



# Assessment of Physicochemical Parameters of Surface Water of Karnaphuli River in Bangladesh Towards Identification of Potential Sources

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## Abstract

In this study, water samples collected from Karnaphuli River, Chittagong, Bangladesh, were analyzed to assess physicochemical parameters to identify the possible potential sources of pollutants. Physicochemical parameters such as pH, alkalinity, acidity, conductivity, TDS, turbidity, total hardness, BOD, COD, ammoniacal-nitrogen, and sodium and chloride were varied from 3.05 to 9.34, 36.50 to 182.50 mg/L as CaCO<sub>3</sub>, 0.00 to 78.00 mg/L as CaCO<sub>3</sub>, 9.75 to 13.11 mS/cm, 6.36 to 10.40 g/L, 6.70 to 150.30 NTU,  $1.37 \times 10^3$  to  $1.95 \times 10^3$  mg/L as CaCO<sub>3</sub>, 5.50 to 45.50 mg/L as O<sub>2</sub>, 10.00 to 185.00 mg/L as O<sub>2</sub>, 0.00 to 12.60 mg/L as NH<sub>3</sub>-N,  $2.27 \times 10^3$  to  $2.92 \times 10^3$  mg/L and  $3.12 \times 10^3$  to  $4.60 \times 10^3$  mg/L in the water samples, respectively. Acidity, TDS, turbidity, total hardness, BOD, COD, and sodium were all very high near the TSP fertilizer factory's point source (site-2), while pH, alkalinity, NH<sub>3</sub>-N, and chloride were very high at KAFCO (site-11). At site-11, BOD and COD levels were also elevated. The results indicate that untreated fertilizer effluents contaminated river water significantly. Pearson correlation matrix for physicochemical parameters and sodium and chloride was also calculated to confirm the potential sources of pollutants in the river water. TSP plant effluent has been shown to cause acidity, TDS, turbidity, BOD, COD and sodium in river water, whereas ammonia-urea plants are found to cause high pH, alkalinity, NH<sub>3</sub>-N, as well as BOD and COD in the Karnaphuli River.

**Keywords:** Karnaphuli River, Physicochemical parameters, Triple Super Phosphate plant, Ammonia-urea plants, Pearson correlation matrix.

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## Introduction

All living things, from tiny cyanobacteria to giant blue whales, need water to survive. Without water, life as we know it would not exist. Like animals and plants, all organisms use water, whether it is salty or fresh, hot or cold, so water is called a universal symbol of life. Due to rapid industrialization and urbanization in Bangladesh, the quality of the surface water, such as rivers, canals, and

lakes, have severely deteriorated through the direct discharge of industrial effluents [1].

The continuously withdrawing groundwater for drinking, industrial and irrigation cause a significant reduction in quality water, however, irrigation provides about 40 percent of the world's food supply globally. A number of different industrial

units, particularly textile/dyeing, leather, pulp and paper, including irrigation, are being used in huge amounts of water [2]. The Himalayan and other northern mountains of Bangladesh are the sources of natural water for Bangladesh, thus many rivers flow over the country. About 230 rivers flow through the country, including 53 international rivers. Industrialization and urbanization are the potential sources of the contamination of these rivers and other water bodies [1]. The continuous, direct discharge of the industrial effluents into the rivers, canals and lakes causes severe pollution day by day [3-8].

The Karnaphuli River is the largest and most important river in the south-east part of Bangladesh. The river originated from the South Lushai Hills of Mizoram province in India with a latitude and longitude of 23°09'60.00" and 92°49'59.99", respectively. The river then enters into the greater Chittagong in the west and south-west directions and finally falls, after a course of about 270 km, into the Bay of Bengal at Patenga-Anwara coastal areas (22°12'38.12", N and 91°48'46.18", E). From the Chittagong Hill Tracts to the Bay of Bengal, the Karnaphuli River has served as the principal inland water transit route [9]. Many industries/factories such as Karnaphuli Paper/Rayon Mills Ltd, Chittagong Urea Fertilizer Ltd (CUFL), Karnaphuli Fertilizer Company Ltd (KAFCO), Diammonium Phosphate Fertilizer Company Ltd (DAPFCL), Triple Superphosphate Company Ltd (TSPCL), Eastern refinery, Chittagong Dry Dock Ltd (CDDL) and as many as metallurgical factories have been set up on its banks to use the inland transport facilities as well as to dump their wastes [9-11]. Consequently, Karnaphuli River has become contaminated through direct discharge of effluents from various industries, and it now faces terrible deterioration of natural water characteristics [9,10]. Chittagong is Bangladesh's second-largest port city, with

about 3.5 million populations. Karnaphuli River is the dumping place of the city and medical and solid wastes as well, thereby resulting in contamination of the river with different types of pollutants like organic, heavy metals, pathogens, etc.

Monitoring of physicochemical parameters of natural water is needed to assess their quality for various uses, including drinking, industrial, agriculture, aquaculture, and so on [12]. Chittagong is a port city, thus groundwater contains high levels of salinity and total dissolved solids (TDS). Therefore, Karnaphuli River water has been used as an alternative to groundwater for the fulfillment of city dwellers and industrial purposes after proper minimal treatment. However, the presence of different industries on its banks has fatally affected the river water quality. Because Chittagong is a port city, its groundwater has high salinity and TDS. As a result, with sufficient basic treatment, Karnaphuli River water has been used as an alternative to groundwater for the satisfaction of city people and industrial reasons. However, the presence of many industries on its banks has had a catastrophic impact on the river's water quality.

