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Assessing the Water Quality and Its Influence on the Chlorophyll-a Concentration in the Karnaphuli River Estuary

Sadia Haque Sadi[1], K M Azam Chowdhury[1]*, Jarin Tasnim[1], Md Minarul Hoque[2], Mohammad Ashifur Rahman Shaheen[3] and Ashraful Moontahab[3]

[1]Department of Oceanography, University of Dhaka, Dhaka 1000, Bangladesh
[2]Faculty of Earth and Ocean Sciences, Bangabandhu Sheikh Mujibur Rahman Maritime University, Dhaka 1216, Bangladesh
[3]Department of Oceanography and Hydrography, Bangabandhu Sheikh Mujibur Rahman Maritime University, Dhaka 1216, Bangladesh

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ABSTRACT: The Karnaphuli river, essential for the economy and biodiversity of Bangladesh, faces increasing threat due to the proximity of industries, necessitating regular water quality monitoring to safeguard both environmental and economic interests. Hence, this study investigates the nutrient distribution and physicochemical parameters (pH, temperature, turbidity, dissolved oxygen, and electric conductivity) in relation to the chlorophyll a dynamics in the Karnaphuli river estuary during the monsoon season for evaluating water quality in the river estuary, stretching about 42 kilometres. Surface and deep-water samples have been collected from five different stations. Nutrients, chlorophyll concentration, and dissolved oxygen have been evaluated using a Continuous Flow Autoanalyzer, spectrophotometer, and DO kit, respectively, while electric conductivity, temperature, turbidity, and pH have been measured using a CTD tool. Spatial mapping and correlation analysis have been conducted as well. Temperature and pH values didn't show much fluctuation within the sampling stations falling within the range of 29°C-31°C and 6.5-7.5, respectively. Positive correlation of pH with ammonia at surface water (r=92) indicates that the effluents of ammonia plants are the primary source of pH in river water. TSP plant effluent has been shown to cause turbidity, evident from the positive correlation between phosphate and turbidity both at surface and deep water (r=91). Increase in turbidity (562.1 NTU) resulted in a decrease in dissolved oxygen (3 mg/L), which poses a serious threat to the survival of aquatic life, including fish, in the river downstream. Decreased water quality at river downstream is evident by comparatively low chlorophyll presence of 1.5 µg/L. However, the shallow coastal region in the study area is indicative of a healthy aquatic ecosystem evident by the presence of high productivity indicated by high chlorophyll concentration of 8.9 µg/L, which is due to comparatively low levels of turbidity and also the water condition there met the standard DO for fisheries (>5mg/L). The findings underscore the critical importance of regular water quality monitoring in the Karnaphuli river to safeguard both the environment and economy of Bangladesh, urging collective action to mitigate the escalating threats posed by industrial activities and ensure the long-term sustainability of the river ecosystem.

Keywords: Karnaphuli River; Water Quality; Physicochemical Parameters; Nutrients; Chlorophyll-a

INTRODUCTION

Water, the ubiquitous symbol of life, is an indispensable element for the preservation of aquatic and terrestrial ecosystems, as well as the intricate interactions between land and atmosphere (Cooper et al., 1998). The maintenance of water quality is a paramount environmental challenge, captivating the attention of diverse specialists, including environmental engineers, geologists, and hydrographers (Zaharin Aris et al., 2014). However, the current state of water resources in Bangladesh raises significant concerns, as a substantial disparity in both quantity and quality exists between surface and groundwater sources. In underdeveloped nations, waterborne diseases are rampant due to domestic, urban, and industrial waste polluting water sources (Effendi et al., 2015). The inexorable rise in water demand to support agriculture, industries, and urban and rural communities has intensified freshwater

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*Corresponding author: K M Azam Chowdhury

