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Assessment of surface water quality using the Water Quality Index (WQI) and multivariate statistical analysis (MSA), around tannery industry effluent discharge areas

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ABSTRACT

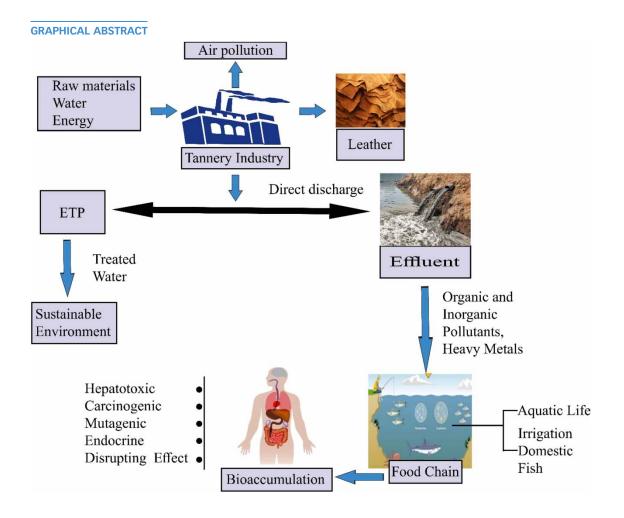
The study attempted to assess the water quality around the tannery effluent discharge areas for suitability for irrigation purposes using different indices (Water Quality Index (WQI)) and statistical analysis in Savar Upazilas, Dhaka, Bangladesh. The samples were collected three times, from monsoon 2021 to pre-monsoon 2023. The analysis results showed that the concentrations of various parameters at most of the sampling points exceeded the surface water standard. Pollution levels were found in the following order: pre-monsoon, post-monsoon, and monsoon. At SW1 point, the CWQI, WWQI, and MWQI of the surface water quality showed a 'poor' category. The IWQI values showed that the surface water at all the sampling points was suitable for irrigation purposes, except for the SW1 sampling point. The NPI indicates that EC, BOD, COD, TSS, Cl⁻, Na⁺, and NO₃⁻-N parameters were potentially responsible for polluting most sampling sites. Multivariate statistical analyses like principal component analysis, cluster analysis, and Pearson correlation matrix showed significant anthropogenic intrusions of these variables in surface water in the area. A strong correlation between these parameters indicated their common origin, i.e., poorly treated tannery industry effluent entered the surface water, suggesting an improvement in the efficiency of the Central Effluent Treatment Plant (CETP).

Key words: characterization, indices, statistical analysis, surface water, tannery industrial effluent

HIGHLIGHTS

- Characterization of discharge effluent.
- Identification of surface water pollutants.
- Identification of sources using multivariate statistical analysis.
- Determination of pollution levels.
- Assessing potential threats using various water quality indices.

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1. INTRODUCTION

The Central Effluent Treatment Plant (CETP) at the Saver tannery industrial zone in Dhaka, Bangladesh, releases poorly treated wastewater into the (Dhaleshwari River) surface water bodies that deteriorate the quality of surface water, which is very harmful to aquatic life and the environment (Al-Shujairi 2013; Hasan et al. 2020). A useful method for communicating water quality data is the water quality index (WQI) (Trivedy et al. 2009). One of the best methods for determining the level of water pollution is the WQI, which is universally recognized and used (Trivedy et al. 2009; Shakil & Mostafa 2021a; Monira et al. 2023a, 2023b). The WQI, a unitless single number, essentially describes the general quality of water at a specific location (e.g., bad, good, marginal, etc.) and is calculated from an amalgamation of various water quality documents obtained by equating measured values with legal requirements (Al-Shujairi 2013; Islam & Mostafa 2021a). The WQI essentially presents complex data on water quality in a way that is mathematically clear and practical for both ordinary people and decisionmakers. To estimate water quality, a number of water quality indicators have been created. First proposed by Horton (1965) in the United States, taking into account the ten most typical water quality factors, and then Brown et al. (1970) weighed each water quality measure individually. The WQI method has experienced numerous revisions that have been validated by a number of researchers throughout the world (Cude 2007; Shakil & Mostafa 2021b; Islam & Mostafa 2021c; Islam & Mostafa 2022a 2022b). A well-known example is the British Columbia Water Quality Index (BCWQI), the Oregon Water Quality Index (OWQI), the Canadian Council of Ministers of the Environment (CCME WQI), and the National Sanitation Foundation's (NSF-WQI) Water Quality Index.

Locally, Bangladesh is referred to as a 'Riverian' country. Formerly the lifeblood of Bangladesh, its rivers are now a foremost national concern due to increased development along their banks without necessary ecological safeguards (Roy & Akash 2018; Shakil & Mostafa 2021b; Islam & Mostafa 2021c). With a length of 160 km, an average depth of roughly 37 m and a maximum depth is 81 m (Hasan *et al.* 2020), the Dhaleshwari River, a significant left-bank distributary of the river Jamuna, flows alongside central Bangladesh (Ahmed *et al.* 2018). The slope of the flood flow water has been measured to be 4 cm/km (BWDB 2012). Residents of the Tannery Industrial Park region claim that after the relocation of the tannery companies, the physical quality of the Dhaleshwari River's water has begun to deteriorate. These claims have also been made in other media. Some worrying news was reported in the media, such as the CETP's poor operation, illegal discharging outlets into the river that obstruct the main CETP line, etc. (Imam 2018; Roy & Akash 2018; Anam 2019). The CETP has a daily capacity of 25,000 m³ of liquid waste. However, 40,000 m³ of waste is formed by the tanners inside the estate per day (Monira *et al.* 2022). The fact that around 15,000 m³ of untreated waste is currently being dumped into the adjoining Dhaleshwari River is fairly depressing. Activated sludge methods are used in the CETP plant, which are mentioned below, with effluent discharge standards (DoE-BD 2023; Ahmed *et al.* 2018).

Firstly, tannery effluent is sent into the fine-screen and vortex-style grit chamber to remove large-size suspended foreign objects and girts then sent to the aeration tank (where physical, chemical, and biological treatments are made). In the aeration tank activated sludge and chemicals are added. Before being qualified for discharge, the treated water enters the disinfection tank, where it is disinfected by adding ClO₂ (chlorine dioxide). The sludge from the oxidation ditch is lifted to the sludge thickening tank, then thickening sludge enters the sludge reaction tank (where PAC (Poly aluminum chloride), PAM (polyacrylamide), and membrane rupture agent will be added to decrease the water content of the sludge). The sludge is lifted by pumps to the Dewatering Integrated Machine (DWIM) for dewatering. Sludge cake will be transported outside for landfilling and filter liquor goes to the piping network inside the pre-aeration equalization tank for treatment (Imam 2018; Roy & Akash 2018; Anam 2019).

The industries using the most water are those involving textile, leather, sugar, pulp and paper production, fertilizer, dyeing, chemicals, and petroleum refineries (Islam & Mostafa 2021b; Rahim & Mostafa 2021; Shakil & Mostafa 2021a; Monira *et al.* 2022). Due to the contamination of local soil, water, and storm drains caused by industrial wastewater discharge, there is a substantial environmental risk (Islam & Mostafa 2018, 2020; Saha *et al.* 2021; Sayed & Mostafa 2021).