In this study, water samples were collected from twelve sampling sites in the Karnaphuli River's Patenga-Anwara industrial zone to investigate the following physicochemical parameters: pH, alkalinity, acidity, electric conductivity (EC), TDS, turbidity, hardness, chemical oxygen demand (COD), biochemical oxygen demand (BOD), NH<sub>3</sub>-N, sodium, and chloride to identify the possible sources of pollutants that significantly contaminate the river water.

## Materials and Methods

### *Study Area*

The Karnaphuli River is located in the east-south part of Bangladesh (Fig. 1). The

river mainly flows through the Hill Tracts and the port city Chittagong from its origin, South Lushai Hills of Mizoram province in India. This is the only means of inland transportation in the greater Chittagong from the Hill Tracts to the city and the Bay of Bengal. Because Chittagong is a port city, its underground water is not appropriate for drinking or industrial usage due to high salinity levels and

TDS. As a result, river water in Bangladesh's east-south region is the preferred option for multipurpose usage with minimal treatment. Fig. 2 (a, b, c) show photographs of the Triple Super Phosphate (TSP), Chittagong Urea Fertilizer Ltd (CUFL) and Karnaphuli Fertilizer Company Ltd (KAFCO), respectively.

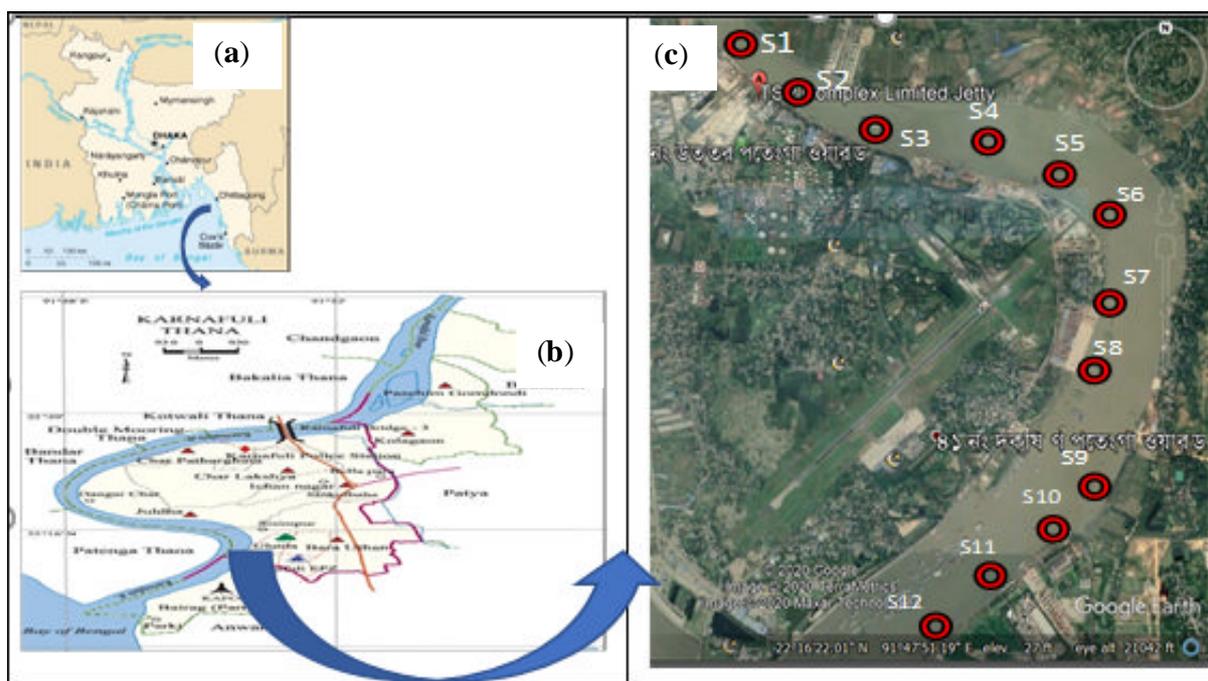


Figure 1. Bangladesh map (a), Karnaphuli river (b) and Sampling sites (c)



Figure 2. Photographs for the point sources of (a) Triple Super Phosphate (TSP), (b) Chittagong Urea Fertilizer Ltd (CUFL) and (c) Karnaphuli Fertilizer Company Ltd (KAFCO)

Table 1. Location of sampling sites, Karnaphuli river, Chittagong, Bangladesh.

