants of major concerns include persistent organic pollutants, nutrients, oils, radionuclides, heavy metals, pathogens, sediments, litters and debris etc. Sarkar et al. (2015) and Sarwar et al. (2010) have reported that rivers are the important surface water sources and are being used for various purposes viz; drinking, household, irrigation, industrial purposes and recreation.

Surface and its surrounding interactions of physicochemical parameters are called corrosion (Vikas et al., 2012; Fianko et al., 2007). Excessive hardness value makes corrosive water that water can damage the water distribution system which has very bad impact on economic and health (Lehtola et al., 2004). Corrosive water can influence with physicochemical parameters character such as pH, alkalinity, and hardness, dissolved oxygen, carbon dioxide, and dissolved solids. High flow rate, high temperature, high concentration of chlorine and high conductivity can increase the corrosion potential of water. The corrosion is determined by the amount of the calcium carbonate in water. According to LSI, RSI index value there have

some term such as water tends to be corrosive and corrosion tendency while it is saturated and super saturated with calcium carbonate, respectively (Bigoni et al., 2014). The Langelier Saturation Index (L.S.I.) is a means of predicting the probable nature of a given water supply i.e. whether it will have predominantly scaling or corrosive tendencies when applied to an industrial system. The Langelier Index is an approximate indicator of the degree of saturation of calcium carbonate in water. It is calculated using the pH, alkalinity, calcium concentration, total dissolved solids, and water temperature of a water sample (AlShamaileh et al., 2017).

(WQI) Indices have been used globally for human use and monitoring the surface water quality (Bilgin, 2018; Zhang, 2019). Find out the river water quality and pollution status (WQI) to be curtailed and empirical method of different physicochemical parameters (Tripathi & Singal, 2019). Multivariate statistical methods like principal component analysis (PCA) and hierarchical cluster analysis (HCA) is an environmetrics (Hamil et al., 2018; Yilma et al., 2018). Many researchers reported that the physicochemical properties of Karnaphuli River in several times but the corrosive characteristics of Karnaphuli river estuarine have not focused or determined. The present study was found out to evaluate concentration of different water qualities of physiochemical parameters and determining the corrosive characteristics of the Karnaphuli River by calculating the WQI, RSI, and LSI index. The aim of study is also to assess the physicochemical contamination and the identification of the source of input in the Karnaphuli river by using WQI and statistical analysis techniques (HCA and PCA).

Materials and Methods

Selection of sampling site

The length of Karnaphuli river is 270 km and it flows southwest through Chittagong Hill Tracts and terminate into the Bay of Bengal. TheTuichawng River, Kawrpui River or Thega River and Phairuang River are the main tributaries. During the 1960s, there was a hydroelectric project lunch in the Kaptai lake called Kaptai Dam that's provides power (230 megawatts) in Chittagong city. Chittagong's sea port is the largest and busiest sea port of Bangladesh which is located in the estuary of Karnaphuli river. In Chittagong, the climatic condition of the riverine area is varied from season to season because of their seasonal wind flow. In the wet season that is hot, overcast and oppressive but in the dry season it is warm, mostly clear and humid. Over the year, the temperature varies from *58°F* to *90°F*. The average annual Rainfall is o*17.8 inches*. The river is surrounding by hill track area and there are huge range of agriculture land, mill and factory covered. The soil is rich of carbonates, Fe and Al etc. For access rainfall, generally the Karnaphuli river's flow higher than wet season to dry season. On the area of the Karnaphuli river, total 30 water samples (sample RK1-RK10 were collected in winter season, RK11-RK21 in rainy season and RK21-RK30 spring season) were collected from 10 different locations which is listed in (Table 1 and Figure 1). Sampling location was selected at low tide of the river system. All the stations lies between 91°48′ to 91°51′ East longitudes and 22°19′ to 22°21′ North longitudes.

Sampling

The water samples were collected for physicochemical parameters from 0.6 m depth from surface by the grab method. The samples were collected 100 ± 2 m into the river from the bank i.e. mid axial during the low tide. For accurate assessment of effluent qualities, the samples were collected carefully, from ten points (Figure 1). Samples were collected during March, 2014 to August, 2015. The plastic bottles were first washed thoroughly with 10% HNO_3 and then distilled water before collecting the sample to make sure that it is completely free from any undesirable materials. During sampling, the sample bottles were first washed with sample. After taking samples, the bottles were labeled accurately by mentioning the name and location of the sampling sites, date, time of collection etc. The collected water samples were then carefully brought and preserved in refrigerator for laboratory analysis. The analytical work was completed as soon as possible after collecting the samples to ensure better results.

Sample analysis

Once a sample was taken, the constituents of the sample should be maintained properly as collected. For proper arrangement of the water quality parameters and making the sample representative; pH, TDS and temperature were recorded immediately

Table 1. Sampling stations with GPS values.

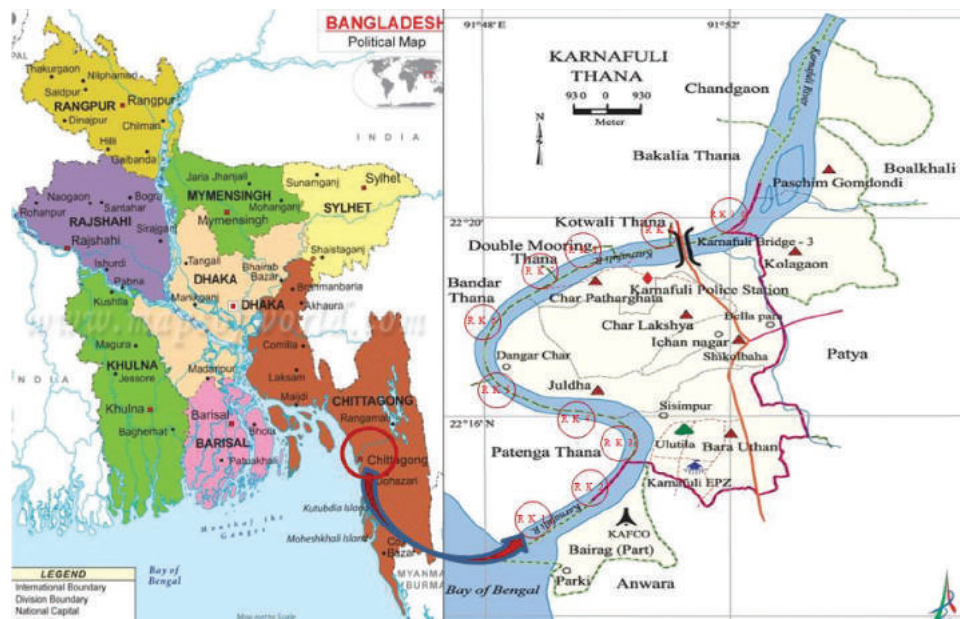| Sampling stations	GPS Value	Sampling stations	GPS Value
Bandor (Rk1)	22°19′9″N & 91°48′56″E	Bangla Bazar Ghat(Rk2)	22°1914″N & 91°4941″E
Anu mazi Ghat (Rk3)	22°19′21″N &91°49′25″E	Mazir Ghat (Rk4)	22°19′22″N &91°49′21″E
Custom Ghat (Rk5)	22°19′26″N&91°49′39″E	Sador Ghat(Rk6)	22°19′28″N&91°49′49″E
Firinghi Bazar Ghat (Rk7)	22°19′32″N&91°50′13″E	Chaktai khal Ghat(Rk8)	22°19′41″N&91°51′11″E
Sha Aamanat Bridge Ghat (Rk9)	22°19′44″N&91°51′22″E	Bhakoliya Khal Ghat(Rk10)	22°20′56″N&91°51′42″E

Figure 1. Sampling sites of the Karnaphuli river (red circles indicating the sampling stations from Bhandor (RK1) to Bhakoliya Khal Ghat (Rk10)).

after collection of each sample within 5–10 min by using Dissolved Oxygen (DO) meter and portable multi-meter. The samples were carefully transferred to the laboratory with minimum and acceptable chemical changes that is recommended for better result. The analysis to be made was fixed, prior to collection of samples. The collected samples were tested in the laboratory and maintain Laboratory Quality Management System (LQMS). A sample of 1.5 L was transferred to amber colored clean plastic bottle for analysis in the laboratory. Samples were preserved using suitable preservation technique. Other parameters such as Acidity, Alkalinity, Total Hardness, Chloride, Phosphorous, Sulfate, and CO_2 were analyzed as per the standard methods (APHA, 2012). Each analysis was done several times and the average was counted. Analytical methods are listed in Table 2.