Email: azam_oceanographer.ocn@du.ac.bd

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scarcity globally. Hence increasing concerns regarding water scarcity, water quality maintenance and its long-term sustainability have garnered attention from governments, industries, and communities worldwide. Bangladesh, renowned as the land of rivers, boasts 230 rivers, including 54 shared with India, flowing through its 24,000 km of arable land. Among these rivers, the 270 km long Karnaphuli River, originating in India's Mizoram state, courses through the Chittagong Hill Tracts before merging into the Bay of Bengal (BIWTA). This river plays a pivotal role in supplying water to Bangladesh, with the nation's major port and commercial hub located on its western bank, endowing it with strategic significance. The Karnaphuli River's ability of natural purification arises from its direct mixing with the Bay of Bengal's waters, resulting in a relatively strong water current (Hasan et al., 2021). Nevertheless, this vital water source is witnessing a concerning decline in its natural water quality (Wang et al., 2016)persistence, and environmental toxicity, especially in developing countries like Bangladesh. Five heavy metals, namely chromium (Cr. As the urban population is growing, increased urban waste production and industries' demand for clean water have led to effluent discharge into the Karnaphuli river, leading to water quality degradation (Sarwar et al., 2010). Water quality encompasses the physical, chemical, biological, and aesthetic attributes that determine its suitability for various applications and its contribution to preserving aquatic ecosystems' health (Department of Water Affairs and Forestry, 1996). The quality of river water can be influenced by factors such as water level fluctuations, reduced dilution due to slow-flowing water, and increased chemical concentrations, including nutrient compounds (Utete & Tsamba, 2017) dire droughts and water abstraction pressures impact shallow man-made reservoirs with multiple designated water uses, often leading to water quality deterioration, and loss of biological integrity and utility value of a lake, threatening the livelihoods of lake shore communities. Thus, water quality information is crucial in setting up guidelines for freshwater resources management. In this study we investigated the water quality, determined the trophic state and assessed the influence of lake zones on the physical-chemical parameters of the Manjirenji Dam, Zimbabwe. Furthermore, we tested the applicability of two customary temperate water quality indices, the Canadian Council of Ministers of the Environment (CCME. Evaluating nutrient and chlorophyll-a (chl-a) concentrations and the extent of eutrophication is crucial for water quality assessment (Yang et al., 2020). Nutrient enrichment is commonly emphasized as a cause of biotic degradation in water bodies, yet little is known about the interaction between nutrients and chl-a in lotic habitats. Hossain (1983) and Jashimuddin (1993) evaluated the Karnaphuli river estuary's dissolved oxygen (DO), salinity, temperature and other parameters for determining water quality. Mahmood et al. (1976) conducted hydrological study of the Karnaphuli estuary. Furthermore, Ali et al. (1985) investigated the physio-chemical parameters of the Moheshkhali channel. Most of these studies concluded that land drainage during the monsoon, industrial wastewater discharge and direct contact of household sewage with water bodies all contribute to the degradation of water quality in rivers and estuaries of Bangladesh. Moreover, disposal of chemical wastes in Karnaphuli river is mostly to be blamed for the deterioration of the water quality in this region (Dey et al., 2015). Also, another study in the lower Meghna River Estuary found a continuous degradation of water quality there by examining parameters like temperature, TSS, pH, DO, BOD (Sharif et al., 2017). Some studies focused on rising levels of pollution in the river water supply that pose a serious threat to Karnaphuli river's aquatic biota and it also focused on why and how this is evident (Craig et al., 2004)catfishes and hilsa shad Tenualosa ilisha, a clupeid, predominate. About 20-30 fishes, mostly blackfishes, which are resident in the floodplain and tolerant of low levels of oxygen provide the majority of the national freshwater fish production. Most of the rural population fish professionally, seasonally or for subsistence. In addition to the harvesters, a further two million people are involved in activities related to the fisheries sector. The yield in the floodplain may vary from 50 to 400kgha-1 per year and the majority of the fishes is eaten fresh. For full-time fishers, conflict over water resources can be intense during the dry season when water is required for irrigation. Flood control, drainage and irrigation schemes may obstruct the lateral migrations of rheophilic whitefish species and the passive drift of larvae from the main channel to the modified floodplains. Existing modifications to the hydrological regimes may cause reductions in catch per unit area and fish biodiversity. The area under flood control is expected to be 5.74×106ha in 2010 resulting in a loss of ca. 151,300t of fishes. There has been a move away from the leasing of water estates ('jalmohals'. Therefore, regular monitoring of the water quality in the Karnaphuli River estuary has escalated in importance due to growing concerns and for preserving ecosystem health and sustaining livelihoods dependent on this essential water resource of Bangladesh. Numerous associations, such as the Department of Environment (DoE), the World Bank, the Environmental Protection Agency (EPA), the World Health Organization (WHO) and Water Aid, amongst others, have each established their own unique standard values for numerous river water parameters. Hence, this study entailed measuring the physicochemical parameters, spatial distribution pattern of chlorophyll a, and nutrients at the surface water and deep water at different points in the Karnaphuli channel including Patenga Estuary as this area is the most polluted due to the existence of the chemical fertilizer, iron, leather, and pharmaceutical sectors, from where poisonous wastewater is directly released into the Karnaphuli River without any treatment. This study aims to investigate the water quality of the Karnaphuli river and its influence on the phytoplankton community by assessing chlorophyll distribution. By identifying polluted and comparatively productive hotspots and understanding their impacts on aquatic life, the findings of this study can contribute to the development of targeted interventions to improve water quality and safeguard the health of ecosystems and communities dependent on these vital resources. It'll also provide evidence-based policy decisions and management strategies aimed at mitigating water pollution in the Karnaphuli river and similar water bodies across Bangladesh.