The effect of the CETP's released effluent since the tannery industrial estate opened on the nearby river's water quality is still unknown. As a result, the present research aims to evaluate the Dhaleshwari River's pollution state through various indexing and statistical analyses for the suitability of irrigation purposes as a result of the newly relocated tannery industrial park.

2. METHODOLOGY

2.1. Study area

The research study area is located in Savar Upazila, in Dhaka district, northwest of Bangladesh's capital city of Dhaka, in the recently relocated (2017) tannery industrial estate (Figure 1). Its coordinates are 23°51′30′′N and 90°16′00′′E/23.8583; 90.2667.

2.2. Sample collection

Surface water samples of the Dhaleshwari River were collected from the tannery industrial estate effluent discharge (CETP) point (SW1), 100 m downstream (SW2), 500 m downstream (SW3), 1 km downstream (SW4), and 2 km downstream (SW5) of the tannery industrial estate effluent discharge areas. The samples had been collected three times a year, from monsoon 2021 to pre-monsoon 2023 (pre-monsoon, monsoon, and post-monsoon). A total of 30 surface water samples were collected. Before the samples underwent a chemical examination in the lab, they were collected in pristine plastic bottles and frozen to prevent degradation.

2.3. Physicochemical parameter analysis

The research considered a total of 19 physicochemical characteristics, i.e., turbidity, TSS, EC, pH, temperature, DO, total hardness (TH), BOD, COD, TDS, Cl^- , HCO_3^- , SO_4^{2-} , NO_3^- -N, PO_4^{3-} , Na^+ , Ca^{2+} , K^+ , and Mg^{2+} . Temperature, turbidity, EC, pH, and DO were directly monitored in the field using digital multi-meters. The UV spectrophotometric technique was used to quantify SO_4^{2-} , NO_3^- -N, and PO_4^{3-} . The Shimadzu AA-7000 atomic

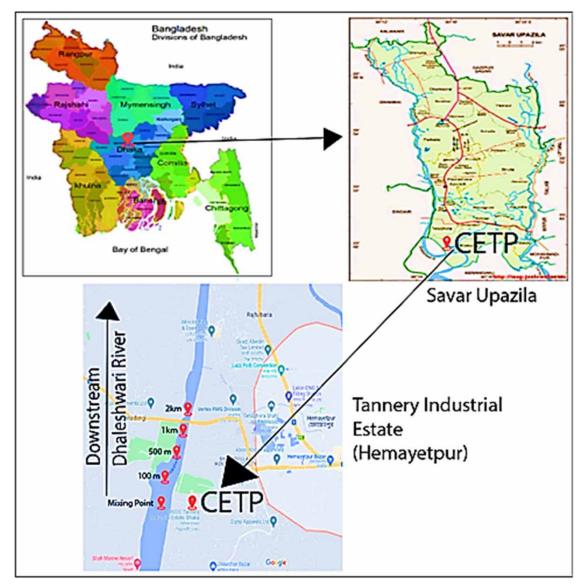


Figure 1 | Location map showing the study area and sampling sites.

absorption spectrophotometer was used to measure Na^+ , $K^{+,} Ca^{2+}$, and Mg^{2+} . The chemical analysis of the selected parameters was measured using the (APHA 2005) standard methods of analysis.

2.4. Index of water quality

2.4.1. Canadian Council of Ministers of the Environment

The WQI of the CCME was used to evaluate the water quality in the research area. Fourteen (14) water quality parameters (EC, temperature, BOD, pH, DO, TSS, COD, TDS, Cl^- , SO_4^{2-} , NO_3^- -N, Na^+ , K^+ , and Ca^{2+}) were used to analyze the WQI score of surface water because turbidity, PO_4^{3-} , total hardness, HCO_3^- , and Mg^{2+} do not have surface water standards in Bangladesh (DoE-BD 2023).

The CCME WQI is calculated using three factors: scope (F1), frequency (F2), and amplitude (F3) (CCME 1999). F1 (Equation (1)) is the percentage of failed parameters that did not achieve their goals at least once throughout the period. F2 (Equation (2)) stands for the proportion of individual tests that fail to achieve their goals (failed tests), and F3 (Equation (3)) stands for the percentage of failed tests that fail to achieve their goals.

The equations are given in the following:

WQI =
$$100 - \frac{\sqrt{(F1^2 + F2^2 + F3^2)}}{1.732}$$
 (1)

where

Scope
$$F1 = \frac{\text{Number of Failed Variables}}{\text{Total Number of Variables}} \times 100$$
 (2)

Frequency,
$$F2 = \frac{\text{Number of Failed Tests}}{\text{Total Number of Tests}} \times 100$$
 (3)

$$\text{Amplitude F3} = \frac{\text{NSE}}{0.01\text{nse} + 0.01} \tag{4}$$

Normalized Sum of Excursions (NSE)
$$= \frac{\sum \text{Excursion}}{\text{Total number of tests}}$$
 (5)

$$\text{Excursion} = \frac{\text{failed tests test}}{\text{standard value}} - 1 \tag{6}$$

The calculated WQI score was then categorized as excellent (95–100), good (80–94), fair (65–79), marginal (45–64), and poor (below 40 or 0–44).

2.4.2. Weighted Average Water Quality Index

Equation (9) was used to calculate the index value of the weighted average WQI approach. Horton's (1965) weighted arithmetic/average WQI technique was utilized to compute the WWQI. Brown *et al.* (1970) and Cude (2007) later expanded on it. With the following three equations (Equations (7)–(9)), the WWQI values were determined:

$$W_i = \frac{K}{S_i} = \frac{1}{\sum (1/S_i)} \div S_i \tag{7}$$

$$Q_i = \frac{(V_n - V_0)}{(S_i - V_0)} \times 100$$
(8)

$$WWQI = \sum_{i=1}^{n} \frac{W_i Q_i}{\sum_{i=1}^{n} W_i}$$
(9)

where V_n is the parameter's experience value, V_0 is the ideal parameter value, and S_i is the standard parameter value. W_i is the *i*th parameter's unit weightage. Q_i is the sub-index of the *i*th parameter. The optimal value for pH is 7, DO is 14.6 mg/L, and other values are normally equal to zero (Inayathulla & Paul 2013; Islam & Mostafa 2021b, 2021c).

That is,

$$Q_{\rm pH} = \frac{(V_{\rm pH} - 7)}{8.5 - 7.0} \times 100 \tag{10}$$

Each parameter's weighting unit (W_i) produced a value that is inversely proportionate to the World Health Organization standard (S_i) .

This index value was calculated using a simple Excel tool. According to this WQI, water quality is rated as excellent (0-25), good (26-50), poor (51-75), very poor (76-100), and unsuitable (>100) according to this WQI. Then, Equation (9) was used to determine the final index (WWQI).

2.4.3. Meireles Water Quality Index

Meireles established the WQI for irrigation purposes and recommended a new categorization for irrigation water (Meireles *et al.* 2010). The factors that affect irrigation water quality the most were chosen.

This method specified five parameters: sodium adsorption ratio (SAR), EC, Na⁺, Cl⁻, and HCO₃⁻. It was recognized that accumulated weights (w_i) and water quality measurement limitations (Q_i) were classified. The parameters recommended by the UCCC (1974) and Ayers & Westcot (1985) were taken into consideration for irrigation water quality while determining the values of Q_i .