Langelier Saturation Index (LSI) and Ryznar Stability Index (RSI)

There are two noticeable evaluating techniques of source water quality which are Langelier Saturation Index (LSI) and the Ryznar Stability Index (RSI). These indices depend on calculated *pH* of saturation for calcium carbonate (*pHs*). The water's actual *pH* and the *pHs* value are used to calculate the index as follows (Tables 3 and 4):

$$LSI = pH - pHs \qquad (1)$$

$$RSI = 2pHs - pH \qquad (2)$$

Table 2. Analytical methods of water quality parameters.

Parameters	Name of Instruments	Method of Analysis/Model
Temperature	DO meter	YK22DO
pH	pH meter	HannaHI-255
Acidity	Tritematric instrument	APHA method
Alkalinity	Tritematric instrument	APHA method
Total Hardness	Tritematric instrument	APHA method
Chloride	IC	HIC-10A(super),Shimad Zu, Japan
TDS	Protable Multi-meter	SENSION(™156)
CO_2	Tritematric instrument	APHA method
Phosphorous	UV-Visible Spectrophoto meter	UV-1650PC(Shimad Zu), Japan
Sulfate	IC	HIC-10A(super),Shimad Zu, Japan

Table 3. Langelier Saturation Index (Shankar, 2014).

Langelier saturation index	Tendency of water
LSI <- 2	Intolerable corrosion
−2.0 < LSI < −0.5	Serious corrosion
−0.5 < LSI < 0	Slightly corrosive but non-scale forming
LSI = 0	Balanced but pitting
0 < LSI < 0.5	Slightly scale forming and corrosive
0.5 < LSI < 2	Scale forming but non corrosive

Table 4. Ryznar Stability Index (Shankar, 2014).

Ryznar Stability Index	Tendency of water
RSI 4.0–5.0	Heavy scale
RSI 5.0–6.0	Light scale
RSI 6.0–7.0	Little scale or corrosion
RSI 7.0–7.5	Corrosion significant

Calcium carbonate saturation index (Langelier stability index) is frequently used to assess the scale forming and scale dissolving tendencies of water. The algebraic difference between the actual *pH* of a sample and its computed *pHs* is known as the Calcium Carbonate Saturation Index.

The value of *pHs* can be calculated using the nomograph or through the use of the following equation (Shankar, 2014).

$$pHs = (9.3 + A + B - (C + D)) \qquad (3)$$

Where, $A = [\log(TDS) - 1/10]$, *TDS* in ppm

$B = [-13.12 \log(T + 273) + 34.55]$, Temperature, *T* in ^{0} C

$C = [\log(Calcium\ hardness) - 0.4]$, *Calcium hardness* in ppm as $CaCO_3$

$D = [\log(Alkalinity)]$, *Alkalinity* in ppm as $CaCO_3$

The temperature affects the results obtained from the above equations. This index is a qualitative indication of the tendency of calcium carbonate to layout or dissolve. Positive value of the index means calcium carbonate tends to deposit whereas negative indicates dissolving of calcium carbonate. If it is zero, the water is at equilibrium.

Water Quality Index (WQI)

The WQI is a measure of the quality of surface or groundwater for most domestic uses. WQI reflects the combined effect of different water quality parameters (Sahu & Sikdar, 2008). WQI is calculated from the point of view of the suitability of surface and/or groundwater for consumption. Hence, for calculation of the WQI in the present study, 6 parameters such as pH, TDS, Total hardness, Alkalinity, chloride and Sulfate were selected (Table 5). There were three steps for computing WQI of water sample.

i. Each of the physicochemical parameters was transformed into a weight (w_i) depending on their influences on primary health or their relative importance in the overall water quality

ii. Relative weight (W_i) was calculated using Eq. (4)

iii. A quality rating scale (q_i) was measured by Eq. (5)

Finally, for counting *WQI*, the water quality sub-index (SI_i) for each chemical parameter is first composed, which is then used to determine the *WQI* as per the Eqs. (6) and (7).

$$W_i = \frac{w_i}{\sum_{n=1}^{n} w_i} \qquad (4)$$

Where W_i is the relative weight, w_i is the weight of each parameter and n is the number of parameters.

$$q_i = \left(C_i / S_i \right) \times 100 \qquad (5)$$

Where q_i= quality rating, C_i =concentration of each chemical parameter in each water sample in mg/L, S_i =Indian drinking water standard for each chemical Parameter in mg/L except for *pH* (BIS, 2012).

$$SI_i = W_i \times q_i \qquad (6)$$

$$WQI = \sum_{i=1}^{n} SI_i \qquad (7)$$

Where SI_i is the sub-index of ith parameter; q_i is the rating based on concentration of ith parameter and n is the number of parameters.

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., correlation analysis, principal component analysis (PCA) and cluster analysis (CA) are generally used in environmental studies (Rahman et al., 2014; Mendiguchia et al., 2004; Han et al., 2006). In the observation, multivariate analysis was executed by using Lab origin software 9.

PCA is widely used to minimize data and to extract a small number of overt factors for analyzing relationships among the observed variables (Farnham et al., 2003; Gou et al., 2007). PCA was verified to take the Principal Components (PC) from river water data and of the sampling point, to assess location variations and possible source of physicochemical parameters in river water. On the other hand, Cluster Analysis (CA) was executed to predict classify elements of different sources on the basis of the similarities of their chemical properties (Rahman et al., 2014).

Table 5. The weight (w_i) and relative weight (W_i) of each of the physicochemical parameters used for WQI determination (Ravi kumar et al., 2013).

Parameters	Observed Mean Value(C_i)	BIS Desirable Limit(S_i)	Weightage(w_i)	Relative Weight(W_i)	Quality Rating(q_i)	Sub-Index $SI_i = W_i \times q_i$
pH	6.25	8.5	3	0.158	73.53	11.93
TDS	778.83	1000	5	0.263	77.88	20.48
Alkalinity	275.63	200	2	0.105	137.82	14.47
Total Hardness	259.29	300	3	0.158	86.43	13.66
Chloride	534.63	250	3	0.158	213.85	33.79
Sulfate	70.74	200	3	0.158	35.37	5.59
			$\sum w_i = 19$	$\sum W_i = 1.0$		$\sum SI_i = WQI = 99.92$

Intuitive similarity relationships between any one sample and the entire dataset will help in the Hierarchical Agglomerative Clustering (HAC) which is generally illustrated by a dendrogram (McKenna, 2003). Some dramatic status gives dendrogram, which helps in the data analysis 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.

Results and Discussion

Physicochemical parameters of the Karnaphuli river water were measured during the three seasons as shown in Table 8. Descriptive statistics including the maximum, minimum, mean, variance and standard deviation values for the Karnaphuli river water are tabulated in Table 9. Environmental risk factor and ecological risk index for physicochemical parameters in the Karnaphuli river are shown in Table 10.

Alkalinity represents the ability of water to neutralize acids and indicates solution's activity to react with acid and buffer its pH that is, the power to keep its pH from changing. It is due to the presence of bicarbonates, carbonates and hydroxide of calcium, magnesium, sodium, potassium, and salts of weak acids and strong bases as borates, silicates, phosphates, etc. Higher concentration of alkalinity offers a bitter taste, harmful for irrigation as it damages soil and hence reduces crop yields (Sundar and Saseetharan, 2008). Table 8 shows that the Alkalinity of the Karnaphuli river varied from 10 to 650 ppm. Sampling station RK2 showed highest Alkalinity during the winter and spring season and lowest during the rainy season. Urea plant, chemical industry, cement industry, soap and detergent are responsible for the higher Alkalinity at sampling station RK2 (Tables 6 and 7). Department of Environment (DoE) sets 200 mg/l as a standard for the surface water Alkalinity. Table 8 shows that the observed values of some parameters in winter & spring season exceeded the acceptable limits for some stations which are listed in Table 10 and also shown in Figure 2.

Hardness is a chemical parameter of water, which scaling the corrosive characteristic of water that represents the total concentration of calcium and magnesium ions. Investigation showed that the Total hardness of the Karnaphuli river varied from 50.1 to 2308.4 ppm. Sampling station RK1 showed highest Total hardness during the winter season and sampling station RK3 showed lowest Total hardness during the rainy season. The higher Total hardness at RK1 is due to the cement industry, soap, and detergent plant (Tables 6 and 7) effluents discharged here. The nature of Karnaphuli river water can be considered according to Table 12 as hard water. Hard water is not suitable for domestic use such as washing, bathing, cooking as

Table 6. The location of the water industries close to the Karnaphuli.

Locations	Numbers	Locations	Numbers
Kaloorghat	150	Fisheryghat	123
Mohra	95	Dry-dock	143
Chandraghona	25	Katgore	60
Chaktai	116	Jaldia	60
Sadarghat	98	Gohira	40
Firingibazar	112	Port	98
	Total	**1120**	

Source: Field survey, 2014

Table 7. The type and number of pollution responsible industries.