MATERIALS AND METHODS

Study Area

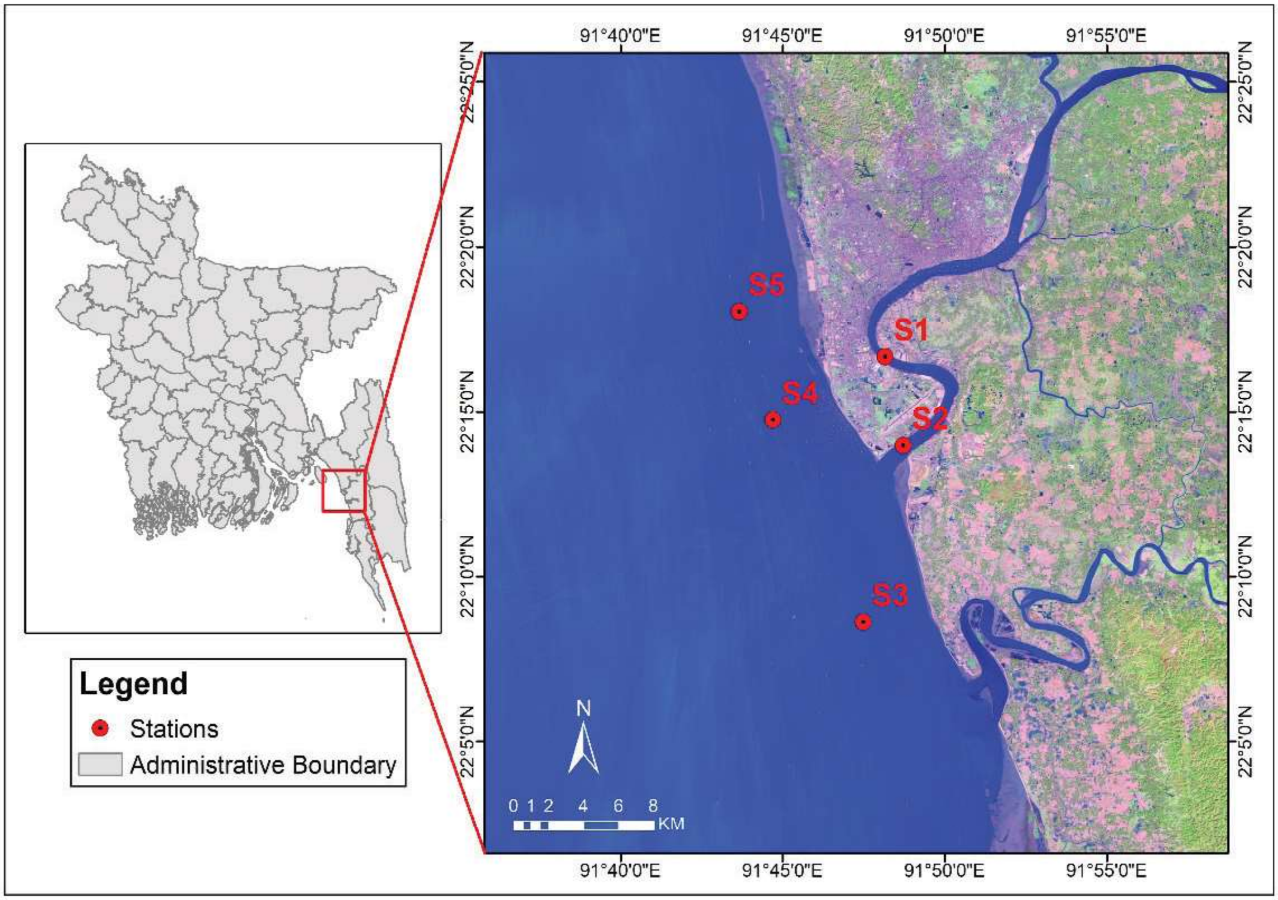

Figure 1: Map of the Study Area (Sampling Stations are Marked with Red Dots and S Indicates Station e.g., S1 Indicates Station 1)

This study was conducted in the Karnaphuli River estuary from 91°48.165 to 91°43.662 E longitude and 22°16.667 to 22°18.047 N latitude, stretching about 42 kilometers during the monsoon season in Bangladesh on August 19th, 2022. Samples were collected from five different stations near the TSP (Triple Super Phosphate) Complex Limited Jetty (S1 in Fig. 1), river estuary (S2 in Fig. 1), and shallow continental shelf off the coast of Chittagong (S3, S4, S5 in Fig. 1).

Sampling and Field Data Collection

Physicochemical parameters, including temperature, turbidity, pH, dissolved oxygen (DO), electric conductivity (EC), ammonia (NH_3), phosphate (PO_4^-), silicate (SiO_3^{2-}), and chl-a concentration for water quality analysis (Kumar et. al., 2012) were monitored using surface and deep-water samples from five downstream sampling stations. For deep-water collection, samples were taken from 6-meter(m) depth at station 1, 10m depth at station 2 and 3 and 13m depth at the next two stations. To analyze nutrient levels and chl-a concentration, 500 ml of water from each station was collected in polypropylene bottles that was previously rinsed with deionized water. Surface water was collected using a clean bucket, while deep water samples were obtained using a Niskin bottle. Sample bottles were sealed and labeled. The samples were transported to Dhaka in an icebox that was covered with black polythene to minimize exposure to sunlight and then stored at -20°C to prevent additional contamination until analysis. The samples were analysed at the laboratory of Bangabandhu Sheikh Mujibur Rahman Maritime University (BSMRMU). A portable GPS meter was used to identify geographic locations. CTD (Sea-Bird model) determined physical properties like temperature, turbidity, pH, and EC. A DO Test Kit (HI-3810) was used to measure dissolved oxygen.

Laboratory Analysis

Measurement of Chlorophyll-a Concentration

Water samples with a volume of 500 ml were collected from each sampling station using a Niskin water sampler and the interior part of the sampler is free from metal parts which is fully made of PVC. The method used for measurement of chl-a and phaeopigment was double extraction hot and cold treatment spectrophotometric method using 90% ethanol as solvent and 2M of HCl (Rai & Marker, 1982). Filtration of the water sample was done with the help of a vacuum filtration device using circle-shaped Whatman GF/F filter paper (47 mm diameter) on the flat circular surface of the filter holder. Calculation of chl-a and phaeopigment were estimated using the following formulae (Marker et. al., 1980):

$Eb = (Eb^{665} - Eb^{750})$

$Ea = (Ea^{665} - Ea^{750})$

Eb/Ea value must be 1.6 or very close to this for more accurate concentration of chl a.

$\text{Chl a } (\mu g/l) = 29.6\,(Eb - Ea) \times v/V \times l$

where,

Eb = Optical density before adding 2M HCl

Ea = Optical density after adding 2M HCl

v = Extracted volume of the pigment in ml

V = Filtered volume of sample water in liter

l = Path length of the cuvette

Nutrient Analysis

Nutrient analysis was performed using a continuous flow autoanalyzer (Skalar San++ Classic segmented flow analyzer) for ammonia (NH_3), orthophosphate (PO_4^-), and silicate (SiO_3^{2-}) measurement. For the analysis, some nutrient-specific reagents and standard solutions had to be provided in the Autoanalyzer. Multiple standard solutions covering a range of concentrations have been used in continuous flow autoanalyzer to construct a calibration curve, enhancing accuracy and precision by calibrating the instrument across a range of analyte concentrations.

Ammonia Analysis Reagents and Standard Solution

For ammonia analysis in the Continuous Flow Analyzer, two buffer solutions have been created and stored at 4°C for a month. Additional solutions include Phenol, Sodium hypochlorite, Sodium nitroprusside, and Air scrubber solutions. Distilled water with a similar salinity to the samples serves as the rinsing liquid. A standard solution of 381.9g of Ammonium chloride (NH_4Cl) has been diluted to create seven working standards of 250, 200, 150, 100, 50, 25, and 5 µg P/liter, for ammonia analysis in the analyzer.

Silicate Analysis Reagents and Standard Solution

Sulfuric acid solution (H_2SO_4), ammonium heptamolybdate solution, oxalic acid solution, L (+) ascorbic acid solution, rinsing liquid sampler, and a standard solution of Sodium metasilicate were needed to be provided into the autoanalyzer of SKALAR. A stock standard solution of sodium metasilicate ($Na_2SiO_3.9H_2O$) has been diluted to create seven more diluted stock solutions of various concentrations (1000, 800, 600, 400, 200, 100, and 20µg Si/liter) for further analysis automatically.