According to Richards (1954), the SAR value of the water sample calculates the relative proportion of Na^+ to Ca^{2+} and Mg^{2+} . SAR was determined by the following Eq.

$$SAR = \frac{Na^{+}}{\sqrt{\frac{(Ca^{2+}+Mg^{2+})}{2}}} (meq/L)$$
(11)

The following equation was used to compute the q_i values

$$q_{i} = Q_{i \max} - \frac{\{(X_{ij} - X_{inf})Q_{iamp}\}}{X_{amp}}$$
(12)

where Q_{imax} is the highest value of Q_i for the related class; X_{inf} is the lower value of the parameter to which the class belongs; Q_{iamp} is the class capacity, and X_{amp} is the class capacity to which the parameter belongs; X_{ij} is the measured value of the parameter.

Each parameter's weight used to calculate the MWQI was normalized so that their combined value is one. Finally, MWQI was determined as follows using Equation (13):

$$MWQI = \sum_{i=1}^{n} q_i w_i$$
(13)

where q_i represents the quantity of the *i*th parameter and w_i represents the normalized weight of the *i*th parameter. Values of q_i were computed using Equation (12), based on the laboratory results of water quality analysis (Table 1). Also, the weight of each parameter used in the MWQI is shown in the same table. The water quality is rated as $85 \le 100$ (no restriction), $70 \le 85$ (low-restriction), $55 \le 70$ (moderate restriction), $40 \le 55$ (high restriction), and $0 \le 40$ (severe restriction).

Table 1 | Biyearly average of physicochemical parameters of surface water in the tannery effluent discharge area

	Mean \pm SD	$an \pm SD$									
	Sample Location										
Parameters	SW1 (mixing point)	SW2 (100 m)	SW3 (500 m)	SW4 (1 km)	SW5 (2 km)	BD SWS (ECR 2023)					
Temp (°C)	$27\ \pm 4.5$	$25.6\ \pm\ 3.8$	$25\ \pm\ 3.6$	$25\ \pm\ 3.6$	$25\ \pm 3.6$	40					
pH	$7.8~\pm~0.5$	$7.6\ \pm\ 0.3$	$7.6\ \pm\ 0.3$	$7.6\ \pm 0.3$	$7.6\ \pm 0.3$	6.0–9.0					
DO (mg/L)	$1.6\ \pm\ 0.1$	$3.4\ \pm\ 0.4$	$5.3\ \pm\ 0.6$	$5.4\ \pm 0.5$	$5.5\ \pm 0.5$	≥ 5					
EC (µS/cm)	$2{,}465\ \pm 1{,}101$	$417\ \pm 257$	$410\ \pm 248$	$407.5\ \pm\ 243.5$	$407.5\ \pm\ 234.1$	1,200					
Turbidity (NTU)	$30.5\ \pm 2.5$	$28.5\ \pm 2.5$	$28\ \pm 2.4$	$28\ \pm 2.4$	$28\ \pm 2.4$	_					
TSS (mg/L)	$265\ \pm\ 4.1$	$231\ \pm 2.5$	$85.8\ \pm\ 34.7$	$71.5\ \pm 28$	$46.5\ \pm\ 5.2$	150					
TDS (mg/L)	1,440 ± 291.7	$832.5\ \pm\ 49.2$	$823.8~\pm 49.4$	$806~\pm 50.9$	$797.5~\pm 32$	1,000					
BOD (mg/L)	$72.8\ \pm 4.6$	$64.5\ \pm\ 1.9$	$53.8~\pm3$	$51.8\ \pm 2.2$	$52.5~\pm 1.9$	30					
COD (mg/L)	$282\ \pm 13.0$	$237\ \pm 12.6$	$228\ \pm 14.4$	$215~\pm10$	$205~\pm19$	100					
Cl ⁻ (mg/L)	1,032 ± 55.5	$25.6\ \pm\ 4.4$	$23.5\ \pm 2.9$	$22.8\ \pm 1.8$	$21.6\ \pm\ 2.9$	600					
SO_4^{2-} (mg/L)	$113.85\ \pm\ 24.5$	$95.25\ \pm 2.2$	$66.8\ \pm\ 21.9$	$62.1\ \pm 7.7$	$60.05~\pm 3.7$	400					
NO ₃ ⁻ N (mg/L)	$13.8\ \pm\ 0.8$	$13.5\ \pm\ 0.5$	$12.1\ \pm\ 4.4$	$8.5\ \pm 0.5$	$4.4\ \pm 0.2$	10					
PO ₄ ³⁻ (mg/L)	$7.08\ \pm\ 0.51$	$6.63\ \pm\ 1.0$	$3.81\ \pm\ 0.32$	3.305 ± 0.35	$2.32~\pm 0.69$	10					
HCO ₃ ⁻ (mg/L)	$240\ \pm\ 101.5$	$166\ \pm\ 181.4$	$139\ \pm 29.51$	$131\ \pm\ 22.8$	117.8 ± 14.3	_					
Na ⁺ (mg/L)	$350\ \pm\ 6.9$	$10.9\ \pm\ 0.5$	$9.9\ \pm\ 0.23$	$9.2\ \pm 1.2$	$8.9\ \pm 0.2$	200					
K^+ (mg/L)	$1.0~\pm~0.45$	$0.45\ \pm\ 0.1$	$0.3\ \pm\ 0.2$	$0.3\ \pm 0.2$	$0.3\ \pm 0.2$	12					
Ca^{2+} (mg/L)	$45~\pm 0.8$	$29.8~\pm 1.5$	$25~\pm 4.2$	$1.7\ \pm 0.05$	$1.3\ \pm 0.5$	75					
Mg ²⁺ (mg/L)	43.8 ± 5	$28\ \pm\ 8.7$	$23.9\ \pm\ 10.1$	$18.4\ \pm\ 11.8$	$15.3\ \pm\ 7.8$	-					

2.4.4. Irrigation Water Quality Index

In addition to IWQI, various indicators were used in this study to examine the fitness of Dhaleshwari River surface water for irrigation uses. The parameters comprise Kelly's Ratio (KR), magnesium adsorption ratio (MAR), SAR, percentage sodium (% Na), and soluble sodium percentage (SSP). The next sections explain their significance and computations.

2.4.4.1. Magnesium Adsorption Ratio. One of the most crucial qualitative factors in establishing the quality of water for irrigation is the MAR, which determines the calcium and magnesium concentrations in water (Joshi *et al.* 2009). In general, calcium and magnesium balance the pH of water, and excess magnesium makes the soil alkaline, which is bad for crops (Nishanthiny *et al.* 2010; Islam & Mostafa 2021c). The formula below is used to compute this ratio (Paliwal 1972):

MAR
$$=\frac{(Mg) \times 100}{(Ca + Mg)}$$
 (concentrations are in meq/L) (14)

2.4.4.2. Sodium Adsorption Ratio. When determining whether water is suitable for irrigation, the sodium content as the SAR must be evaluated because it has an impact on the soil's penetration rate salinity, and TH (Subramani *et al.* 2005; Shakil & Mostafa 2021b; Islam & Mostafa 2021b). The SAR increases when Na (sodium) concentrations increase to Ca (calcium) and Mg (magnesium) concentrations (Vyas & Jethoo 2015; Islam & Mostafa 2021c). This sodium risk is also linked to a variety of factors such as soil type, salinity, and so on. Sandy soils, for example, may be better able to withstand high SAR water (Richards 1954; Islam & Mostafa 2021b). The SAR is expressed in Equation (10).