Industries	Numbers	Industries	Numbers
Tannery	25	Steel Mill	03
Textile	65	Paper and rayon mill	03
Oil refinery	05	Soft drinks industry	10
T.S.P. plant	07	Cement factory	07
Urea plant	02	Soap and detergent	05
D.D.T. plant	03	Insect killer production plant	05
Chemical industry	04	Paint and X-ray production unit	07
Fish processing plant	60	Others industry	105
Asphalt bitumen plant	03		
	Total	**313**	

Source: Field survey, 2014

well as other purposes. Hard water is also not suitable for industrial and agricultural use. It damages the delicate machineries and affects the quality, stability and glossiness of the final product. According to the Environmental Conservations Rules (ECR) guideline, the range of Total hardness should be 200–500 ppm (ECR, 1997). Table 8 shows that most of winter and all rainy seasonal observed values exceeded the acceptable limit which is listed in Table 10 and also shown in Figure 3.

The Sulfate concentration of Karnaphuli river water fluctuated from 0.57 to 274 ppm. Sampling station RK1 showed highest Sulfate concentration during the winter and lowest during the rainy season. The presence of Carbon dioxide (CO_2) in this estuary is due to high salt concentrations discharged by the industries and from municipal waste which enriched with high concentration of sulfates, chlorides and bicarbonates. According to the ECR (1997) guideline, the acceptable limit of Sulfate concentration in wastewater should be 400 ppm. The observation showed that the concentration of Sulfate in the Karnaphuli river is pleasant tolerable level (Table 10) and (Figure 4).

Chloride is one of the most important parameters in assessing the water quality. The higher concentration of Chloride indicates higher degree of organic pollution (Munwar, 1970). It was shown that the Chloride of the Karnaphuli river varied from 7.82 to 2263.4 ppm. Sampling station RK1 showed highest Chloride during the winter while RK10 showed lowest Chloride during the rainy season. Sewage is such a rich

Table 8. Concentration of physico-chemical parameters in the three seasons.

Samples→ Parameters↓	Season	RK1	RK2	RK3	RK4	RK5	RK6	RK7	RK8	RK9	RK10
Temp(^{0} C)	Winter	26.50**	25.50	25.60	25.80	25.5	25.20	25.50	25.20	25*	25*
	Spring	29.20	29.40	29.30	29.10	29.20	29	28.70*	29.10	32**	32**
	Rainy	30.10	29.10*	29.90	29.90	30.00	31**	30.30	30	30.40	30.60
pH	Winter	6.76	6.50	6.33*	6.78**	6.47	6.38	6.56	6.38	6.71	6.62
	Spring	6.68	6.28*	7.01**	6.54	6.35	6.34	6.35	6.46	6.37	6.33
	Rainy	5.80	5.60*	5.70	5.80	5.70	5.70	5.70	5.60*	5.70	6**
Alkalinity	Winter	320	400**	320	350	385	280*	500	620	270	320
(ppm)	Spring	500	650**	30*	390	330	270	320	380	360	400
	Rainy	50	10*	30.00	140	70	50	160**	50	90	100
Acidity	Winter	15	15	30	35**	15	20	30	25	15	14.90*
(ppm)	Spring	35**	25	15	15	15	15	10*	10*	10*	35**
	Rainy	20	30**	20.00	20	20	20	25	15*	15*	20
TDS	Winter	2950**	2150	1660	1477	1235	959	605	788	360	171.40*
(ppm)	Spring	1249	1362	1239	1289	1386**	1343	1248	237*	673	312
	Rainy	98.90	71.60	56.20*	130.5**	123	66.60	73.30	68.10	150.40	90.90
Chloride	Winter	2263**	1643	1334	1153	1015	266	1061	554	92.58	17.93*
(ppm)	Spring	953	1024	939	959	1075	1254**	403	72.92	50.6*	104.1
	Rainy	20.12	32.05	22.12	73.5	54.98**	8.59	8.63	8.31	9.21	7.82*
Total hardness	Winter	2308.4**	562.2	621.4	357.8	335.2	256.5	323.7	168.1	145.7	87.7*
(ppm)	Spring	393.6	474.3**	357.6	351.8	439.7	387	379.4	285.8	204.8*	274.2
	Rainy	78.4	62.8	50.10*	84.9	102	53.7	65.2	56.3	113.3**	79.9
Sulfate	Winter	274**	199	160	139	124	33.8	128	71.7	19.37	5.52*
(ppm)	Spring	124	123	116	115	133	152**	59.9	16.41*	62.1	27.08
	Rainy	0.57*	10.27	7.36	21**	11.8	7.33	5.68	7.53	6.29	6.66
CO_2	Winter	13.2	13.2	26.4	30.8**	13.1*	17.6	26.4	22	13.2	13.2
(ppm)	Spring	30.8**	22	13.2	13.2	13.2	13.2	8.8*	8.8*	8.8*	30.8
	Rainy	17.6	30.8**	17.60	17.6	17.6	17.96	22	13.2*	13.2*	17.6
Phosphorous	Winter	0.57	0.91	0.68	0.64	1.38	1.02	6.19**	0.16*	1.16	1.44
(ppm)	Spring	0.99	0.94	0.77	0.92	1.52	1.16	6.19**	0.68	0.65*	1.1
	Rainy	0.64	0.39*	0.59	1.88**	1.08	0.39*	0.47	0.77	0.49	0.89

**→Seasonal Highest Value & *→Seasonal Lowest Value

Table 9. Statistics valued of physiochemical parameters in the studies area.

Parameters	N	Min	Max	Mean	Variance	Std. Deviation
Temperature(^{0} C)	30	25	32	28.35	5.16	2.07
pH	30	5.6	7.01	6.25	0.169	0.38
Acidity (ppm)	30	10	35	19.75	56.04	4.99
Alkalinity(ppm)	30	10	650	275.63	32160.60	165.93
TDS(ppm)	30	56.20	2950	778.83	546463.25	631.17
CO_2(ppm)	30	8.8	30.8	18.03	46.67	5.19
Phosphorous(ppm)	30	0.16	6.19	0.904	1.96	0.299
Total- hardness	30	50.1	2308.4	259.29	168695.48	167.33
Chloride (ppm)	30	7.82	2263	534.63	382683.95	535.31
Sulfate (ppm)	30	0.57	274	70.74	5132.99	61.29

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

source of Chloride, a high concentration may indicate pollution of water by sewerage effluent. According to the guideline of WHO (2011), the acceptable Chloride limit is 250 ppm while according to ECR (1997) the range lies between 150 to 600 ppm. Table 8 showed that some of the winter, spring as well as all the rainy season observed values of most of the stations exceeded the acceptable limits as listed in Table 10 and also shown in Figure 5.

pH is used to understand the corrosive nature of water. Lower pH indicates higher corrosive nature of water. Photosynthesis quantity depends on the pH value of water. By the decrease of photosynthesis rate, the emission of carbon dioxide and bicarbonates increases which are eventually responsible for increase in pH. Investigation shows that the pH of the Karnaphuli river fluctuated from 5.6 to 7.01. In the assessment, sampling stations RK2 and RK3 showed highest temperature during the spring while RK2 and RK8 showed lowest temperature during the rainy season. The higher pH at sampling stations RK2 and RK3 are due to the steel mills and tannery industries (Tables 6 and 7) effluents discharged there. According to the different standards, the acceptable pH range lies between 6.5 to 8.5 as listed in Table 10 (ECR, 1997; WHO, 2006). Sarwar et al. (2010) reported that Karnaphuli river water pH lies between 6.2 and 7.0 while this study showed that the pH in Karnaphuli river water is acidic as listed in Table 9 and also shown in Figure 6.

Total Dissolved Solids (TDS) basically represent the presence of different types of minerals and metallic ions which comprised both colloidal and dissolved solids in water. Turbidity of water increases with the increase of TDS value. Sampling station RK1 shows highest TDS during the winter season sampling station RK3 shows lowest TDS during the rainy season. Sampling

Table 10. Environmental risk factor and ecological risk index for physicochemical parameters in the Karnaphuli River.