Phosphate Analysis Reagents and Standard Solution

Ammonium heptamolybdate solution, L (+) ascorbic acid and rinsing liquid sampler as reagent, and stock solution of potassium di-hydrogen phosphate (KH_2PO_4) is needed for the analysis of phosphate in the sample water through the continuous flow analyzer. For the stock solution, 439.4 mg of potassium di-hydrogen phosphate (KH_2PO_4) has been diluted to create seven diluted stock solutions of various concentrations (250, 200, 150, 100, 50, 25, 5 µg P/liter) for further analysis. After preparing reagents and the standard solution, the Autoanalyzer was initiated and rinsed with distilled water. Seven empty test tubes were positioned in their designated slots. Samples were poured into 100 ml test tubes and placed in the sample slots. The computer program and settings for the autoanalyzer were configured. Input tubes were immersed in the appropriate reagents and solutions, and the autoanalyzer was instructed to commence the analysis. Upon completion, the autoanalyzer generated tables, graphs, and statistical data for the analyzed nutrients.

Statistical Analysis

It is necessary to characterize the range of the data and the relationships between the different variables. For this purpose, descriptive statistics (median, maximum, minimum, standard deviation) and correlation analysis has been done. The Pearson correlation is applied to determine the degree to which two variables are related to one another. The percentage of variance in the dependent variable that may be attributed to differences in the independent variables is denoted by the correlation coefficient, r. The presence of a positive sign or value denotes a positive correlation between two variables, whereas the presence of a negative sign or value denotes a negative correlation (Magroliya et al., 2018).

Calculation of Karl Pearson's correlation coefficient formula is as follows:

$$r = \frac{n(\sum xy)-\sum(x)\sum(y)}{\sqrt{[n\sum x^2-(\sum x)^2][n\sum y^2-(\sum y)^2]}}$$

where,

r = Karl Pearson's correlation coefficient

y = Dependent Variable

n = Total Number of Observations

x = Independent Variable

The strength of the correlation is determined by the magnitude of the coefficient, with values close to -1 or +1 indicating a strong correlation, and values close to 0 indicating a weak correlation. This information can be used to develop strategies for water quality management and improve the overall water quality.

RESULTS AND DISCUSSION

The water samples were taken from the surface and deep water of the Karnaphuli river estuary over the marked domain in the study area (Figure 1). Table 1 depicts a wide range of measured electric conductivity, DO, physicochemical parameters, and turbidity. Depending on the location both high and low tides were covered during the sample collection.

Table 1: Details of the Sample Points Including Physical Parameters, DO, and Tide Values along with the Measured Concentration of the chl-a and Nutrients

Station No	**1**		**2**		**3**		**4**		**5**	
Condition	**4th hour of Low Tide**		**5th Hour of Low Tide**		**Last hour of Low Tide**		**1st Hour of High Tide**		**1st Hour of High Tide**	
Depth	**0 m**	**6m**	**0 m**	**10 m**	**0 m**	**10 m**	**0 m**	**13 m**	**0 m**	**13m**
Temperature (°C)	30.9	31.0	30.2	30.1	29.7	29.7	29.6	29.6	29.5	29
pH	6.5	7.3	6.7	7.0	6.9	6.9	7.2	7.1	7.5	7.3
EC (S/m)	0.6	0.2	0.5	0.8	0.3	0.6	0.2	0.7	0.2	0.8
DO (mg/L)	2.9	3	4	3.4	4	5	4.5	5.6	4.5	6.5
Turbidity (NTU)	169.3	562.1	127.7	294.7	80.3	288.5	46.9	285	56.1	185.6
Chlorophyll-a (µg/L)	1.5	1.5	3.0	3.0	3.0	4.4	4.4	4.5	4.4	8.9
Ammonia (NH_3-N) (µg/L)	4.2	4.5	5	4.4	5.1	5	5.4	5.8	5.6	6.6
Phosphate (PO_4^{3-}) (µg/L)	13.3	12.9	11.8	12.2	11.9	12	10.8	11.7	11.4	11
Silicate (SiO_3^{2-}) (µg/L)	235.5	178.8	354.2	107.1	304.1	12.7	154.1	178.2	145.4	258.5

Distribution of Physicochemical Parameters

pH levels at the surface water and deep water of sampling sites were nearly similar with a highest value of 7.5 at the surface water of station-5 and the lowest value of 6.5 at the surface water of station-1. The mean pH value were 6.96 at surface water and 7.12 at deep water, indicating nearly neutral pH at all the sampled stations (Table 2). The standard temperature for the survival of aquatic life in Bangladesh is 20°C-30°C (ECR, 1997). The fluctuation of temperature in the Karnaphuli River estuary was very low. As shown in Table 1, the highest observed temperature during the study period was at the deep water of station-1 (31°C) with a mean temperature of 29.98°C at the surface and 29.88°C at deep water, which mostly comply with the national standard. The comparatively higher temperature at station-1 was supported by higher turbidity at this station (Table 1). As shown in Table 1, at deep water highest turbidity was observed at station-1 which was 562.1 Nephelometric Turbidity Unit (NTU) and the lowest value was at station-4 (46.8947 NTU). A comparatively lower temperature of 29.6°C was also observed at station-4. Turbidity results from suspended solids present in the water which absorbs solar radiation and consequently causes an increase in water temperature (Patel et. al., 2015). This statement complies with the values obtained from the study area as the highest temperature was observed at station-1, where the turbidity was also high. This relationship between temperature and turbidity highlights the complex interplay of environmental factors in the study area, emphasizing the importance of understanding these dynamics for effective ecosystem management and conservation efforts. As per the observation, the turbidity of deep water was comparatively higher than that of the surface.