Sample No.	Sampling locations (DMS N-E)	Industrial zones	Site codes	Distance from a point source of TSP plant
1	22°16'46.55" N 91°47'57.51" E		S1	-50 m
2	22°16'38.07" N 91°48'09.86" E	TSP plant	S2	03 m
3	22°16'22.12" N 91°48'27.82" E		S3	30 m
4	22°16'20.82" N 91°48'35.18" E		S4	200 m
5	22°16'16.16" N 91°49'01.33" E	Meghna Oil Jetty	S5	500 m
6	22°16'09.27" N 91°49'46.06" E	DryDoc	S6	1000 m
7	22°15'55.89" N 91°50'04.05" E	Boat Club	S7	1500 m
8	22°15'24.90" N 91°50'06.19" E		S8	2000 m
9	22°14'38.53" N 91°49'57.01" E	Ghat DAP	S9	2500 m
10	22°14'19.40" N 91°49'42.87" E	CUFL	S10	3000 m
11	22°14'04.27" N 91°49'12.40" E	KAFCO	S11	3200 m
12	22°13'46.86" N 91°48'55.30" E		S12	3500 m

DMS (N-E) degree minute second (northeast) of geographic coordinates of the sampling sites

### Chemicals and Reagents

Nitric acid, hydrochloric acid, sulphuric acid, sodium hydroxide, ammonia solution, Eriochrome Black T, ethylenediaminetetraacetic acid disodium salt dihydrate, potassium dichromate, mercuric sulphate, Mohr's salt, ferroin indicator, manganese sulphate, alkali iodide-azide solution, sodium thiosulphate, sodium potassium tartrate, Nessler's solution and mercuric nitrate were purchased from Merck, Darmstadt, Germany.

### Sampling

Water samples were collected in pre-cleaned 500 mL polyethylene terephthalate (PET) bottles (cleaned with 5% nitric acid and dried in an oven at 105°C) from the Patenga-Anwara industrial zone of the Karnaphuli River, Chittagong, during October 2018. Before sampling, the PET bottles were rinsed

twice with the river water in each case. The water samples were collected at a 10-15 cm depth from twelve sites along the river during movement of the tide out to sea (Fig. 1 and Table 1) [13].

### Methodology

#### Analysis of pH, EC, turbidity and TDS.

The pH, EC, turbidity and TDS of the collected water samples were measured immediately after collection using a portable multifunctional water checker (HORIBA, Japan, Model: U-5000) [13].

#### Alkalinity and acidity

**Alkalinity.** 50 mL of water was poured to a 250 mL conical flask, along with 4-5 drops of methyl orange solution, and titrated with 0.05 M hydrochloric acid until the color change from yellow to salmon pink was

observed. The total alkalinity was calculated by the following equation (1):

$$\text{Total Alkalinity} \left( \text{as } \frac{\text{CaCO}_3 \text{ mg}}{\text{L}} \right) = \frac{\text{BR} \times \text{M} \times 50 \times 1000 \times 1000}{\text{Sample volume (mL)} \times 100} \quad (1)$$

Where BR and M stand for burette reading and molarity of HCl, respectively and 1000 mL 1M HCl = 50 g CaCO<sub>3</sub>.

*Acidity.* 50 mL of water was placed into a 250 mL conical flask, and a few drops of phenolphthalein indicator was added to the water sample. When 0.05 M of standard NaOH solution was added, the color changed from colorless to pink, which was used to determine the endpoint. The total acidity was calculated using the equation (2):

$$\text{Total Acidity} \left( \text{as } \frac{\text{CaCO}_3}{\text{L}} \right) = \frac{\text{BR} \times \text{M} \times 50 \times 1000 \times 1000}{\text{Sample volume (mL)} \times 1000} \quad (2)$$

where M stands for molarity of NaOH. 1000 mL 1M NaOH = 50 g CaCO<sub>3</sub>.

*Total hardness.* 5 mL of the water sample was diluted to 50 mL in a 250 mL conical flask. After adding about 1 mL of ammonia buffer solution, 3-4 drops of Eriochrome Black T indicator were added. The water sample was then titrated with a standard 0.05M Na<sub>2</sub>EDTA solution until the color changed from wine red to pure blue. The total hardness was calculated using the equation (3):

$$\text{Total Hardness} \left( \text{as } \frac{\text{CaCO}_3 \text{ mg}}{\text{L}} \right) = \frac{\text{BR} \times \text{Molarity of EDTA} \times \text{Mol wt of CaCO}_3 \times 1000 \times 1000}{\text{Sample in mL} \times 1000} \quad (3)$$

where 1000 mL 1M EDTA = 100 g CaCO<sub>3</sub> mg/L.

*COD.* 50 mL of the water sample was taken in a quick fit flask of the reflux apparatus. Then 25 mL of 0.017M K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>

solution and 1 g of mercuric sulphate were added into the quick fit conical flask, and then it was fixed up with the apparatus. 20 mL of conc. H<sub>2</sub>SO<sub>4</sub> with silver sulphate was added through the condenser. The sample was refluxed for 1.5 hr. The remaining K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> was titrated with 0.1M (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub> solution upon the addition of 2 drops of ferroin indicator. A blank sample was run with the same procedure. 0.1M (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub> solution was standardized with a standard 0.017M K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution. The COD was calculated using equation (4):

$$\text{COD} = \frac{(\text{Blank} - \text{Sample}) \times (\text{Normality of FAS}) \times 8 \times 10^6 \text{ mg}}{(\text{Sample Volume}) \times 1000} \text{ as } \frac{\text{mg}}{\text{L}} \quad (4)$$

*BOD.* Two stoppered ground bottles were filled with the water sample, followed by the addition of 2 mL of 40% MnSO<sub>4</sub> solution and 2 mL of alkali iodide-azide solution. The bottle was agitated two times using a shaker for 10 min. Then 2 mL of concentrated H<sub>2</sub>SO<sub>4</sub> was added and again agitated using the shaker. The whole solution was transferred in a conical flask and titrated with 0.025 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solutions using 1-2 mL starch solution as an indicator. Dissolved oxygen was calculated using equation (5):

$$\text{DO} = \frac{(\text{Titration reading}) \times (\text{Molarity}) \times 8 \times 10^6}{(\text{Sample Volume in mL}) \times 1000} \text{ mg L}^{-1} \text{ as } \text{O}_2 \quad (5)$$

Where 1000 mL 1M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution = 8 mg O<sub>2</sub>.