Parameters	Season	N	Exceeded Samples	BSTI Std. Limit	WHO Std. Limit	ECR(1997) Std. Limit
Temp	Winter	10	—	—	—	30(sewage)
(^{0} C)	Spring	10	RK9, RK10			20–30(DoE)*
	Rainy	10	RK1, RK6, RK7, RK9, RK10			
pH	Winter	10	RK3, RK5—RK8	6.4–7.4	—	6.5–8.5*
	Spring	10	RK2, RK5—RK10			6–9(waste)
	Rainy	10	RK1—RK10			
Acidity	Winter	10	—	—	—	—
(ppm)	Spring	10	—			
	Rainy	10	—			
Alkalinity	Winter	10	RK1—RK10	—	—	200 (DoE)*
(ppm)	Spring	10	RK1, RK3—RK10			
	Rainy	10	—			
CO_2 (ppm)	Winter	10	—	—	—	—
	Spring	10	—			
	Rainy	10	—			
Phosphorous	Winter	10	—	—	—	8(waste)
(ppm)	Spring	10	—			
	Rainy	10	—			
Total	Winter	10	RK1—RK3, RK5—RK10	300	—	200–500*
Hardness	Spring	10	—			
(ppm)	Rainy	10	RK1—RK10			
TDS	Winter	10	RK1—RK5	500	1000*	2100(waste)
(ppm)	Spring	10	RK1—RK7			
	Rainy	10	—			
Chloride	Winter	10	RK1—RK5, RK7, RK9, RK10	250	250	150–600*
(ppm)	Spring	10	RK1—RK7			600(waste)
	Rainy	10	RK1—RK10			
Sulfate (ppm)	Winter	10	—	—	250	400*
	Spring	10	—			
	Rainy	10	—			

*→This value is considered for finding exceeded sample above the table; N→ Number
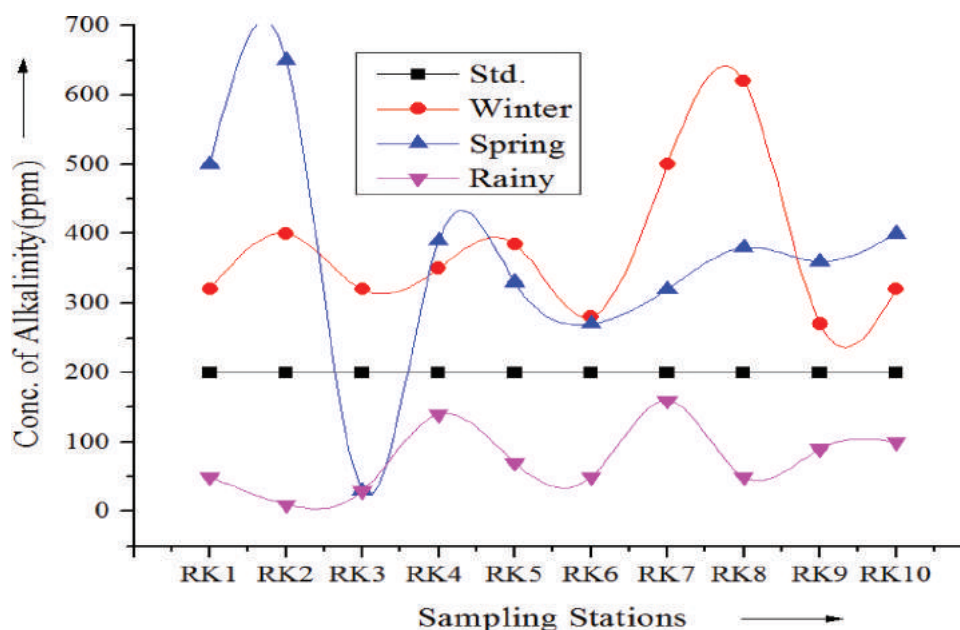
Figure 2. Concentration vs Sampling site of Alkalinity.

station RK1 showed highest TDS during the winter while sampling station RK3 showed lowest TDS during the rainy season. High TDS detected was due to the various dying stuff, which are used in the textile mills and they might be major sources of the heavy metals. It is noted that, the increase of heavy metal concentrations in the river sediment could increase the suspended solids concentrations (Kambole, 2003). TDS fluctuated from 56.20 to 2950 ppm. According to the guidelines of World Health Organization (WHO), the TDS should not exceed 500 ppm and 1000 ppm, respectively. Table 8 shows that winter and spring observed values exceeded the acceptable limits for most of stations as listed in Table 10 and also shown in Fig. 7.

Water temperature is one of the most important parameters for understanding the surface water systems and thermodynamic process in water environment.
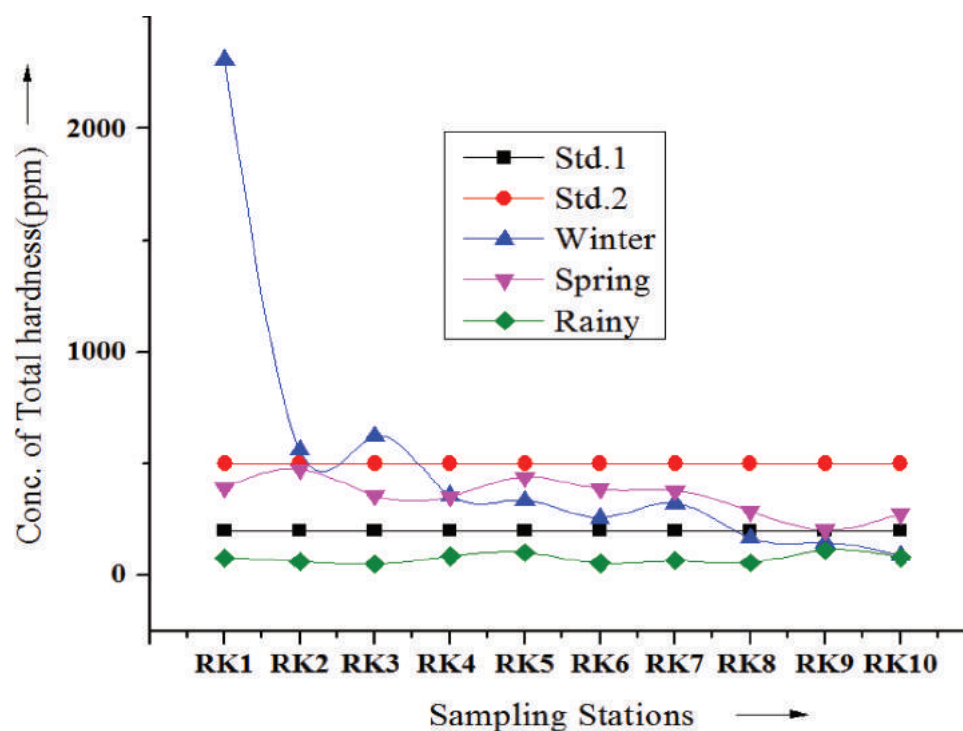
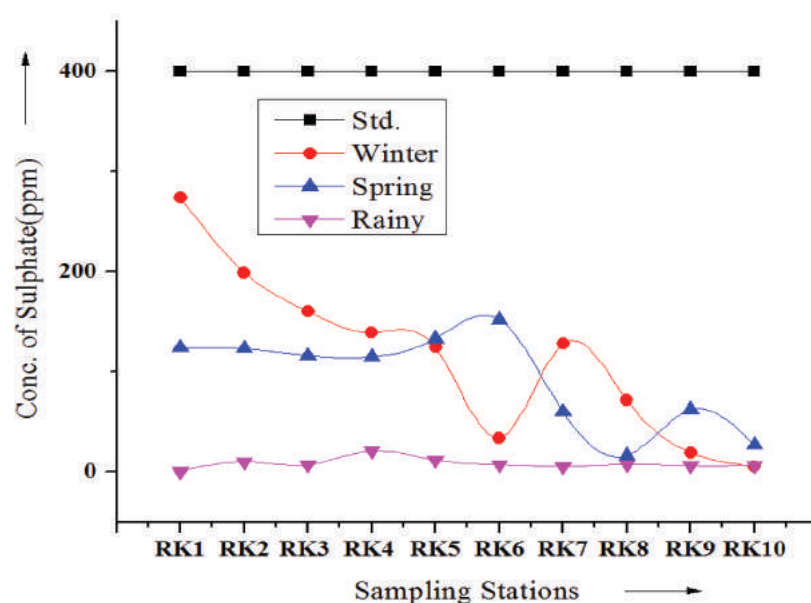**Figure 3.** Concentration vs sampling site of Total Hardness.

Figure 4. Concentration vs Sampling site of Sulfate.

Investigation shows that the temperature of the Karnaphuli varied from 25 to 32° C. Sampling stations RK9 and RK10 show highest temperature during the spring season and lowest during the winter season. The reason of higher temperature is the greenhouse effect or climate change fact and solar radiation. Besides, there are many mills and factories (listed in Tables 6 and 7) constructed on the banks of Karnaphuli river and use Karnaphuli's water for cooling purpose. After cooling they drained out their effluent into Karnaphuli river which increases the temperature. According to different standards, the surface water temperature limit is 20–30 ºC (DoE, 1997; ECR, 1997; WHO, 2006). Table 8 shows that some rainy and spring seasonal observed values exceeded the acceptable limits for all stations which as listed in Table 10 and shown in Figure 8.