2.4.4.3. *The SSP.* It is calculated as follows and represents the ratio of sodium and potassium to the total concentration of cationic ions (Shammi *et al.* 2016; Islam & Mostafa 2021b):

$$SSP = \frac{(Na + K) \times 100}{(Ca + Mg + Na + K)} (meq/L)$$
(15)

2.4.4.4. Percentage of sodium (% Na). Percentage sodium is another crucial consideration when determining whether water is suitable for irrigation due to the high fraction of sodium (% Na) in the water, which inhibits plant growth and lowers soil absorbency (Richards 1954; Islam & Mostafa 2021b). It is computed as displayed below (Islam *et al.* 2017; Islam & Mostafa 2021b):

% Na =
$$\frac{(Na) \times 100}{(Ca + Mg + Na + K)}$$
 (ions are expressed in meq/L) (16)

2.4.4.5. *Kelly's Ratio*. Whenever assessing water for irrigation, KR is employed, with sodium being compared against calcium and magnesium, which stand in for the alkali hazards. The following formula is used to compute the ratio (Kelly 1951):

$$KR = \frac{(Na) \times 100}{(Ca + Mg)} \text{ (ions are expressed in meq/L)}$$
(17)

2.4.5. Nemerow's Pollution Index (NPI)

Nemerow's Pollution Index (NPI) is expressed by the following Eq.

NPI =
$$\frac{C_n}{S_n}$$
 (18)

where C_n is the concentration of the *n*th parameter; S_n is the prescribed standard limits of the *n*th parameter. The result of the NPI calculation will be:

NPI values ≤ 1 NPI values > 1

If water parameter NPI value > 1:

1. It indicates its presence in surplus amount or concentration and

2. The particular parameter has the potential to contribute to pollution in the water bodies studied.

2.4.6. Statistical analysis

Using SPSS (version 24), Principal Component Analysis (PCA) and Cluster Analysis (CA) were carried out on the original data set without any weighting or standardization. To reduce the variances of the factor loadings across variables for each factor, a varimax normalized rotation was performed after PCA. To determine the relationship between physicochemical characteristics and to support the results of multivariate analysis, Pearson's correlation matrix was used (Bhuiyan *et al.* 2010; Islam & Mostafa 2021c).

3. RESULTS AND DISCUSSION

3.1. Characterization

Table 1 shows the physicochemical properties of surface water around the tannery industrial estate effluent release area. The temperature ranged from 25 to 27 °C in this investigation, which was below the permitted limit stated by the Bangladesh Surface Water Standard (BD SWS 2023). The average pH readings were within the acceptable range, ranging from 7.6 to 7.8. The dissolved oxygen (DO) concentration was below the required limit and ranged from 0.5 to 1.6 mg/L. DO depletion in surface water was produced by the BOD load from the leather effluent discharge. Low DO is responsible for ecosystem imbalance, aquatic fisheries decrease, acute stress, and the death of organisms (Connolly *et al.* 2004). Chowdhury *et al.* (2013) made a similar observation.

Electrical conductivity (EC) values ranged from 407.5 to $2465 \,\mu$ S/cm (Table 1) at various locations of the leather effluent discharge zones. Except for the SW1 point, it was within the allowed limit at most of the sites. According to several reports, the high EC value suggested the presence of numerous mineral ions and salts, particularly sodium and chromium salts employed in the tanning and pickling stages. The high volume of EC is harmful to the aquatic ecosystem (Shannon *et al.* 2020; Shakil & Mostafa 2021a). The turbidity varied between 28 and 30.5 NTU.

Total suspended solids (TSS) concentrations ranged from 46.5 to 265 mg/L (Table 1), and at the SW1 and SW2 points, they exceeded the standard level, but at other sampling sites, they were within the permissible range. TSS represents the suspended impurities in water bodies. A high TSS value changes the water-holding capacity and porosity of soil and decreases soil fertility (Chowdhury *et al.* 2015). Hasan *et al.* (2020) expressed a similar observation.

The total dissolved solids (TDS) concentration fluctuated from 797.5 to 1,440 mg/L (Table 1) and originated within the standard level at all sampling sites except for the SW1 point. The concentrations of biochemical and chemical oxygen demand (BOD and COD) exceeded the acceptable limit, ranging from 51.8 to 72.8 mg/L and 205 to 282 mg/L, respectively, at all sampling sites. High BOD and COD values decrease DO levels and cause the deaths of fisheries and aquatic organisms (Trivedy *et al.* 2009). Organic and inorganic pollutants emitted by leather effluent are caused by a high concentration of COD and BOD in the surface water. These findings were supported by Chowdhury *et al.* (2013).

The TH values ranged from 123 to 262.5 mg/L at different sites in the leather effluent discharge areas. TH is the measure of the reacting capacity of water with soap to form leather. Hard water is responsible for the corrosive effect (Phiri *et al.* 2005). There is no permissible limit for total hardness.

The chloride (Cl⁻) and sulfate (SO₄²⁻) concentrations ranged from 21.6 to 1,032 mg/L and 60.05 to 113.9 mg/L, respectively (Table 1), and were found to be within the acceptable limit at all sampling sites except for Cl⁻ at the SW1 sampling point. Due to the excess use of chloride salt during the preservation and processing of raw hides, higher chloride concentrations were found (Shannon *et al.* 2020). The nitrate-nitrogen (NO₃⁻-N) concentration ranged from 4.4 to 13.8 mg/L, which exceeded the allowable limit at the majority of the investigated sites around the leather effluent discharge zones. A higher value of nitrate and phosphate is responsible for eutrophication, anoxia, and algal blooms in surface water bodies (EPA 2021). The phosphate (PO₄³⁻) and bicarbonate (HCO₃⁻) varied from 2.32 to 7.1 mg/L and 117.8 to 240 mg/L, respectively. However, there is no surface water

standard (DoE-BD 2023) for bicarbonate in Bangladesh. Various additives like dyes, deformers, scale inhibitors containing phosphate, and nitrogen compounds may contribute to the concentration (Connolly *et al.* 2004).

The sodium (Na⁺) and potassium (K⁺) ions (Table 1) varied from 8.9 to 350 mg/L and 0.3 to 1.0 mg/L, respectively. The sodium (Na⁺) ion content was acceptable except for the SW1 sampling point, whereas the potassium ion was within the permissible limit at all sampling sites. The weathering of various rocks and the excess use of sodium salt during the preservation and processing of raw hides are responsible for higher sodium concentrations (Bhuiyan *et al.* 2010). The concentrations of calcium (Ca²⁺) and magnesium (Mg²⁺) ions varied from 1.3 to 45 mg/L and from 15.3 to 43.8 mg/L, respectively. The concentration of calcium ions (Ca²⁺) was within the standard limit of DoE-BD 2023. However, the magnesium (Mg²⁺) ion has no surface water standard in BD.