A sufficient amount of DO is required to keep the water quality maintained, which is necessary for the survival of aquatic organisms and the decomposition of waste materials by microorganisms (Islam & Meghla, 2010). DO level in the study area ranged from 2.9 mg/L to 6.5 mg/L with the highest value at station-5 and the lowest value at station-1 (Table 1), which is consistent with the temperature distribution at the study area as less oxygen is held by warm water than by cool water (Patel et. al., 2015).

In this study, the average value of DO was 3.9 mg/L and 4.7 mg/L at surface and deep water, respectively (Table 2). According to Boyd (1998), the ideal DO values for fisheries ranged from 4 to 6 mg/L. This is the threshold below which majority of aquatic organisms will not survive. The current analysis showed that the measured DO concentrations were much below the ECR-mandated maximum (5.0 mg/L) for water bodies, specially at station-1 and station-2. However, a high value of DO was observed at the deep water of station-3, 4 and 5 (5 mg/L, 5.6 mg/L and 6.5 mg/L, respectively).

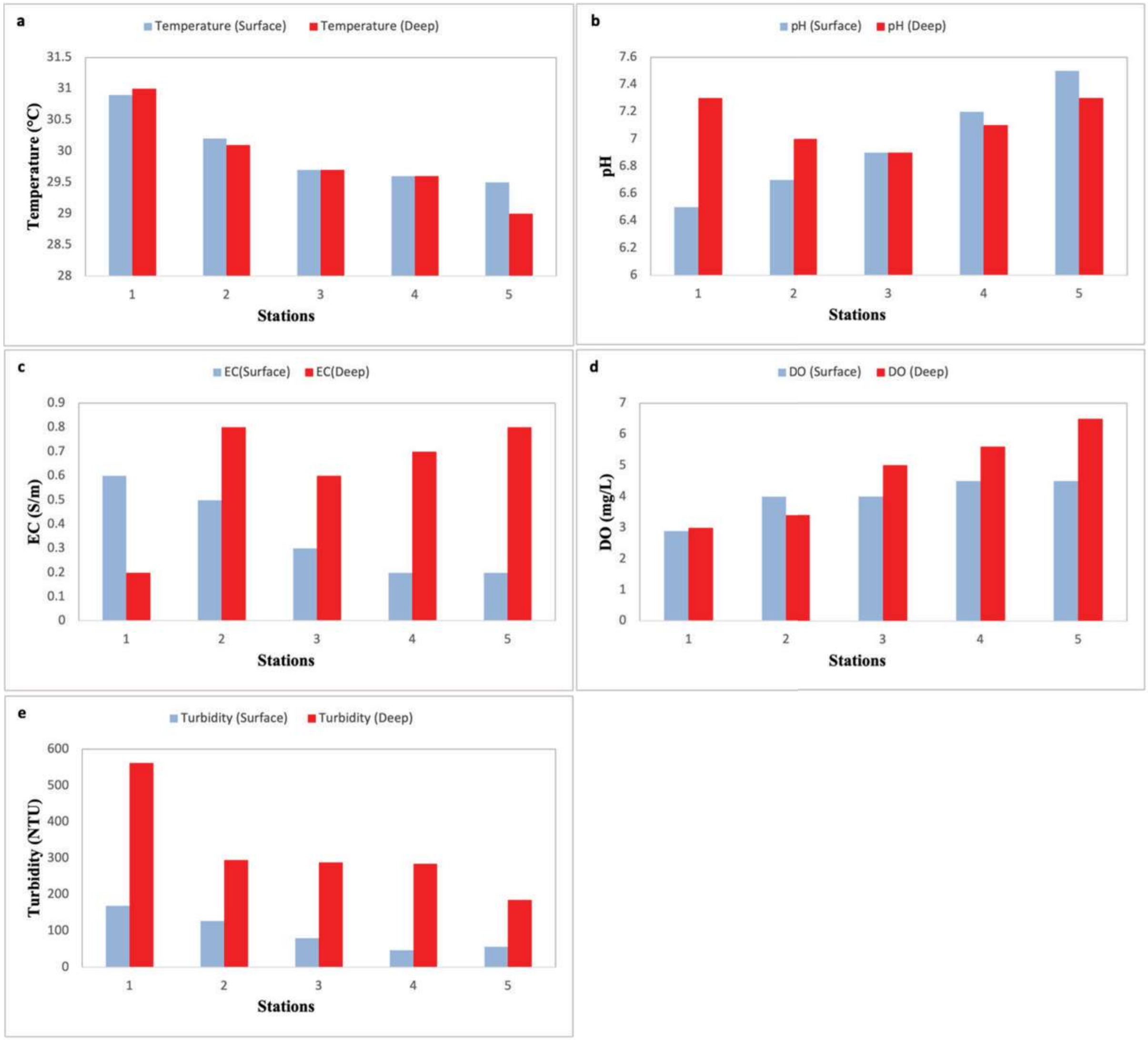

Figure 2: Variation in the Concentration of Physicochemical Parameters at Different Stations

The dynamic pattern of dissolved oxygen in the estuary results from intricate interactions among physical, chemical, and biological processes (Borsuk et al., 2001). The highest electric conductivity was observed at the deep water of station-4 (0.787509 S/m) the sample of which was collected at the time of high tide (Table 1). Salinity and conductivity levels in rivers are affected by the influx of salty water from the Bay of Bengal during high tide. At the time of low tide, saline water is drawn back into the ocean, which caused conductivity to decrease in river estuary. The lowest level of conductivity was observed at the deep water of station-1 (0.182014 S/m) at the time of low tide. Table 2 compares measured values with standard values for physicochemical parameters (EQS,1997) and chl-a concentration (Rahaman et al., 2013).