Carbon dioxide is the end product of organic carbon degradation in almost all aquatic Environments and its variation is often a measure of the net ecosystem metabolism (Hopkinson, 1985; Smith, 1997). CO_2
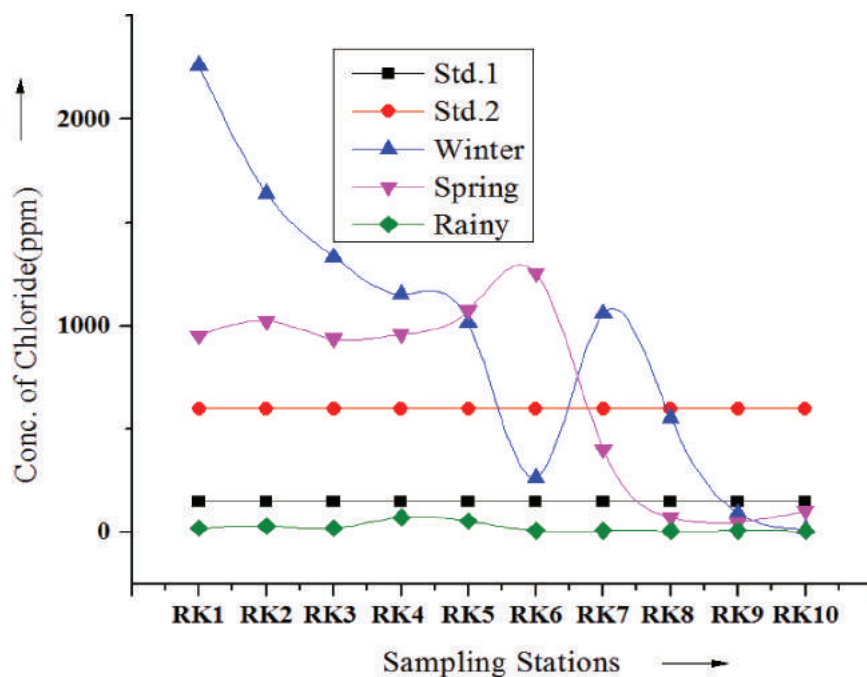
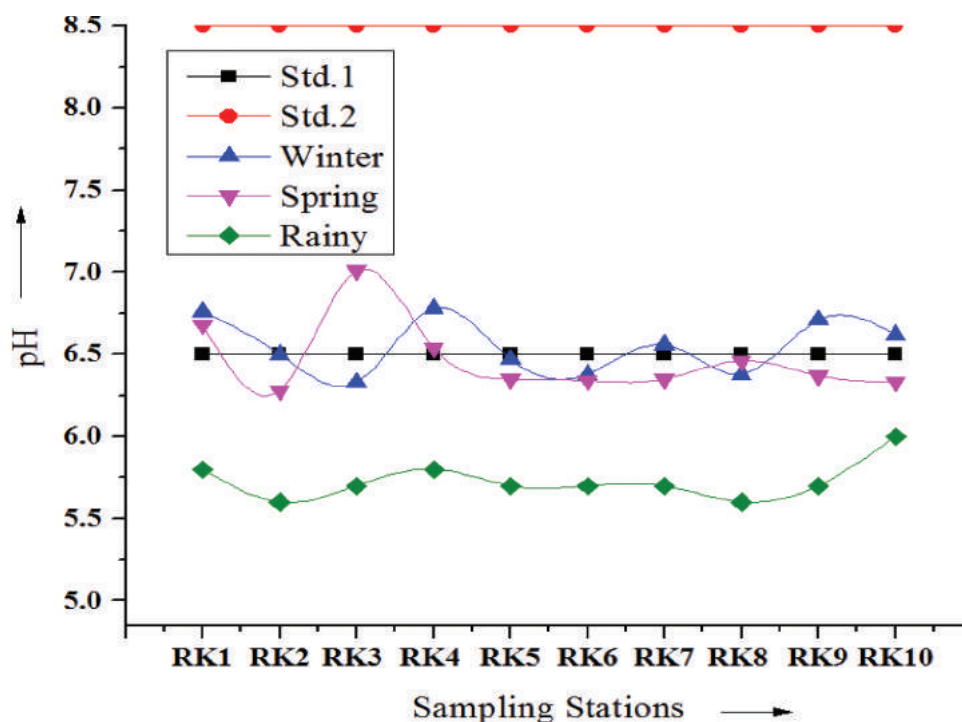**Figure 5.** Concentration vs sampling site of Chloride.

Figure 6. Concentration vs Sampling site of ig. 7. Concentration vs sampling site of TDS.

is also the most important greenhouse gas on the earth. Its snivel across the air-water or sediment–water interface is among the most important concerns in global change studies and is oft a measure of the total ecosystem production or metabolism of the aquatic system. Table 8 and Figure 13 show that the Carbon dioxide of the Karnaphuli river varied from 8.8 to 30.8 ppm. Sampling stations RK4, RK1, RK10, and RK2 show highest Carbon dioxide during the winter,

spring, and rainy season, respectively, and lowest carbon dioxide during the spring season at sampling stations RK7, RK8 and RK9. The higher carbon dioxide at RK4, RK1, RK10, and RK2 are due to the urea plant, chemical industry, fish processing plant, asphalt bitumen plant, soft drinks industry and other factory effluents discharged (Tables 6 and 7).

The phosphorous concentration of the Karnaphuli river water varied from 0.16 to 6.19 ppm. Sampling
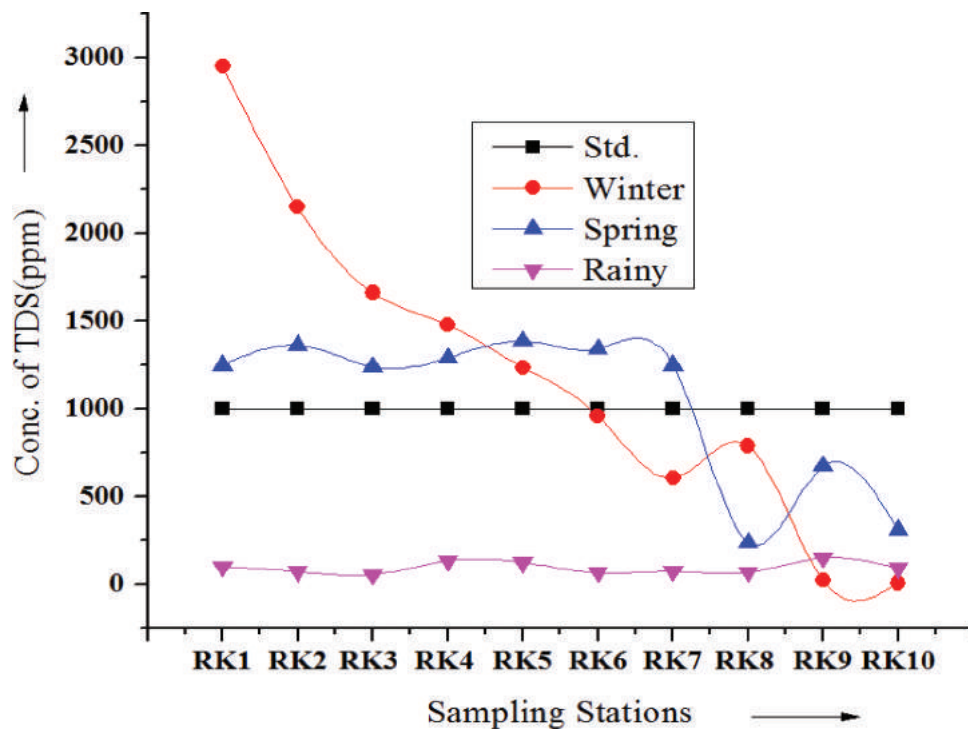
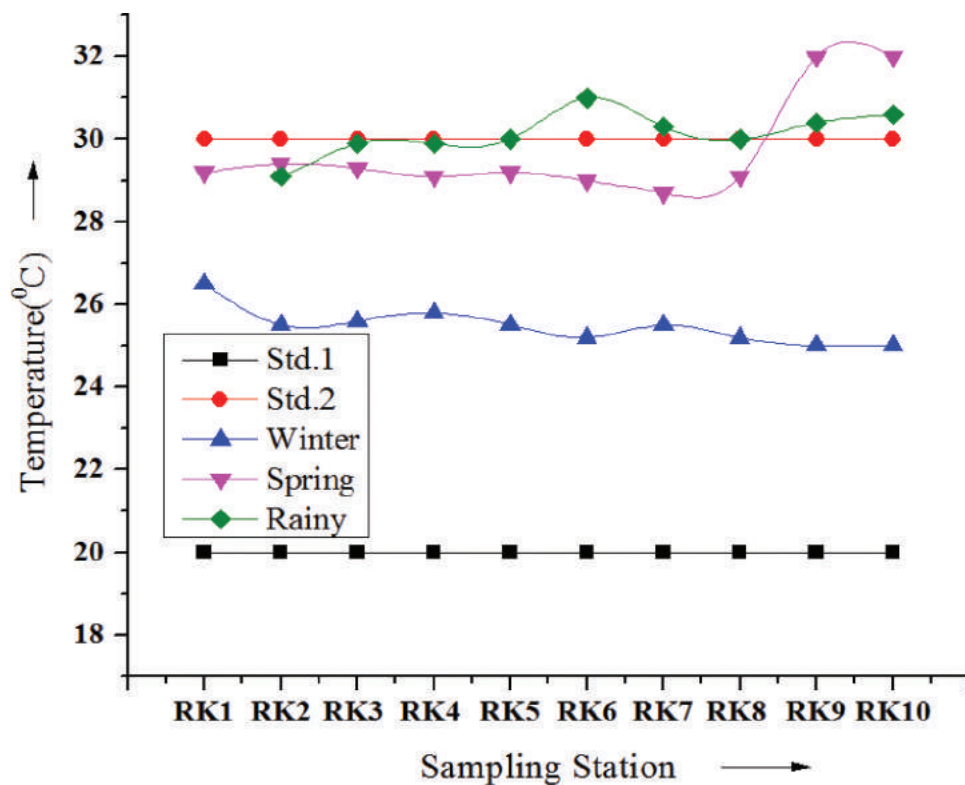**Figure 7.** Concentration vs Sampling site of Temperature.