*Determination of initial DO:* After filling the BOD bottle with sample and diluted water, dissolved oxygen (DO) was measured immediately by Winkler Method (Azide modification) in bottle 1 for initial DO.

*Determination of Final DO:* Determination of dissolved oxygen (DO) in bottle 2 after 5 days of incubation at 20°C.

Therefore, the BOD of the water sample was calculated using equation (6):

$$\text{BOD}_5 = (\text{DO before incubation} - \text{DO}_5 \text{ after incubation}) \times \text{Dilution Factor} \quad (6)$$

**Ammoniacal nitrogen.** About 1 mL saturated  $\text{ZnSO}_4$  solution was added to a 100 mL aliquot of the water sample to remove the turbidity. Then a solution of NaOH was added slowly until pH of the water sample was achieved at 10.5. The mixture was kept for 10 min to settle down the precipitate and then filtered. The requisite volume of the transparent water sample was taken into a 50 mL Nessler tube with ammonia free water. About 2-3 drops of sodium potassium tartrate solution were added to it in order to prevent cloudy tubes, followed by the addition of 1 mL of Nessler's solution (solution of potassium tetraiodomercurate (II)). The mixture was kept for 30 min and recorded the absorbance at 425 nm using UV-1800 (Shimadzu, Japan). Prior to doing this, a series of standard ammoniacal-nitrogen solutions of 1.0, 2.0 and 4.0 mg/L were prepared from the stock solution (1000 mg/L) upon successive dilution in order to construct an analytical calibration curve. Concentrations of the standard solution were plotted along the x-axis and the corresponding absorbance was on the y-axis. Concentrations of ammoniacal nitrogen for the water samples were calculated by knowing the absorbance of the water samples.

**Chloride.** 5 mL sample was diluted to 50 mL taken in a 150 beaker upon addition of deionized water followed by addition of 0.5 mL mixed indicator. The color of the water sample became purple. After that, 0.1 M  $\text{HNO}_3$  solution was added until the color turned yellow and then titrated with standard  $\text{Hg}(\text{NO}_3)_2$  solution. The appearance of permanent dark purple indicated the endpoint of the titration. Chloride concentration was calculated using the equation (7):

$$\text{Cl}^- = \frac{(\text{Sample} - \text{Blank}) \times M \times 35.45 \times 10^6}{(\text{Sample Volume}) \times 1000} \text{ mgL}^{-1} \quad (7)$$

where M stands for  $\text{Hg}(\text{NO}_3)_2$ .

**Sodium.** Inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Shimadzu, ICPE-9820, Japan) was applied to determine the amount of sodium in the water samples. To construct an analytical calibration curve, a series of standard sodium solutions ranged from 0.5 to 4.0 mg/L were prepared through dilution of 1000 mg/L sodium standard solution (ICP standard, KRIAT Co., Ltd., South Korea) (Fig. 3). Each of the points in the calibration curve was averaged with replication three ( $n = 3$ ).

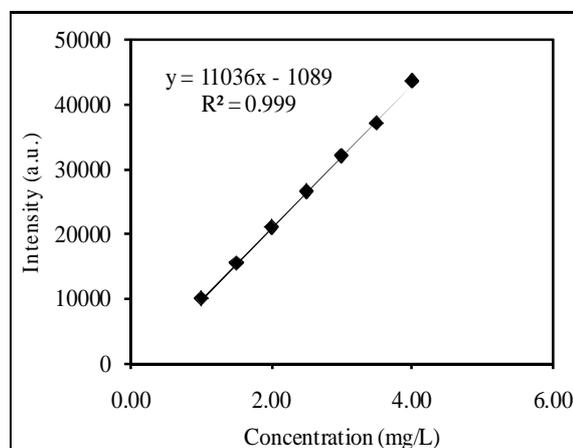


Figure 3. Calibration curve for measurement of sodium using ICP-OES

The calibration curve was used to estimate sodium concentration in the water samples along with SD, RSD and linear range correlation coefficient ( $R^2$ ). The value of  $R^2$  was found to be 0.999. In order to ascertain the analytical accuracy of ICP-OES, a certified reference material (CRM) of sodium (1000 mg/L Na in  $\text{HNO}_3$  (2%) of total 100 mL, Cat No: ICP-Na, KRIAT Co., Ltd., South Korea) was used. The CRM solution was diluted to a concentration within the calibration curve's concentration range, and replication three ( $n = 3$ ) was performed. Using the mean and SD values, the RSD was calculated and found to be less than 0.5%.

### Statistical analysis

Statistical software SPSS version 18.0 (SPSS, USA) was used to calculate the correlation matrix of the physicochemical parameters of Karnaphuli River water.