3.2. Seasonal variation

The biyearly average temperature of all collected surface water samples varied from 22.6 to 27.8 °C. The maximum and minimum mean temperatures were observed in the pre-monsoon (27.8 °C) and post-monsoon (22.6 °C) seasons with a standard deviation (SD) of 2.5 and 2.7, respectively (Table 2). The pre-monsoon is a summer season in which temperatures naturally remain high. Sultan *et al.* (2009) observed that the mean maximum and minimum temperatures were 28 and 22 °C in the pre-monsoon and post-monsoon seasons, respectively, which was similar to the present study results. The biyearly mean pH of all collected surface water samples varied from 6.5 to 7.3. The average surface water pH was about neutral (7.3) during the monsoon season due to an increase in the surface water volume. Then pH decreased (6.9) in the post-monsoon due to the presence of organic acids like humic, fulvic acids, etc. (Yusuff & Sonibare 2005). In the pre-monsoon season, the pH was lower (6.5) than in other seasons due to a decrease in the volume of water. Phiri *et al.* 2005 conveyed a similar consideration.

The biyearly average DO and standard deviation (SD) of all collected surface water samples varied from 4.02 to 4.5 mg/L and 1.2 to 1.45, respectively (Table 2). For the same reason (dilution effect), the mean DO was found in the following order: monsoon (4.5 mg/L) > post-monsoon (4.2 mg/L) > pre-monsoon (4.02 mg/L). Sunil & Harada (2001) found the highest (5.0) DO concentration in the monsoon period, which showed similarity with the present study.

	Mean ± SD								
Parameters	Monsoon (2021–2022)	Post-monsoon (2021–2022)	Pre-monsoon (2022–2023)						
Tem (°C)	$26.2~\pm 2.5$	22.6 ± 2.7	$27.8~\pm 2.8$						
pH	$7.3\ \pm 0.81$	$6.9\ \pm\ 0.44$	$6.5\ \pm\ 0.18$						
DO (mg/L)	$4.5~\pm1.45$	$4.2~\pm 1.2$	$4.02~\pm 1.3$						
EC (µS/cm)	$677\ \pm\ 442$	$741.7\ \pm\ 185$	$1,045.3 \pm 105$						
Turbidity (NTU)	$27.3\ \pm 2.8$	26 ± 2.5	$32.5~\pm2.5$						
TSS (mg/L)	$135\ \pm\ 5.2$	$140~\pm 5.1$	$145~\pm 5.9$						
TDS (mg/L)	$820.36\ \pm\ 50.1$	$944.6~\pm 48.2$	$1,054.2 \pm 40.1$						
BOD (mg/L)	53.28 ± 15.9	$60.38 \ \pm \ 10.3$	$63.5~\pm~10.3$						
COD (mg/L)	183.4 ± 29.30	233.4 ± 15.30	$283.4\ \pm\ 15.45$						
TH (mg/L)	102.46 ± 28.4	$193\ \pm 25.9$	169.46 ± 32.2						
Cl^{-} (mg/L)	215.32 ± 13.1	223.72 ± 2.8	$236.26\ \pm 2.5$						
SO ₄ ²⁻ (mg/L)	$81.74\ \pm\ 14.50$	$714\ \pm\ 5.45$	124.72 ± 5.30						
NO ₃ ⁻ -N (mg/L)	$6.5\ \pm 5.3$	$8.7\ \pm 5.0$	$15.3~\pm 5.1$						
PO ₄ ³⁻ (mg/L)	$3.22~\pm 0.51$	$4.42~\pm0.32$	$6.22\ \pm\ 0.60$						
HCO ₃ ⁻ (mg/L)	$111~\pm101$	$121~\pm 180$	$243.8\ \pm\ 29.5$						
Na ⁺ (mg/L)	$74.42\ \pm 5.7$	$76.06\ \pm\ 0.5$	82.86 ± 0.25						
K ⁺ (mg/L)	$0.296\ \pm\ 0.40$	$0.714\ \pm\ 0.49$	$0.402\ \pm 5.1$						
Ca^{2+} (mg/L)	$19.76\ \pm\ 4.3$	21.32 ± 4.12	$20.6~\pm 4.15$						
Mg^{2+} (mg/L)	$19.48\ \pm\ 2.5$	27.08 ± 3.2	$31.08\ \pm\ 2.1$						

 Table 2 | Biyearly average values and standard deviations of the physicochemical parameters in the surface water around the industrial effluent discharge area

The biyearly mean of EC, TDS, TSS, turbidity, BOD, and COD (Table 2) for all collected surface water samples varied from 677 to 1,045.3 μ S/cm, 820.4 to 1,054 mg/L, 135 to 145 mg/L, 26.0 to 32.5 NTU, 53.3 to 63.5 mg/L, and 183.4 to 283.4 mg/L, respectively. The standard deviation (SD) of EC, TDS, TSS, turbidity, BOD, and COD (Table 2) for all collected surface water samples varied from 105 to 442, 40.1 to 50.1, 5.1 to 5.9, 2.5 to 2.8, 10.3 to 15.9, and 15.30 to 29.30, respectively. During the pre-monsoon season, water is evaporated, which increases EC, TDS, TSS, turbidity, BOD, and COD concentration and is found in the following order: pre-monsoon > post-monsoon > monsoon. Various studies delivered the same observations (Peavy *et al.* 1985; Davis & Cornwell 1998; Phiri *et al.* 2005; Sultan *et al.* 2009). The higher value of these parameters is an indication of polluted water. So, pollution levels were found to be higher in the pre-monsoon season as compared to other seasons.

In the case of TH during the pre-and post-monsoon, the water samples were of the hard to very hard type and were in the following order: post-monsoon > pre-monsoon > monsoon. Jasmin & Goni (2009) found that the value of TH varied from 112 to 195 mg/L, which is similar to the present study.

Biyearly average values of the anionic parameters like Cl⁻, SO₄²⁻, NO₅⁻-N, HCO₅⁻, and PO₄³⁻ (Table 2) in the surface water around the CETP discharge area varied from 215.32 to 236.26 mg/L, 81.74 to 714 mg/L, 6.5 to 15.3 mg/L, 111 to 243.8 mg/L, and 3.22 to 6.22 mg/L, respectively. The standard deviation (SD) of Cl⁻, SO₄²⁻, NO₅⁻-N, HCO₅⁻, and PO₄³⁻ for all collected surface water samples varied from 2.5 to 13.10, 5.30 to 14.50, 5.1 to 5.3, 29.5 to 101, and 0.32 to 0.60, respectively. The biyearly anionic parameter (Table 2) concentrations were found to be higher in the pre-monsoon season due to a decrease in the water level and anthropogenic sources including fertilizers and human and animal waste. Several studies conveyed the same explanations (Phiri *et al.* 2005). The average anionic parameter concentration of the surface water samples in the study area was in the following order: pre-monsoon > post-monsoon.

The biyearly cationic parameter concentration (Table 2) was found to be lower in the monsoon compared to other seasons due to the dilution effect of rainwater. A parallel reflection was stated by various studies (Davis & Cornwell 1998). The average cationic parameter concentration of the surface water samples in the study area was in the following order: pre-monsoon > post-monsoon > monsoon. The higher value of these parameters is an indication of polluted water. So, pollution levels were found to be higher in the pre-monsoon season as compared to other seasons.