Figure 8. Concentration vs Sampling site of Temperature.

station RK7 showed highest phosphorous concentration during the winter and spring season and lowest phosphorous concentration was shown in sampling station RK8 during the winter season. Soil erosion and Triple Superphosphate (TSP) fertilizer plant are responsible for the higher phosphorous concentration in river water. The increase in phosphorous concentrations in the rivers leads to eutrophication and depletion of dissolved oxygen concentrations (Davie, 2008). ECR (1997) limits acceptable phosphorous

Table 11. Results of physicochemical analysis of samples along with their saturation indices.

Parameters name→	Temp (^{0} C)	pH	TDS (ppm)	Calcium-hardness (ppm)	Alkalinity (ppm)	LSI	RSI
Winter mean value	25.48	6.55	1235.54	86.01	373	−2.81	12.18
Spring mean value	29.71	6.47	1033.8	96.74	390	−2.66	11.88
Rainy mean value	30.18	5.73	92.95	36.01	75	−3.45	12.70
Mean value	28.46	6.25	778.83	72.92	279.33	−3.06	12.36

concentration to 8 ppm for wastewater. It was shown that the concentration of Phosphorous in Karnaphuli river is pleasant tolerable level (Table 10).

The Acidity of the Karnaphuli river water varied from 10 to 35 ppm. Sampling stations RK4, RK1 and RK10 showed highest acidity concentration during the winter and spring seasons and lowest acidity was shown in sampling stations RK7, RK8, RK9 during the spring season.

Physicochemical analysis of samples along with their saturation indices are shown in Table 11 and classification of water depending upon the hardness is shown in Table 12. Investigation showed that the LSI value of Karnaphuli river water was −3.06, which indicates that this water is intolerable corrosive while RSI value was 12.36 (Tables 3 and 4). If water dumped by industries is not treated properly it would pollute the ground water (Olayinka & Alo, 2004).

Table 13 shows Water Quality Index (WQI) score and the equivalent Water Quality status. Water quality index technique used to assess the suitability of surface water. In the investigation, WQI was found to be 99.92, which indicated that Karnaphuli river water quality is poor according to Table (13). The Karnaphuli river water used for domestic, industrial, and irrigation purposes and without purification its water is not safe.

A correlation matrix was calculated by the statistics tools of MS Excel. Physicochemical parameters of water exposed significant correlations with a strong relation with each other as shown in Table 14. This correlation matrix of river water was calculated in order to ascertain the relationship among the physicochemical parameters where strong correlation

Table 12. Types of water hardness (WHO 2006).

Classification Hardness	Range (mg/L)
Soft	0–75
Medium hard	75–150
Hard	150–300
Very hard Above	300

Table 13. Water Quality Index (WQI) and status of water quality (Chatterji and Raziuddin 2007).

Water quality 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

($p <.01$) and significant correlation ($p <.05$). The temperature showed a negatively significant correlation with Alkalinity (r =−0.43), pH (r =−0.55), TDS (r = −0.45), Sulfate (r =−0.43) and Chloride (r =−0.48) and negatively insignificant correlation with Phosphorous (r =−0.18). The pH showed a negatively significant correlation with temperature (r =−0.55) and positive significant correlation with Alkalinity (r =0.62), Total hardness (r =0.47), TDS (r =0.66), Sulfate (r =0.64) and Chloride (r =0.62) also positively insignificant correlation with Phosphorous (r =0.18). The Alkalinity showed a negatively significant correlation with temperature (r =−0.43) and positive significant correlation with pH (r =0.62), TDS (r =0.50), Sulfate (r =0.52) and Chloride (r =0.49) also positively insignificant correlated with Acidity(r =0.20), Total hardness (r =0.29), CO_2 (r =0.16) and Phosphorous (r =0.23). The TDS showed a negatively significant correlation with temperature (r =−0.45) and positive significant correlation with pH (r =0.66), Alkalinity (r =0.50, Total hardness (r =0.82), Sulfate (r =0.96) and Chloride (r =0.95). The Chloride showed a negatively significant correlation with temperature (r = −0.48) and positive significant correlation with pH (r =0.62), Alkalinity (r =0.49), Sulfate (r =0.99), Total hardness (r =0.78) and TDS (r =0.95). The Total hardness showed a positive significant correlation with pH (r =0.47), Sulfate (r =0.79), Chloride (r =0.78) and TDS (r =0.82) also negatively insignificant correlated with temperature (r =−0.29). The Sulfate showed a negatively significant correlation with temperature (r =−0.43) and positive significant correlation with pH (r =0.64), Chloride (r =0.99), Total hardness (r =0.79), Alkalinity (r =0.52) and TDS (r =0.96). The CO_2 showed a positively significant correlation with Acidity (r =−0.99) and positively insignificant with Alkalinity(r =0.16). The Phosphorous showed a negatively in significant correlation with Temperature (r = −0.18) and positively insignificant with Alkalinity (r =0.23).

The scree plot (Figure 9) showed three PCs of Eigen values loaded 80.27% 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 shown in Table 15. Principal Component Analysis (PCA) is showing Table 15 of the samples.

Principal component analysis (PCA) was executed on the river water quality data using Multivariate Analysis technique, which was used to expand the

Table 14. Correlation of among the physicochemical parameters.

	Temp(°C)	pH	Alkalinity (ppm)	Acidity (ppm)	TDS (ppm)	Chloride (ppm)	Total hardness (ppm)	Sulfate (ppm)	CO_2 (ppm)	Phosphorous (ppm)
Temp(°C)	1									
pH	−0.55**	1								
Alkalinity (ppm)	−0.43**	0.62**	1							
Acidity (ppm)	−0.07	−0.03	0.20*	1						
TDS(ppm)	−0.45**	0.66**	0.50**	−0.04	1					
Chloride (ppm)	−0.48**	0.62**	0.49**	0.08	0.95**	1				
Total hardness (ppm)	−0.29*	0.47**	0.29*	−0.08	0.82**	0.78**	1			
Sulfate (ppm)	−0.43**	0.64**	0.52**	0.05	0.96**	0.99**	0.79**	1		
CO_2(ppm)	−0.05	−0.06	0.16*	0.99**	−0.07	0.06	−0.09	0.03	1	
Phosphorous (ppm)	−0.18*	0.18*	0.23*	−0.05	0.06	0.09	0.005	0.09	−0.06	1

Bold digits are significant at 95% and 99% confidence level as denoted by * (95%) and ** (99%).
*Correlation is significant at the 0.05 level (2-tailed).
**Correlation is significant at the 0.01 level (2-tailed).

observed relationship of cluster variables in simple ways, expressed in the pattern of variance and covariance between the variable and similarities between observations (Figure 10).

The PC1, PC2 and PC3 for river water quality data were elucidated the total variance of 47.13%, 20.73% and 12.42%, respectively. The PC2 in the data sets explained 20.73% of total variance, and it was positive loaded with Acidity and CO_2, which were significantly distributed in RK4 and RK9. The PC2 was also derived from several industries such as cement, chemical and steel mill industries that are located in the study area, which are responsible for physicochemical pollution. The PC3, accounting for 12.42% of total variance, was negatively loaded on Phosphorous which was widely distributed in RK10. The PC3 was mixed from chemical fertilizers industry in the river water.