## Results and Discussion

### pH, Alkalinity and Acidity Measurements

Table 2 illustrates the pH values of the water samples on-site within a range from 3.80 to 9.34 with a mean value of  $7.26 \pm 1.47$ . The lowest (3.80) and the highest (9.34) values were found at sites-2 and 11, respectively. The direct discharge of effluent from the TSP fertilizer factory, which contains unused phosphoric/sulphuric acid, leads to an extremely low pH (3.80) at site-2. However, the alkaline pH of the river water detected at site-11 is caused by effluent from the ammonia-urea plants of the KAFCO limited (Table 2). This is because the effluents of ammonia-urea plants include free ammonia. The pH of water samples collected from the Turag river, an urban river in Dhaka, Bangladesh, was assessed by Rahman *et al.* and Ahmed *et al.* [14, 15], with values ranging from 7.0 to 8.0 and 6.11 to 8.37, respectively. According to FAO and DoE, the acceptable pH ranges for irrigation are 6.5-8.4 [16] and 6.5-8.5 [17], respectively. The WHO recommended a pH range of 6.5-8.5 for drinking water [12]. For aquaculture, the suitable pH range is 6.8-9.0 [18,19].

The water samples' alkalinity was within acceptable limits, ranging from 36.50 to 182.50 mg/L as  $\text{CaCO}_3$ , with a mean of  $91.25 \pm 33.82$  mg/L. Because of unused phosphoric acid and sulphuric acid in the TSPCL's effluents, the low level of alkalinity at site-2 (36.50 mg/L as  $\text{CaCO}_3$ ) is reasonable. The maximum alkalinity for aquaculture is 200 mg/L [18,19]. However, the range of suitable alkalinity for aquaculture is 50-300 mg/L.

The acidity of the river water was measured as  $\text{CaCO}_3$  and ranged from 0.0 to 78.0 mg/L, with a mean value of  $19.72 \pm 19.21$  mg/L (Table 2). The acidity of the river water was quite high (78.0 mg/L, site-2) due to the direct discharge of the TSPCL effluent. The TSP complex effluents contain high levels of unused phosphoric and sulphuric acid, which is the main cause of the elevated acidity at site-2 (Table 2). On the other hand, the acidity near the ammonia-urea plant (site-11) was recorded at 0 mg/L of  $\text{CaCO}_3$ . This is reasonable because of the existence of free ammonia in the effluent discharged from the ammonia-urea plant (Table 2).

### EC and TDS

The results show that the EC levels in the water samples ranged from 9.75 to 13.90 mS/cm, with a mean of  $11.89 \pm 1.30$  mS/cm (Table 2). Hossen *et al.* also estimated the EC of the Karnaphuli River water at the port area and Sandwip channel and found only  $1.56 \pm 0.55$  and  $6.70 \pm 4.82$  mS/cm, respectively [11]. The EC levels in urban river water (Turag river) were remarkably low, ranging from 0.77 to 1.43 mS/cm [15]. In another investigation, the EC levels of the Turag river water were measured and found to be 0.73-1.98 mS/cm [20]. Because of the direct discharge of effluents from many industrial units, it is expected that urban river water, such as the Turag River, will be significantly contaminated compared to the Karnaphuli River. The results suggest that several industrial units along the Karnaphuli River's banks contribute to the degradation of river water quality.

However, according to Bangladesh standards, the recommended EC for irrigation is only 2.25 mS/cm [17]. According to the WHO, the recommended EC value for drinking water is just 1.40 mS/cm [12]. The DoE, Bangladesh, recommended 0.70 and 1.0

mS/cm for drinking and irrigation water, respectively [17]. On the basis of different standards, it is, therefore, concluded that the river water cannot be used directly for either domestic or irrigation purposes. The high levels of EC in the river water suggested the presence of various ions such as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and their salts in the river water.

The levels of TDS varied from 6.36 to 10.404 g/L with a mean of  $8.22 \pm 1.34$  g/L (Table 2). The highest TDS value was recorded near the TSPCL point source (site-2) (Table 2). Hossen *et al.* reported that the TDS levels in the Karnaphuli River water at the port area and Sandwip channel were  $1.21 \pm 0.40$  g/L and  $4.62 \pm 3.45$  g/L, respectively [8]. TDS levels in Turag river water were measured by Rahman *et al.* and Ahmed *et al.* were low at 0.17-0.44 and 0.58-0.66 g/L, respectively [14,15]. Turag, as previously stated, is an urban river in Dhaka that has been used to load effluents from numerous industrial units since Bangladesh's industrial revolution in the 1950s. It is unusual to observe such low levels of TDS in the Turag river water. According to WHO, USEPA and DPHE, the permitted levels of TDS for drinking water are 0.50, 0.50 and 0.60 mg/L, respectively [12,21,22]. The high level of TDS in river water is undesirable to customers in various applications, including drinking, cooking, and industry.

### **Turbidity**

Turbidity measurements ranged from 6.7 to 150.3 NTU, with a mean value of  $60.55 \pm 38.96$  NTU (Table 2). The maximum level was observed at site-2 (150.3 NTU), which is close to the TSP fertilizer factory's point source; nevertheless, the lowest level was recorded at site-3 (6.7 NTU), which is just 30 m downstream of the TSP fertilizer

factory's point source (Table 2). The turbidity of another urban river, Turag, was measured and found to be 24.5-41.1 NTU [15]. The turbidity of Turag river water was just 27.4 NTU in another study [23].