Table 2: Comparison of Measured Parameters with Standard Value

Parameter	**Surface Water**			**Deep Water**			**Standard**
	Min.	**Max.**	**Mean±SD**	**Min.**	**Max.**	**Mean±SD**	**Value**
Temperature(°C)	29.5	30.9	29.98±0.58	29	31	29.88±0.74	20-30
pH	6.5	7.5	6.96±0.40	6.9	7.3	7.12±0.17	6.5-8.5
EC(S/m)	0.2	0.6	0.36±0.18	0.2	0.8	0.62±0.24	0.08-0.1
DO (mg/L)	2.9	4.5	3.90±0.65	3	6.5	4.7±1.48	4-6
Turbidity(NTU)	46.9	169.3	96.06±51.5	185.6	562.1	323.18±140.9	10
Chl-a (µg/L)	1.5	4.4	3.26±1.20	1.5	8.9	4.46±2.77	0.24-3
Ammonia (µg/L)	4.2	5.6	5.06±0.54	4.4	6.6	5.26±0.93	0.5
Phosphate(µg/L)	10.8	13.3	11.84±0.92	11	12.9	11.96±0.69	6

The pH and temperature values were almost identical to the standard values. The measured turbidity levels were significantly greater than the standard values, indicating more polluted water. On the other hand, standard DO values were higher than observed values. The measured values for electric conductivity, ammonia, phosphate, and chl-a were higher than the standards as well.

Spatial Distribution of Nutrients and Chl-a Concentration in Surface and Deep Water

Silica is a major nutrient content of water. In surface water, the concentration of silicate in the study zone varied from 145 µg/L to 354 µg/L. On the other hand, in deep water, it varied from 12.74 µg/L to 258.45 µg/L. In the ocean, the amount of silica found in surface water was lower than in deep water. The hyperpycnal flow of water in the estuary is responsible for the pattern (Geyer et al., 2004). However, the concentration of silicate was lower in the mouth of the river or the estuary than in the channel of the river. In river channels, silicate is supplied from the weathering of rocks and soils in the upstream catchment areas. However, as river water flows into the estuary, it undergoes mixing with seawater, and this mixing can lead to the dilution of certain freshwater-derived constituents, including silicate. Additionally, estuaries are sites of biological activity where diatoms and other siliceous phytoplankton species thrive. These organisms readily utilize silicate for their growth, which can further deplete silicate concentrations in estuarine waters. The complex interactions of physical mixing, dilution, and biological processes contribute to lower silicate concentrations in estuaries compared to river channels (Anderson, 1986). Consequently, silicate is an essential nutrient for diatoms, a group of phytoplankton, and its availability can affect phytoplankton growth and composition. Silica is a crucial ingredient for aquatic organisms such as diatoms, radiolaria, and sponges, as it helps create their skeletons and spicules (Amann et al., 2014).

In surface water, the concentration of phosphate in the study zone varied from 10.8 µg/L to 13.3 µg/L. On the other hand, in deep water, it varied from 10.9 µg/L to 12.9 µg/L. The concentration of phosphate was higher in the channel than in the mouth of the river. Natural sources including the weathering of rocks and minerals, contributes to background phosphate levels and riverine transport nutrients into the estuary (Alam et al., 2023). The comparatively lower value in coastal part could be attributed to the utilization of phosphate by phytoplankton. Phosphate is known to be the main limiting nutrient for the growth of phytoplankton and chl-a (Correll, 1999). Phosphates are critical minerals that support organism growth and limit aquatic production. Inorganic phosphorous has a dynamic role in aquatic ecosystems when present in low concentrations, but high concentrations can promote eutrophication (Manikannan et al., 2011). The impacts of differing phosphates are significant; elevated phosphate levels can lead to promoting algal blooms that deplete oxygen when they decompose, negatively affecting water quality, aquatic biodiversity, and the overall ecological balance of the estuary (Li et al., 2011; Sterner, 1994; Vitousek et al., 1997). Anthropogenic causes, on the other hand, involve industrial discharges, agricultural runoff containing phosphorous-based fertilizers, and untreated sewage discharge, which introduce excess phosphates into the estuary (Smith & Longmore, 1980). In surface water, the concentration of ammonia in the study zone varied from 4.4 µg/L to 6.6 µg/L. On the other hand, in deep water, it varied from 4.2 µg/L to 5.6 µg/L. Ammonia concentration was relatively lower at river downstream and estuary than at coastal region. Elevated nitrate, phosphate, and ammonia levels can lead to water pollution, promoting eutrophication and harmful algal blooms. These blooms can deplete oxygen when they decompose, negatively affecting aquatic ecosystems, fisheries, and overall water quality. Though low nitrate and phosphate levels can limit primary production, potentially disrupting the estuarine food web, lower nitrite, and ammonia concentrations are generally preferred for a healthy aquatic ecosystem, as they are less harmful to aquatic organisms and contribute to better overall water quality (Tyrrell, 1999). In surface water, the concentration of chl-a in the study zone varied from 1.48 µg/L to 4.4 µg/L. On the other hand, in deep water, it varies from 1.48 µg/L to 8.88 µg/L. Chl-a concentration in the estuary and river channel is very low both in surface and deep water. But in coastal seawater, the chl-a shows the opposite scenario in both surface and deep water. Ammonium ion acts as an indicator of reservoir pollution level. Pollution of water decreases primary productivity (Ghazaryan et al., 2012). From the estuary towards the coastal region, the chl-a concentration at the surface was high when the ammonium concentration was high as well. The same scenario persists in deep water. Karnaphuli estuary receives not only freshwater inputs from rivers but also tidal inflows of nutrient-rich seawater. The mixing of these two water sources creates favorable conditions for phytoplankton growth. Additionally, estuaries serve as nurseries for various aquatic organisms, leading to high biological activity and the release of organic matter, which can serve as a nutrient source for phytoplankton. The confinement of estuarine water and sediment can also result in the retention of nutrients, promoting algal blooms. This dynamic interplay of nutrient inputs, mixing, and biological processes leads to elevated chlorophyll-a concentrations in estuaries (Cloern, 2001). In the river downstream, where chlorophyll-a concentrations were low, ammonia concentrations were also relatively low, limiting primary production and thus chlorophyll-a synthesis. On the contrary, in coastal seawater, higher concentration of chlorophyll-a was observed, coinciding with elevated levels of nutrients like ammonia. These nutrients fuel the growth of phytoplankton, leading to higher chlorophyll-a concentrations. This relationship highlights the significant role of nutrient enrichment in coastal waters, promoting primary productivity and supporting a diverse and productive marine ecosystem.