The CA results mostly similar with that of PCA. Q-mode CA was used to identify the spatial similarities and site grouping among the sampling points. Particular group or class shows similar properties 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 (Figure 11). Cluster 1 consists of 15 sampling points. These 15 sampling points are RK1, RK2, RK4, RK15, RK5, RK14, Rk3, RK16, RK11-RK13, RK3, RK8, RK7, and RK22. Sampling points RK2 to RK8 were highest contaminated due to close to river industrial effluents discharged. Sampling points RK1 and RK22 are less polluted since contamination sources are at far distance while RK2 and RK3 are the mostly polluted region. Cluster 2 included to 10 sampling sites which are RK6, RK17, RK9, RK19, RK23, RK25, RK26, RK28, RK29 and RK30 and most of the industries situated in the sampling stations RK9 whereas cluster 3 consists of 5 sites which are RK10, RK27, RK18, RK20 and RK24, these sites are mostly less contamination of river water due to leaching of parent material and agricultural runoff.

Figure 11. shows that winter, spring and rainy seasonal sampling points were RK1 to RK10, RK11 to RK21 and RK21 to RK30, respectively.

Cluster analysis (CA) has three main clusters for datasets of analyzed parameters which led to forecast physicochemical groupings in the ground water or river water datasets and the results are shown in Figure 12. Parameters associated to the same cluster were likely to be found from a same source. Cluster 1 includes pH, TDS, Chloride, Alkalinity, Total Hardness, and Phosphorous, which might be explained by combining mixed sources, domestic, sewage, agricultural, and leaching of fertilizers from the rock or soil horizon to the aquifer. Cluster 2 consists of Acidity and CO_2 and it lighted the influence of greenhouse gas pollution and make the water acidic condition. Cluster 3 covers water temperature, if it was
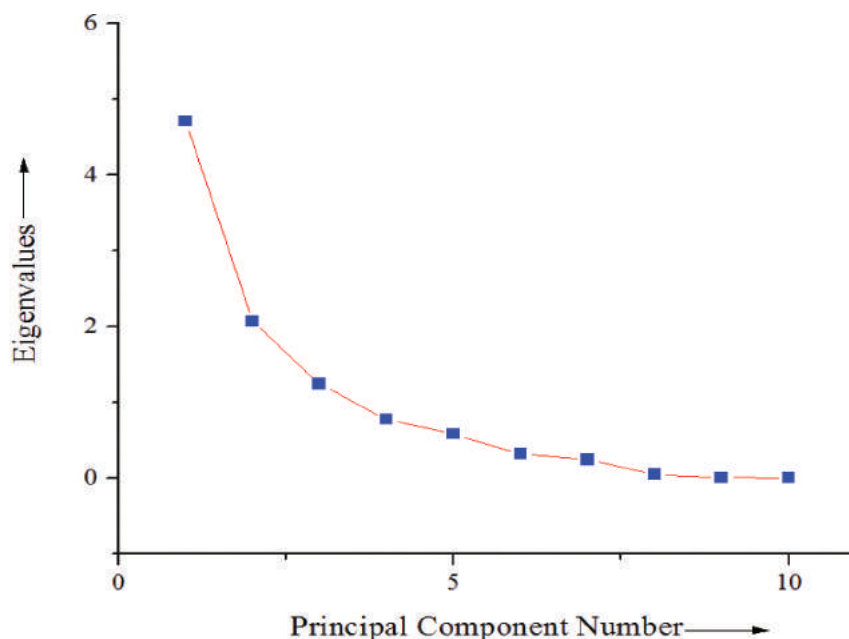
Figure 9. The Eigenvalues Vs Principal component analysis.

Table 15. Principal Component Analysis (PCA) for river water samples.

Parameters	PC1	PC2	PC3
R mode			
Temperature	−0.27112	−0.05925	0.35943
pH	0.35663	−0.03338	−0.26764
Alkalinity	0.29143	0.17482	−0.36969
Acidity	0.02217	0.68788	0.06548
TDS	0.4369	−0.076	0.17403
Chloride	0.43711	0.01285	0.17089
Total hardness	0.3667	−0.11636	0.32318
Sulfate	0.43872	−0.0068	0.175
CO_2	0.00788	0.68616	0.08373
Phosphorous	0.07028	−0.03598	−0.67576
Eigenvalues	4.713	2.037	1.242
% of variance	47.13	20.73	12.42
Cumulative %	47.13	67.86	80.27
Q mode			
RK1	−0.27112	−0.05925	0.35943
RK2	0.35663	−0.03338	−0.26764
RK3	0.29143	0.17482	−0.36969
RK4	0.02217	0.68788	0.06548
RK5	0.4369	−0.076	0.17403
RK6	0.43711	0.01285	0.17089
RK7	0.3667	−0.11636	0.32318
RK8	0.43872	−0.0068	0.175
RK9	0.00788	0.68616	0.08373
RK10	0.07028	−0.03598	−0.67576

drastic change of water temperature which is fatal for fish and biota (Patil, Sawant, & Deshmukh, 2012).

Conclusion

Pollution is unavoidable part of all economic activities. Rapid growth of the industrial sectors has greatly improved the quality of our life but has also contributed largely to pollution. Industrial pollution in Chittagong, especially industrial waste water pollution is increasing at an alarming rate and may create a great problem in near future and river will lost its navigability. It is apparently observed that the Karnaphuli river undergoes severe pollution. Firingi Bazar Ghat (RK7) and Custom Ghat (RK3) were the highest polluted stations; the second highest polluted stations were Bandhar (RK1), Anu Mazi Ghat (RK3) & Shador Ghat (RK6), respectively. The comparative observations showed high variance of winter to rainy seasonal variations of those parameters. Globally commercial coastal areas and marine fisheries are being damaging day by day due to pollution, which have been reported by researchers, therefore, control of hydrophyte pollution has been found as an immediate need for sustained management and conservation of the subsisting fisheries and aquatic resources.