The turbidity of the water can represent the presence of suspended colloidal particles in the aquatic system. The presence of unused phosphate rock as fine particles in the TSPCL's effluents is indicated by a high level of turbidity in the water at the point source. Fluorinated calcium triphosphate,  $\text{CaF}_2 \cdot \text{Ca}_3(\text{PO}_4)_2$  is a chemical phosphate rock that is highly insoluble in water [24]. The presence of calcium fluoride causes the insolubility of tricalcium phosphate. Fluorine's smaller size facilitates its high electron density, which repels the lone pair electrons of the oxygen atom in water molecules, preventing the phosphate rock from dissolving and instead of appearing as fine particles in effluents and river water. High turbidity in natural water is undesirable because it reduces sunlight penetration into natural water basins. Photosynthesis reactions in phytoplankton require a certain amount of light. A clear water body with an NTU of less than 25.0 can grow 12.8 and 5.5 times more plankton and fish than one with an NTU of greater than 100 [25]. The acceptable limit of NTU for aquatic life in natural water is only 8.0 NTU, however, we found above 8.0 NTU throughout the sampling region, with the exception of site-5 [26].

### **Total Hardness**

Total hardness in river water was found to be quite high, ranging from 1370 to 1950 mg/L as  $\text{CaCO}_3$ , with a mean of  $1729.50 \pm 186.61$  mg/L (Table 2). However, Ahmed *et al.* found only 180-345 mg/L in Turag river water [15]. Moniruzzaman *et al.* reported similar results in Turag river water [27]. The recommended hardness for

aquaculture is only 300 mg/L [25]. According to the DoE and DPHE, the permitted levels are 300 and 200-500 mg/L, respectively [17, 22]. Based on total hardness levels, water can be classed as soft (up to 70 mg/L), moderately soft (70-150 mg/L), hard (> 300 mg/L), and very hard ( $\geq$  800-900 mg/L) [28]. According to the current findings, the water in the Karnaphuli River has become highly hard and cannot be used directly for domestic or industrial purposes.

### BOD and COD

Table 2 shows the results of BOD and COD in water samples, with mean values of  $18.00 \pm 11.23$  and  $63.42 \pm 47.48$  mg/L. The highest levels of BOD (45.50 mg/L) and COD (185.0 mg/L) were detected at site-2, which is quite close to the point source of the TSP fertilizer factory (Table 1). The second highest

levels of BOD (28.5 mg/L) and COD (91.0 mg/L) were found at site-11, which is the point source for the KAFCO fertilizer factory's ammonia-urea plants (Table 2).

However, in April 2018, Hossen *et al.* collected water samples from the Karnaphuli River and found only  $4.10 \pm 0.57$  and  $12.68 \pm 2.01$  mg/L of BOD and COD at the Chittagong port area and  $5.44 \pm 1.21$  and  $15.15 \pm 1.19$  mg/L of BOD and COD at Sandwip channel, respectively [11]. Sarwar *et al.* on the other hand, found extremely high levels of BOD and COD in water samples collected from the Karnaphuli River (between January 2003 and January 2008), with mean values of  $247.47 \pm 73.22$  and  $560.27 \pm 160.21$  mg/L, respectively [10]. The BOD and COD levels in Turag, an urban river, were 20-52 and 180-382 mg/L, respectively [14].

Table 2. Physicochemical parameters of the water samples collected from Karnaphuli River during October 2018.

Sampling Sites (ID)	pH	Alkalinity mg/L as CaCO <sub>3</sub>	Acidity mg/L as CaCO <sub>3</sub>	Conductivity mS/cm	TDS g/L	TH mg/L as CaCO <sub>3</sub>	Turbidity NTU	COD mg/L as O <sub>2</sub>	BOD mg/L as O <sub>2</sub>	NH <sub>3</sub> -N mg/L as N	Cl ( $\times 10^3$ ) mg/L	Na ( $\times 10^3$ ) mg/L
S-1	6.80	85.17	15.0	9.75	6.624	1470	75.5	70	21.5	1.15	3.64	2.27
S-2	3.05	36.5	78.0	12.41	10.404	1950	150.3	185	45.5	2.15	4.08	2.92
S-3	7.30	73.0	20.5	10.67	6.904	1850	23.6	36	12.5	1.18	3.63	2.38
S-4	7.32	85.2	15.4	10.47	6.360	1764	50.2	28	11.0	0.73	3.12	2.38
S-5	7.39	109.5	15.35	10.6	7.340	1568	6.7	68	14.5	0	3.15	2.48
S-6	7.47	97.34	20.47	11.42	8.268	1862	45.5	25	7.8	0	3.28	2.70
S-7	7.62	85.16	15.35	12.57	9.172	1862	80.5	85	25.5	0	3.28	2.70
S-8	7.10	73.00	10.2	13.90	10.100	1764	15.3	10	5.5	0	3.26	2.70
S-9	8.10	85.16	20.5	11.94	7.344	1862	60.0	17	8.0	0.2	3.21	2.81
S-10	7.75	97.34	15.35	13.11	8.828	1372	53.0	78	18.5	1.5	3.57	2.81
S-11	9.34	182.5	0	12.76	8.096	1568	95.5	91	28.5	12.60	4.60	2.81
S-12	7.84	85.17	10.5	13.10	9.212	1862	70.5	68	17.0	0.15	4.60	2.81
<b>Mean<math>\pm</math>SD</b>	7.26 $\pm$ 1.47	91.25 $\pm$ 33.82	19.7 $\pm$ 19.21	11.89 $\pm$ 1.30	8.221 $\pm$ 1.34	1729.5 $\pm$ 186.6	60.6 $\pm$ 39.0	63.4 $\pm$ 47.5	18.0 $\pm$ 11.2	1.64 $\pm$ 3.53	3.62 $\times 10^3$ $\pm 0.53$	2.65 $\times 10^3$ $\pm 0.21$