Correlation Analysis

Pearson correlation matrix have been evaluated among the physicochemical parameters, nutrients and chl-a concentration based on 95% statistical significance. Table 3 and 4 depicts the Pearson correlation coefficients among all the observed physical parameters, nutrient constituents, and chl-a concentrations at surface and deep water, respectively. The study reveals that chl-a exhibits a significant and strongly negative correlation with turbidity (r= -0.94 at surface water), indicating a decrease in chlorophyll concentration with increasing rate of turbidity. DO drives the primary productivity and exhibits a strong positive correlation with chl-a holding r values of 0.97 and 0.91 at the surface and deep water, respectively. DO exhibits negative correlation with EC (r=-0.89) at the surface water as the higher the conductivity levels, the lower the DO levels in the water (Atlas Scientific, 2021). The positive correlation of pH with ammonia at the surface water (r = 0.92) indicates that ammonia plant effluents are the primary source of pH in the river water.

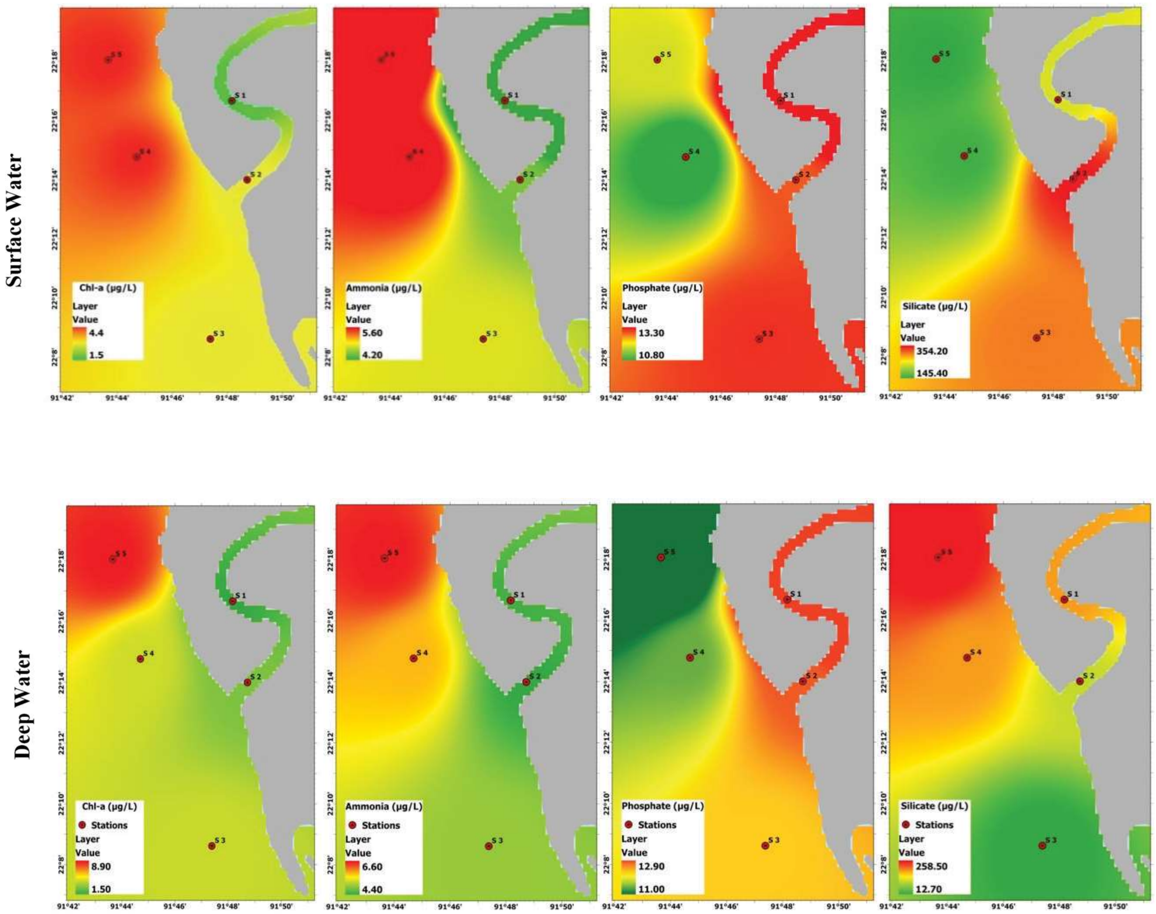

Figure 3: The Spatial Variation of Nutrients and Chlorophyll in Surface and Deep Water

Table 3: Pearson Correlation Coefficients (r) among Physiochemical Parameters and Dissolved Nutrients in the Surface Water of the Karnaphuli River Estuary. [Bold Numbers Indicate the Correlation is Significant at 0.05 Level and the Italic Numbers Indicate p Value

	Temperature (°C)	*pH*	*EC (S/m)*	*DO (mg/L)*	*Turbidity (NTU)*	*Chl-a (µg/L)*	*Ammonia (µg/L)*	*Phosphate (µg/L)*	*Silica (µg/L)*
Temperature (°C)	1.00	*0.047*	*0.009*	*0.01*	*0.005*	*0.03*	*0.007*	*0.04*	*0.53*
pH	**-0.88**	1.00	*0.02*	*0.06*	*0.03*	*0.02*	*0.03*	*0.12*	*0.17*
EC (S/m)	**0.96**	**-0.93**	1.00	*0.04*	*0.001*	*0.03*	*0.03*	*0.06*	*0.28*
DO (mg/L)	**-0.95**	0.86	**-0.89**	1.00	*0.02*	*0.005*	*0.002*	*0.01*	*0.55*
Turbidity (NTU)	**0.97**	**-0.91**	**0.99**	**-0.93**	1.00	*0.02*	*0.02*	*0.03*	*0.34*
Chl-a (µg/L)	**-0.92**	**0.93**	**-0.92**	**0.97**	**-0.94**	1.00	*0.005*	*0.01*	*0.33*
Ammonia (µg/L)	**-0.96**	**0.92**	**-0.92**	**0.99**	**-0.94**	**0.97**	1.00	*0.02*	*0.49*
Phosphate (µg/L)	**0.89**	-0.78	0.86	**-0.97**	**0.91**	**-0.95**	**-0.93**	1.00	*0.54*
Silica (µg/L)	0.38	-0.71	0.60	0.60	0.54	-0.55	-0.41	0.36	1.00

Table 4: Pearson Correlation Coefficients (r) among Physiochemical Parameters and Dissolved Nutrients in the Deep Water of the Karnaphuli River Estuary. [Bold Numbers Indicate the Correlation is Significant at 0.05 Level and the Italic Numbers Indicate p value.]