3.3. Water Quality Index

3.3.1. Canadian Council of Ministers of the Environment

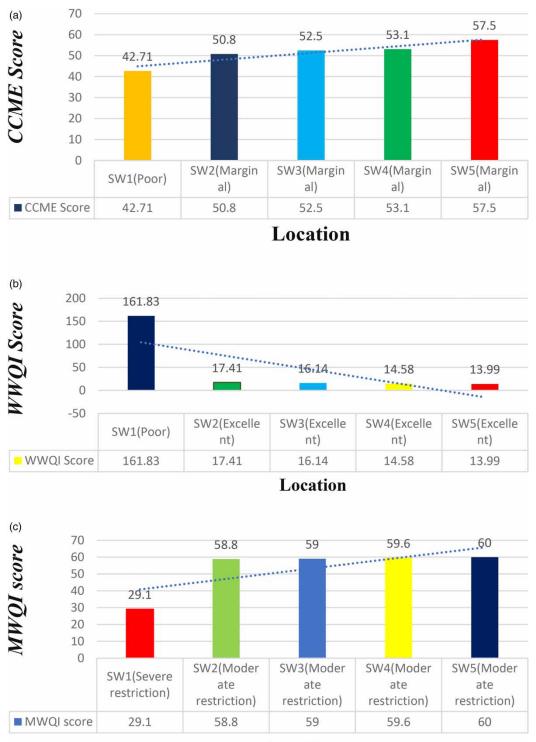
To evaluate the quality of the water near the locations where leather effluent is discharged, the CCME WQI was used. The WQI score was computed using the parameters' standard values. Figure 2(a) provides the surface water's CCME WQI calculated terms. The surface water's WQI score ranged from 42.71 to 57.5. The majority of the sampling locations had marginal water quality ratings, which showed that those places' surface water quality was in danger and frequently departed from natural or desirable conditions. But at the SW1 sampling point, surface water quality was 'poor' indicating the water's quality was often protected but rarely threatened and occasionally deviated from acceptable or natural levels, and no aquatic life could survive at the SW1 sampling point. The high values of EC, TSS, TH, BOD, COD, turbidity, HCO_3^- , Cl^- , NO_3^{-} -N, SO_4^{2-} , Ca^{2+} , Mg^{2+} , and Na^+ were responsible for influencing the lowering of the *C*WQI values. Hasan *et al.* (2020) illustrate a similar observation.

From sites SW1 to SW5 (Figure 2(a)), the WQI ratings of surface water near leather industries are increasing. This pattern suggests that the surface water quality at the discharge site (SW1) was negatively impacted by leather effluent and that the water quality has since gradually improved.

The performance of the CWQI model was realistic when at least ten parameters were included over at least 2 years and were used in the index calculation (Nishanthiny *et al.* 2010). In this regard, the study expected that the present dataset provided good enough information about the water quality because the inputs (parameters and station) were sufficient and the study followed the WHO 2011 guidelines for water quality standards. However, the CWQI method has some limitations because all variables were given the same importance and were easy to manipulate, and Scope F1 did not respond when a few variables were measured. So the study considers the other remaining indexing models.

3.3.2. Weighted Average Water Quality Index

Figure 2(b) shows the premeditated terms of the WWQI for surface water. The surface water's WQI score ranged from 13.99 to 161.83. The water quality scores were 'excellent' for most of the test sites, indicating that the surface



Location

Figure 2 | (a) CCME; (b) WWQI; and (c) MWQI score of the surface water body around the leather industrial effluent discharge areas.

water quality in those areas was adequate for irrigation. But at the SW1 sampling point, surface water quality was 'poor' indicating the quality of the water was not suitable for irrigation as well as aquatic biota. The high EC value of the present samples showed a higher WWQI value at the SW1 sampling point. High values of EC, TDS, turbidity, and TH (Ca^{2+} , Mg^{2+} , and HCO_3^-) also contributed to high index values at the SW1 sampling point, i.e., the effluent discharge point.

The surface water WQI ratings near the leather industry show a downward tendency from SW1 to SW5 (Figure 2(b)). This trend implies that the leather effluent degraded the quality of surface water at the discharge point (SW1) and that the water quality is gradually taming with respect to the expanse.

Here, BOD and COD parameters were not taken into consideration. So, it may not provide adequate information about the actual water quality. The absence of a single bad parameter concentration can affect this model. However this model is easy to calculate, and various important water quality parameters were used to assess the irrigation water quality for this study.

3.3.3. Mireles Water Quality Index

Considering the demerits of the CWQI and WWQI models, this study uses the MWQI to evaluate the water quality for irrigation purposes. According to Islam & Mostafa (2021c), MWQI is the best method for assessing the water quality for irrigation purposes. Figure 2(c) shows the premeditated terms of the MWQI for surface water. The surface water's WQI score ranged from 29.1 to 60. The water quality rankings were 'moderate' for most of the test sites, indicating that the surface water quality in those areas was suitable for irrigation. However, at the SW1 sampling point, the surface water quality fell under the 'severe' category, which indicated the water quality was not suitable for irrigation and aquatic life. Water in the 'severe' category should not be utilized for soils since it has a high risk of generating salinity and sodicity issues (Meireles *et al.* 2010). Most plants are highly poisonous in these water sources. As a result, it should be avoided for salt-sensitive plants (Bhuiyan *et al.* 2010). Here, only five parameters, which are briefly discussed in the methodology sections, are taken into consideration. The high values of EC, HCO_{3}^{-} , Cl^{-} , and Na^{+} were responsible for influencing the lowering of the MWQI values. This method is considered only aimed at the investigation of irrigation water quality for better yield production. That's why the study chose this model.

This pattern (Figure 2(c)) suggests that the quality of the surface water at the discharge point (SW1) was negatively impacted by leather effluent and that the water quality has since steadily improved as it relates to distance.

3.3.4. Irrigation Water Quality Index

In addition to the IWQI, additional indicators were used in this study to examine the fitness of the Dhaleshwari River water on behalf of irrigation purposes because several researchers assessed the irrigation water quality using indices like the MAR, SAR, SSP, % Na, and KR (Bhuiyan *et al.* 2010; Islam *et al.* 2017; Ahmed *et al.* 2018).

Table 3 shows the calculated terms of the MAR for surface water. The surface water's MAR score ranged from 59.4 to 92.9. The water quality rating was greater than 50 (MAR > 50 harmful to soil and aquatic life), which indicated they were harmful to soil and aquatic life (Ayers & Westcot 1985). When the MAR exceeds 50, it has a negative impact on the soil (Gupta *et al.* 1987). Additionally, soil containing high concentrations of exchangeable Mg^{2+} causes infiltration complications (Ayers & Westcot 1985). In general, calcium and magnesium balance the pH of water, and excess magnesium makes the soil alkaline, which is bad for crops (Nishanthiny *et al.* 2010; Islam & Mostafa 2021c). The high concentration of magnesium plays the dominant part in this investigation. A parallel observation was delivered by Ahmed *et al.* (2018).