The present results indicate that the Karnaphuli river water was primarily contaminated by inorganic pollutants, whereas the urban river, Turag, was contaminated by excessive bacteria/microorganisms, which could have resulted from industrial and domestic wastewater that depleted dissolved oxygen, resulting in increased biochemical oxygen demand in the river water [29]. Since the main seaport is located on the Karnaphuli River's bank, merchant ships and fishing vessels discharge grease, fish oil, bilge, garbage, and other pollutants, causing severe pollution. As a result, it is believed that the TSP complex and ammonia-urea plants are primarily responsible for the significant contamination of the Karnaphuli River. The wastewater, including phosphoric acid, sulphuric acid, bleaching powder, and other chemicals, is primarily responsible for the elevated COD and BOD levels seen at site-2. Furthermore, non-biodegradable organic substances such as lubricating oils, seal oils, and unused ammonia and urea contribute to high COD levels at site-11 (ammonia-urea plant, KAFCO). Ships, cargo vessels, oil tankers, fishing vessels, trawlers, and river crafts are the main sources of oil in the Karnaphuli river, which comes through handling, transit, ballast and bilge water and accidents, as the port authority lacks an oil reception facility.

The high level of biodegradable organic matter in effluents leads to BOD levels and reduces DO in receiving ecosystems. The permissible limits of BOD for drinking, recreation, and irrigation are 2, 3, and 10 mg/L, respectively, while 0-5 mg/L of COD indicates a very clean aquatic body [14,17,21,22]. COD in drinking water is limited to 4 mg/L [17,21,22]. However, according to the current findings, the mean BOD and COD values in river water were  $18.00 \pm 11.23$  and  $63.42 \pm 47.48$  mg/L, respectively (Table 2). The findings imply that river water can be used for drinking,

industrial, and agricultural applications after proper treatment.

#### *Ammoniacal-nitrogen (NH<sub>3</sub>-N)*

The results demonstrate that concentrations of ammoniacal-nitrogen varied from 0.0 to 12.6 mg/L with a mean value of  $1.64 \pm 3.53$  mg/L in the sampling area (Table 2). Site-11 is the point source of the ammonia-urea plant (KAFCO), which was reasonably contaminated with a high level of ammoniacal-nitrogen (12.6 mg/L), but it is below the detection limit in sites 5-8 (Table 2). In fact, on sites 5-8, there is no heavy industry except the Meghna oil jetty. Hence these sites were not contaminated with ammonia, resulting in NH<sub>3</sub>-N levels that were below the detection limit. The mean value of NH<sub>3</sub>-N in this study was  $2.46 \pm 4.15$  mg/L, although the permissible level is only 0.5 mg/L [30]. Most fish species are hazardous to 1.2-3.0 mg/L of free ammonia or ammonium (NH<sub>4</sub><sup>+</sup>), while the highest permitted limit for aquatic life is only 0.89 mg/L at 25°C [30]. Site-11 also meets the DoE effluent standard (50 mg/L ammonia N). As a result, it is considered that direct discharge of wastewater from ammonia-urea factories may pose a threat to the survival of fish within the point source area of site-11.

#### *Sodium and chloride*

The mean concentrations of Na<sup>+</sup> and Cl<sup>-</sup> ranged from 2.27 to  $2.92 \times 10^3$  and 3.12 to  $4.60 \times 10^3$  mg/L, with the mean concentrations of  $2.65 \pm 1.98 \times 10^3$  and  $3.61 \pm 0.51 \times 10^3$  mg/L, respectively (Table 2). Sites-2 and 11 had the highest concentrations of sodium ( $2.92 \times 10^3$  mg/L) and chloride ( $4.60 \times 10^3$  mg/L), respectively. However, the maximum chloride level in drinking water is only 4.60 mg/L [12], and it is just 4.0 mg/L for irrigation [31]. As stated previously, the highest levels of acidity, turbidity, hardness, TDS, BOD, COD, etc. were found at site-2, which is very close to the TSP fertilizer

factory's point source, whereas pH, alkalinity and so on were detected with high values at site-11 (near to the point source of ammonia-urea plants of KAFCO). As a result, it can be concluded that the excessive sodium in the river water at site-2 is attributable to the direct discharge of the TSPCL's effluent, while site-11 is very close to the sea.

In seawater, sodium ( $\text{Na}^+$ ) and chloride ( $\text{Cl}^-$ ) are the most common ions. The maximum values of sodium and chloride in the Bay of Bengal are about  $2.50 \times 10^3$  and  $3.80 \times 10^3$  mg/L, respectively [32]; nevertheless, these two ions are roughly  $3.0 \times 10^3$  and  $4.60 \times 10^3$  mg/L in seawater. Because of its geographical location, the Bay of Bengal has a low sodium chloride level. The Bay of Bengal is located in the northeastern part of the Indian Ocean, having an east coast border with the Indian supercontinent. As a result, the sea receives a significant amount of fresh water from rivers, rainfall, and surface runoff. The study's sampling region was the Karnaphuli River's Patenga-Anwara industrial zone, which is close to the Bay of Bengal's estuary (Fig. 1). The level of water in the downstream segment of the Karnaphuli River

is thus controlled by the tides and ebbs of the sea.