Rivers constitute the major inland surface water sources for domestic, agricultural, and industrial purposes and these are essential for the development of human civilization. Chittagong City, the commercial capital of Bangladesh, is one of the most overcrowded cities in the country with a population of more than onemillion. The livelihood of the Chittagong city is directly or indirectly dependent on the Karnaphuli river. During the dry season the pollution level becomes higher due to the reduced Mean Daily Discharges (MDD) of the river which provides with a potential health and environmental risks to the general public. Government and non-government organizations will be taken into responsibility to protect the Karnaphuli river. With the help of the stakeholders the river must be revived-pollutant sources must be
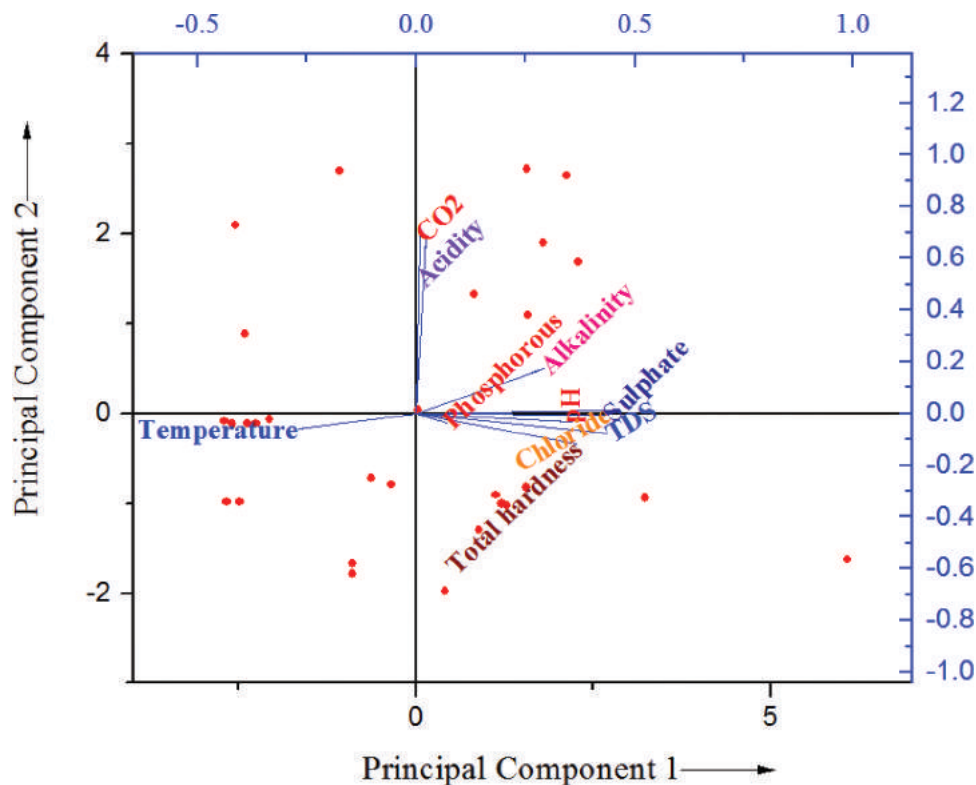
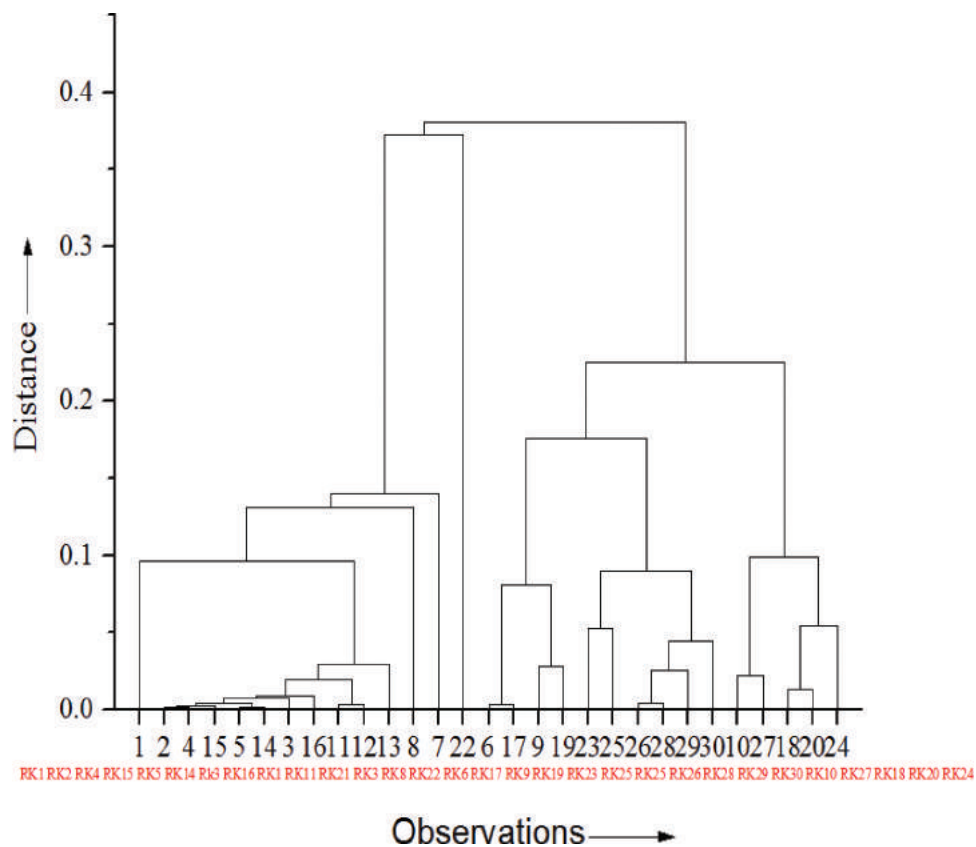**Figure 10.** PC2 vs PC1.

Figure 11. Distance vs Observations.

stopped so that the karnaphuli flows with its natural water. It is urgent to control the pollution source by the government body to stickily implementing laws or monitoring the ETP and save the river ecosystem. It is also needed to monitor the water quality parameter and remove the water pollutant by applying some method such as Aeration, Chemical Oxidization, Water Diversion to Flush out Pollutants, Phyto-
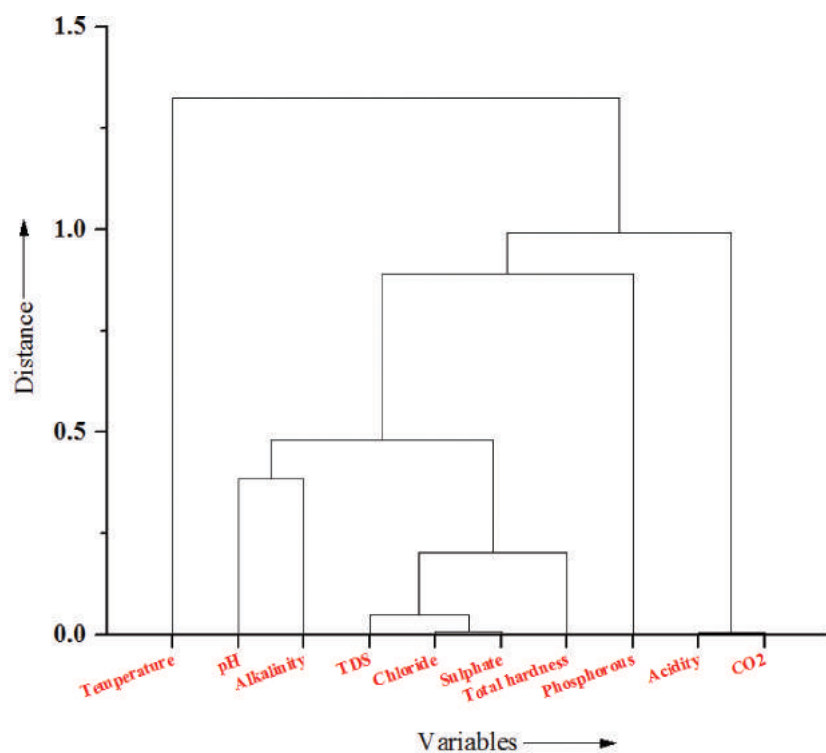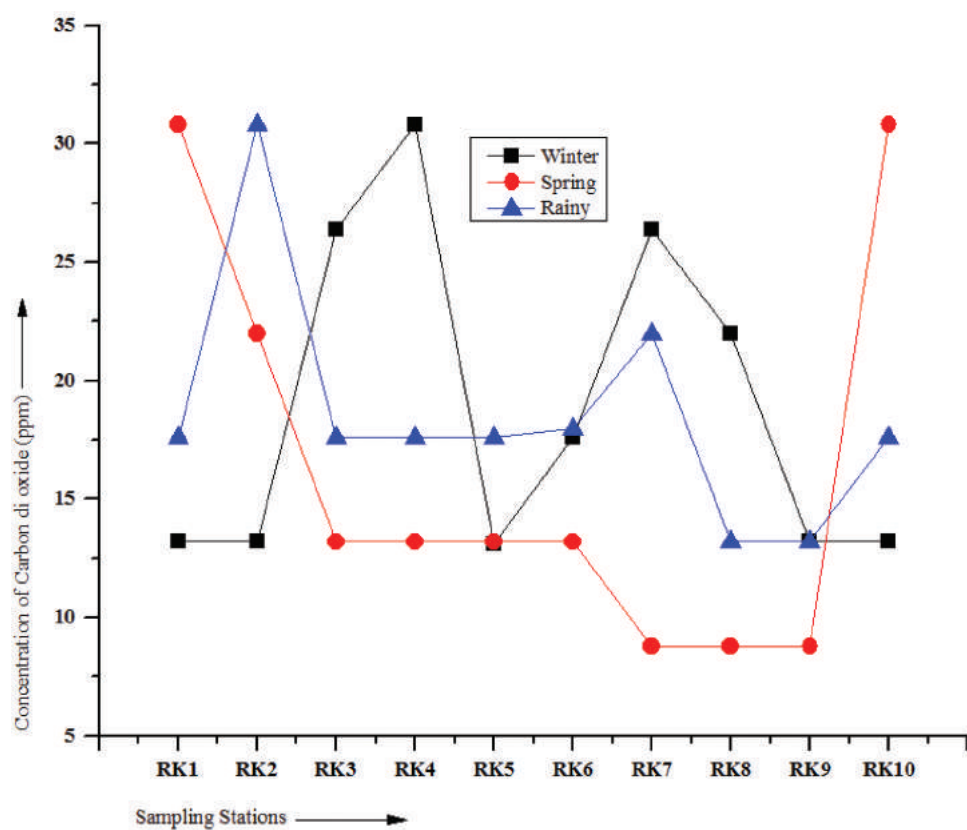
Figure 12. Distance vs Variable Parameters.

Figure 13. Concentration vs Sampling site of CO_2.

Remediation, Bio-film Technology, Remediation Technology with Aquatic Plants, and Aquatic Animals etc.

ORCID

Md. Ripaj Uddin [iD] http://orcid.org/0000-0002-9200-8039
Md. Moazzem Hossain [iD] http://orcid.org/0000-0002-3433-2500

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