Table 3 shows the premeditated terms of the SAR for surface water. The surface water's SAR score ranged from 3 to 8.8. The water quality rankings were <10, (SAR < 10 Excellent) in almost all of the sampling sites, indicating they are suitable for irrigation (Ayers & Westcot 1985). Here, sodium plays a vital role and also illustrated similar observation by Islam & Mostafa (2021c). The presence of Na⁺ in irrigation water reacts with soil to restrict permeability, and frequent use makes the soil impermeable, whereas high Na⁺ causes alkali soil formation. High

	Sampling point	Sampling point									
Indexing name	SW1	SW2	SW3	SW4	SW5						
MAR	61	60.5	59.4	93.8	92.9						
SAR	8.8	0.4	0.3	0.4	0.5						
SSP	72	11.8	11.4	20.4	22.7						
% Na	21.13	4.31	3.61	2.01	1.81						
KR	257	13.2	12.5	25	28.8						

Table 3 | The IWQI calculated terms for the surface water body in the industrial effluent discharge areas

 Na^+ saturation also causes Ca^{2+} insufficiency. Frequent irrigation with high Na^+ water for an extended period of time makes the soil flexible and sticky when wet and forms clods and crust when dry. In contrast, the presence of Ca^{2+} or Mg^{2+} salts in irrigation water mitigates the negative effects of sodium by improving soil permeability (Punmia & Lal 1981; Asaduzzaman 1985).

Table 3 shows the premeditated terms of the SSP for surface water. The surface water's SSP score ranged from 11.4 to 72. Practically all of the sampling sites had water quality values < 20 or 20–40 except (SSP < 20 Excellent; 20–40 Good) for SW1, which indicates that besides mixing point surface water, all other surface water is appropriate for irrigation (Islam *et al.* 2017). High SSP levels in irrigation water may hinder plant development and impair soil permeability (Joshi *et al.* 2009). The high concentration of sodium and potassium plays a significant role in this analysis. An analogous statement was delivered by Ahmed *et al.* (2018).

Table 3 shows the calculated terms for the % Na in surface water. The surface water's % Na score ranged from 1.81 to 21.13. The water quality values were <40 (% Na < 40 Recommended) in practically all of the sampling sites, which indicates they are recommended for irrigation purposes (US SL 1954). Excess Na⁺ also causes concerns with agricultural water uptake, seedling emergence, aeration, plant and root infections, and so on (Ayers & Westcot 1985).

KR in water suggests a balance of Na⁺, Ca²⁺, and Mg²⁺ ions. A KR greater than one indicates an overabundance of Na⁺ in the water. Kelley (1963) recommended that the ratio of irrigation water should not exceed 1. Table 3 shows the premeditated terms of the KR for surface water. The surface water's KR score ranged from 12.5 to 257.6. The water quality rating was greater than one (KR >1 bad water, high level of Na⁺) in practically all of the sampling sites, which indicates they are unsuitable for irrigation purposes due to excess levels of Na⁺ (Kelly 1951; Shammi *et al.* 2016; Shakil & Mostafa 2021b, 2021c).

However, considering the results of MAR and KR, the samples from all the sampling sites were not suitable for irrigation purposes as the Ca and Mg concentrations were found to be higher at all sampling points, whereas SAR and *%Na* showed the opposite information. The SSP analysis results illustrated that, except for the SW1 sampling point, surface water was suitable for irrigation purposes. However, the overall indices for water quality at all the sampling points were suitable for irrigation purposes, except for the SW1 sampling point.

3.3.5. The NPI

NPI methods indicated which parameters were responsible for polluting the sampling sites. In this method, the mean value was divided by the standard value of surface water (DoE-BD 2023). An NPI value greater than one means they are responsible for polluting the sites. The study showed that COD, EC, BOD, TSS, Cl^- , NO_3^- -N, and Na⁺ are responsible for polluting most of the sampling sites (Table 4).

3.3.6. PCA and CA

The PCA considered the extracted PCs from the variables with eigenvalues greater than 1.00 for the surface water samples. Two PCs were extracted for the surface water PCA (Table 5). The variance explanations for the PCs are 88.902 and 8.912% for PC1 and PC2, respectively. PC1 was found to be strongly correlated with temperature, COD, pH, BOD, EC, TDS, turbidity, TSS, TH, Cl^- , SO_4^{2-} , HCO_3^- , Na^+ , K^+ , and Mg^{2+} but the role of the second component (PC2) in this variable is very insignificant because their eigenvalues were less than 1.00 (Jimenez-Espinosa *et al.* 1993). PC1 was also found to be negatively correlated with DO, PC2 with TSS, BOD, SO_4^{2-} ,

Parameters	NPI for SW1	NPI for SW2	NPI for SW3	NPI for SW4	NPI for SW5
Do	3.1	1.5	0.94	0.93	0.91
EC	2.1	0.35	0.34	0.34	0.34
TSS	1.8	1.54	0.57	0.45	0.31
BOD	2.42	2.2	1.8	1.7	1.8
COD	2.8	2.4	2.3	2.2	2.1
Cl ⁻	1.72	0.04	0.04	0.04	0.04
NO_3^N	1.38	1.35	1.21	0.85	0.44
Na ⁺	1.75	0.06	0.05	0.05	0.05

Table 4 | The NPI calculated terms for the surface water body in the industrial effluent discharge areas

	Component	
Parameters	PC1	PC2
Temperature	0.991	_
pH	0.937	0.344
DO	-0.977	0.130
EC	0.939	0.340
Turbidity	0.983	0.176
TSS	0.898	-0.392
TDS	0.952	0.299
BOD	0.964	-0.185
COD	0.989	_
TH	0.967	0.255
Cl ⁻	0.939	0.341
SO_{4}^{2-}	0.956	-0.244
NO_3^-	0.707	-0.619
PO ₄ ³⁻	0.872	-0.471
HCO_3^-	0.999	_
Na ⁺	0.939	0.339
\mathbf{K}^+	0.985	0.164
Ca ²⁺	0.890	-0.352
Mg^{2+}	0.988	_
Eigenvalue	16.891	1.693
% Variance	88.902	8.912
Cumulative %	88.902	97.815

Table 5 | Varimax normalized factor loading matrix of physicochemical parameters for surface water

 NO_3^- , PO_4^{3-} , and Ca^{2+} , therefore, they were not contributing to the variables (Irabar *et al.* 2008). The source of PC1 loading could be released from anthropogenic sources, specifically industrial effluent in the study area. In the PCA for surface water, all extracted PCs from the variables that had eigenvalues larger than 1.00 were kept and considered. The total sample variance of the two PCs extracted was about 97.815%, and it was the combination of PC1 (88.902) and PC2 (8.912). About 88% of the total variance is displayed in the first loadings (Table 5). The axis with the greatest variance becomes the first principal component (PC1), and the axis with the second greatest variance becomes the second principal component (PC2), and so on (Kaiser 1960). The parameters that contribute most to the components typically have a high degree of commonality (Islam & Mostafa 2022a 2022b).