### Pearson correlation matrix

A correlation (r-value) matrix was calculated for the physicochemical parameters of the water samples to establish inter-parameter relationships to assess the possible sources of the parameters. This research aids in evaluating the possible sources of pollution in the Karnaphuli River caused by human activity. The matrix is tabulated in Table 3. As seen in Table 3, the alkalinity of the river water is significantly correlated with pH ( $r = 0.769$ ) and  $\text{NH}_3\text{-N}$  ( $r = 0.767$ ).

However, the acidity exhibits insignificant negative correlations with pH ( $r = -0.939$ ) as well as with alkalinity ( $r = -0.671$ ), indicating that acidity is inversely proportional to pH and alkalinity in the river water. The result also negatively correlates acidity and  $\text{NH}_3\text{-N}$  ( $r = -0.186$ ). As a result, it may be concluded that the effluents of ammonia-urea plants are the primary source of alkalinity and pH in river water.

**Table 3:** Correlation matrix of physicochemical parameters and sodium/chloride for the water samples collected from the Karnaphuli River.

	pH	Alkalinity	Acidity	EC	TDS	Hardness	Turbidity	COD	BOD	$\text{NH}_3\text{-N}$	Cl	Na
pH	1											
Alkalinity	0.769**	1										
Acidity	-0.939**	-0.671*	1									
EC	0.070	0.057	-0.018	1								
TDS	-0.405	-0.278	0.400	0.842**	1							
Hardness	-0.357	-0.504	0.445	0.139	0.301	1						
Turbidity	-0.489	-0.107	0.607*	0.192	0.386	0.215	1					
COD	-0.627*	-0.137	0.684*	0.144	0.459	0.006	0.811**	1				
BOD	-0.566	-0.072	0.631*	0.130	0.408	0.030	0.875**	0.976**	1			
$\text{NH}_3\text{-N}$	0.312	0.767**	-0.186	0.182	-0.014	-0.301	0.390	0.310	0.419	1		
Cl	0.008	0.308	0.063	0.350	0.312	-0.010	0.572	0.524	0.555	0.629*	1	
Na	-0.102	0.047	0.296	0.832**	0.774**	0.269	0.484	0.386	0.353	0.240	0.412	1

\*\* Correlation is significant at the 0.01 level (2-tailed).

\* Correlation is significant at the 0.05 level (2-tailed).

Acidity, on the other hand, has a positive relationship with turbidity ( $r = 0.607$ ), COD ( $r = 0.684$ ), and BOD ( $r = 0.631$ ). COD ( $r = 0.811$ ) and BOD ( $r = 0.875$ ) both have substantial positive correlations with turbidity (Table 3). COD has a good correlation with BOD ( $r = 0.976$ ). This data implies that different types of unused inorganic chemicals in TSP-effluents produce BOD via reducing DO of water due to inorganic pollutants' oxidation processes. As a result, it is concluded that effluents from the TSP factory are a common cause of acidity, COD, BOD, and turbidity in the Karnaphuli River's water. The significant positive correlation of chloride with  $\text{NH}_3\text{-N}$  ( $r = 0.629$ ) suggests that the ammoniacal-nitrogen from the urea plant at site-11 is a common source. Furthermore, the positive correlation of chloride with turbidity ( $r = 0.572$ ), COD ( $r = 0.524$ ), and BOD ( $r = 0.555$ ) in river water suggests common sources. Sodium, a seawater analog to chloride, has a strong positive relationship with conductivity ( $r = 0.832$ ) and TDS ( $r = 0.774$ ). These findings indicate that the source of prevalent sodium in seawater is distinct from the source of chloride in seawater. The highest level of TDS at site-2 is due to the direct discharge of effluents from the TSPCL unit, making TSPCL's effluent one of the potential sodium sources in river water. Because one of the potential sources of EC is TSPCL effluent, the positive correlation of sodium with electrical conductivity confirms its source of TSP effluent.

## Conclusion

The point source areas of TSPCL and Karnaphuli fertilizer factory are vulnerable due to the discharge of untreated and/or partially treated effluents from many industries, particularly phosphate and ammonia/urea units. Most of the vital physicochemical parameters, such as turbidity, BOD, COD, conductivity etc., exceeded the tolerance limits generally in the whole

sampling area. The high level of  $\text{NH}_3\text{-N}$  at site-11, the point source of Karnaphuli Fertilizer Factory (KAFCO), is alarming for the aquaculture in the river as well as in the Bay of Bengal. The Karnaphuli river is also polluted due to the discharge of urban wastages, land washout, shipping activities, city run-off, asphalt road constructions, atmospheric fallout, etc. It is mentioned that the Chittagong Urea Fertilizer Factory (CUFF) was shut down during the sampling period. The degree of contamination gradually decreases with increasing distance of the point sources, however, the coastal area of the Bay of Bengal is being contaminated by the upstream industrial pollutants. Therefore, properly functioning of the effluent treatment plants (ETPs) at the TSP complex and urea plants is a crying need to save the Karnaphuli River that might play a vital role in the development of the east-south part of the country. The fact that TSPCL and KAFCO are now working together to reduce river pollution by treating effluent.

## Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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