	Temperature (°C)	*pH*	*EC (S/m)*	*DO (mg/L)*	*Turbidity (NTU)*	*Chl-a (μg/L)*	*Ammonia (μg/L)*	*Phosphate (μg/L)*	*Silicate (μg/L)*
Temperature (°C)	1.00	*0.85*	*0.08*	*0.02*	*0.01*	*0.03*	*0.07*	*0.003*	*0.74*
pH	0.11	1.00	*0.56*	*0.89*	*0.62*	*0.71*	*0.53*	*0.91*	*0.04*
EC (S/m)	-0.83	-0.34	1.00	*0.29*	*0.02*	*0.24*	*0.40*	*0.11*	*0.93*
DO (mg/L)	**-0.93**	0.09	0.60	1.00	*0.11*	*0.03*	*0.01*	*0.02*	*0.57*
Turbidity (NTU)	**0.95**	0.30	**-0.94**	-0.80	1.00	*0.09*	*0.21*	*0.03*	*0.92*
Chl-a (μg/L)	**-0.92**	0.23	0.65	**0.91**	-0.82	1.00	*0.03*	*0.01*	*0.43*
Ammonia (μg/L)	-0.84	0.38	0.49	**0.95**	-0.67	**0.92**	1.00	*0.03*	*0.26*
Phosphate (μg/L)	**0.98**	-0.07	-0.79	**-0.94**	**0.91**	**-0.96**	**-0.91**	1.00	*0.51*
Silicate (μg/L)	-0.20	**0.90**	0.05	0.34	-0.06	0.46	0.61	-0.40	1.00

A strong positive correlation between turbidity and phosphate is observed with a r value of 0.91 at both the surface and deep water. This indicates that turbidity likely originates from phosphate sources, specifically TSP plants located downstream of the river. Turbidity exhibits strong positive correlation with temperature as well, with r values of 0.97 and 0.95 at the surface and deepwater, respectively. The turbidity levels increase with rising water temperature, as elevated turbidity results in greater absorption of sunlight by suspended particles, thereby further elevating the water temperature (Paaijmans et al., 2008). The strong positive correlation between pH and silicate at the deepwater (r=0.90) indicates high solubility of silicate at higher pH level. The strong correlations suggest that these parameters have emanated from identical sources, specifically from household waste products, agricultural supplies, and industrial byproducts.

CONCLUSIONS

The environmental health of the aquatic system was diagnosed in this study, where all the indices support each other results and have found a good research result representing the condition of surface water and deep-water quality of the Karnaphuli river estuary. However, the conditions in some stations are fair (Station 3, 4 and 5) compared to other sampling stations (Station 1 and Station 2). This study will encourage and help the researchers to evaluate the water quality of one of the most dynamic river systems of Bangladesh. The study area surrounds shipping and port operations, welding factories, and oil companies. The Karnaphuli river plays a crucial role in supplying water to over 800 industries in the Chittagong region. However, its water quality is deteriorating especially at the downstream, with elevated turbidity (highest 562.1 NTU), posing a threat. Temperature and pH values exhibited minimal fluctuation across the sampling stations. pH levels were relatively stable, ranging from 6.5 to 7.5. These values fall within the acceptable range for aquatic life (6.5-8.5), indicating that pH is not a major stressor. However, the positive correlation between pH and ammonia in surface waters (r = 0.92) suggests that ammonia effluents from industrial sources are influencing the river's pH, particularly in areas closer to pollution sources. Excessive nutrients may lead to phytoplankton overgrowth, depleting oxygen and harming aquatic life. EC values were observed to be higher than typical standards, particularly in deeper waters where EC ranged from 0.2 to 0.8 S/m (mean 0.62 ± 0.24 S/m), significantly exceeding the standard threshold (0.08-0.1 S/m). This elevated conductivity suggests increased ion concentration due to the influx of industrial effluents, potentially leading to adverse effects on freshwater organisms that are sensitive to ionic changes. Chlorophyll-a concentrations varied across the study area, reflecting the productivity of the aquatic ecosystem. The seaward region showed higher chlorophyll-a and nutrient concentrations but lower turbidity. The shallow coastal regions within the study area exhibited high chlorophyll-a levels, reaching 8.9 μg/L, indicative of a healthy and productive aquatic environment. This is likely due to the lower turbidity and higher DO levels. Conversely, in areas with higher turbidity (562.1 NTU) and lower DO (3 mg/L), chlorophyll-a levels were notably low, with concentrations as low as 1.5 µg/L in the downstream regions. This indicates diminished primary productivity, likely due to the stressed environmental conditions. Urgent action is needed to control pollution, as water parameters have already exceeded standard tolerance limits. Strict regulations and public awareness are vital to safeguard the Karnaphuli river's future.

Future Scope of the Study

For future research, the continual collection of samples and reassessment of data regarding the physicochemical parameters of the water are essential to develop an effective management plan and a deeper comprehension of the hydrology and river water quality of the Karnaphuli River. It is suggested that the research be expanded even further by considering the seasonal variance throughout the year. The governing organizations responsible for enforcing water policy in these regions will have this report as a reference database for future use as well.

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