The CA was used to visualize the groupings in the measured variables of the surface water. The CA results are exposed in Figure 3. The results of the CA were performed using SPSS software. The parameters fitting clusters are possible to originate from a communal source. Numerous mutual features were detected in that plot, and those were very comparable to those examined in the PCA. In this study, two different clusters, which closely relate to the group of physicochemical parameters, are evident: cluster (1) temperature, COD, pH, BOD, EC, TDS, turbidity, TSS, TH, Cl⁻, SO₄²⁻, HCO₃⁻, Na⁺, K⁺, and Mg²⁺ and cluster (2) DO. The same clusters or groups of parameters are likely to have originated from the same source (Ahmed *et al.* 2018). In CA analysis, the most similar variables are placed in one cluster and linked to closely related clusters, which in turn produce clusters with fewer relatives, all of which are linked to make one large cluster (Chegbeleh *et al.* 2020). That justifies the PCA because in the PCA (Table 5), only DO values were found to be negative (-0.997) for PC1, which proves that DO will produce another cluster, which was proven in CA by producing a separate cluster (Cluster II).

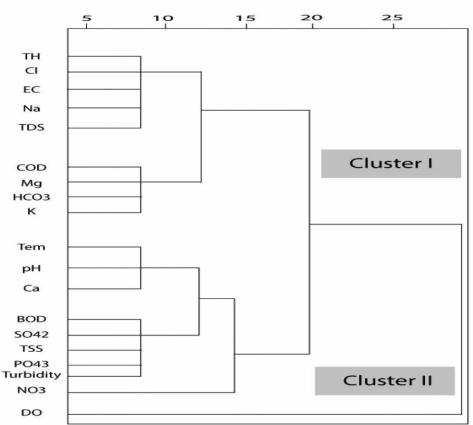
3.3.7. Correlation matrix

Using the SPSS (version 24) program, the Pearson correlation matrix was constructed. The results of PCA are often consistent with correlations between physicochemical characteristics, which helps corroborate

relationships between parameters that were not discussed in earlier studies. According to the values of correlation coefficients in surface water (Table 6), a strong positive correlation exists between temperature with turbidity, and K⁺, pH and EC with TDS, TH, Cl⁻, and Na⁺, TSS with PO_4^{3-} , BOD with SO_4^{2-} , COD with Mg^{2+} , and SO_4^{2-} with PO_4^{3-} at a significant level of 0.01. However, DO shows a negative correlation with all parameters at a significant level of 0.01 and justifies the PCA and CA analyses. The strong correlation among these variables indicates their common origin, especially from industrial effluent, which is responsible for enriching these variables in surface water.

4. CONCLUSION

Physicochemical characterization of the surface water around the tannery industrial estate effluent discharge areas showed that the concentrations of BOD and COD at all sampling points, EC, Na⁺, and Cl⁻ at the SW1 point, and TSS, NO₃⁻-N, at the SW1 and SW2 points, exceeded the permissible limit for surface water standard, however, the DO concentration varied from 1.60 to 5.5, originating under the Department of Environment (DoE-BD 2023) standard. According to seasonal variation, pollution levels were to be found in the following order: pre-monsoon > post-monsoon > monsoon, because of lower inflow and higher evaporation in the pre-monsoon season. Except for the SW1 sampling point, in the majority of sampling locations, the CWQI of the surface water quality was classified as a 'marginal', and the MWQI was in a 'moderate' category. At the SW1 point, the CWQI, WWQI, and MWQI of the surface water quality for irrigation purposes because this method is considered only aimed at the investigation of irrigation water quality for better yield production. The IWQI values showed that the surface water at all the sampling points was suitable for irrigation purposes, except for the SW1 sampling most sampling points. The study observed that no aquatic life could survive



Dendrogram using Average Linkage (Between Groups) Rescaled Distance Cluster Combine

Figure 3 | Hierarchical CA of physicochemical parameters.

	1^{**}	0.83	0.91*	1^{**}	10.0**	0.81	0.47	0.65	(
3	0.98**	0.93*	0.96*	1^{**}	0.98**	0.91*	0.58	0.79	(
9*	0.76	0.90*	0.93*	0.77	0.73	0.91*	0.90*	0.91*	(
0*	0.92*	0.95*	1**	0.93*	0.90*	0.95*	0.80	0.90*	(

SO42-

 NO_3^-

PO4³⁻

HCO₃

 Na^+

Ca²⁺

 \mathbf{K}^+

Mg²⁺

*Highly correlated; **Very highly correlated.

Temperature	1																		
pH	0.95*	1																	
DO	-0.97^{**}	-0.86	1																
EC	0.96*	1.0**	-0.86	1															
Turbidity	1**	0.98**	-0.95*	0.98**	1														
TSS	0.88	0.70	-1^{**}	0.70	0.82	1													
TDS	0.96**	1**	-0.9*	1^{**}	0.97**	0.73	1												
BOD	0.96*	0.83	-1^{**}	0.83	0.92*	0.97**	0.85	1											
COD	0.96**	0.91*	-1^{**}	0.91*	0.96*	0.89*	0.93*	0.94*	1										
TH	0.98**	1**	-0.9*	1^{**}	0.99**	0.76	1**	0.88*	0.94*	1									
Cl^{-}	0.96*	1**	-0.86	1^{**}	0.98**	0.70	1**	0.83	0.91*	1**	1								
SO_4^{2-}	0.94*	0.80	-0.99**	0.81	0.90*	0.99**	0.82	1^{**}	0.94*	0.89	0.81	1							
NO_3^-	0.62	0.47	-0.72	0.47	0.57	0.82	0.51	0.73	0.78	0.53	0.47	0.77	1						
PO_4^{3-}	0.84	0.65	-0.93*	0.65	0.78	1^{**}	0.68	0.95*	0.88*	0.72	0.65	1^{**}	0.88	1					
HCO_3^-	0.99**	0.93*	-0.98**	0.93*	0.98**	0.90*	0.95*	0.96**	0.99**	0.96**	0.93*	.96*	0.73	0.88*	1				
Na^+	0.96*	1**	-0.86	1^{**}	0.98**	.70	1**	0.83	0.91*	1^{**}	10.0**	0.81	0.47	0.65	0.93*	1			
\mathbf{K}^+	1**	0.98**	-0.95*	0.98**	1**	0.83	0.98**	0.93*	0.96*	1^{**}	0.98**	0.91*	0.58	0.79	0.98**	0.98**	1		
Ca^{2+}	0.83	0.72	-0.88	0.73	0.80	0.89*	0.76	0.90*	0.93*	0.77	0.73	0.91*	0.90*	0.91*	0.89*	0.73	0.81	1	
${\rm Mg}^{2+}$	0.96**	0.90*	-0.96*	0.90*	0.95*	0.90*	0.92*	0.95*	1**	0.93*	0.90*	0.95*	0.80	0.90*	0.99**	0.90*	0.95*	0.94*	1

 Table 6 | Pearson correlation matrix of physicochemical parameters in surface water

EC

DO

Temperature pH

Turbidity TSS

TDS

BOD

COD

ΤН

 CI^-

at the SW1 sampling point. Each index represents pollution levels that decrease with increasing distance. Multivariate statistical investigations such as the PCA, CA, and correlation matrix showed that anthropogenic activities influenced the higher values of EC, BOD, COD, TSS, Cl^- , Na^+ , and $N-NO_3^-$ in surface water in the study area. A strong positive correlation between these parameters indicates their common origin, i.e., poorly treated tannery industrial effluent is responsible for the enrichment of these variables as they enter surface water. The study found that the discharge of untreated tannery industrial estate effluent poses a threat to the environment. Hence, continuous monitoring is necessary, and tannery industry effluent must undergo proper treatment before discharging into surface water bodies.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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