

**ASSESSMENT OF CENTRAL EFFLUENT TREATMENT PLANT  
(CETP) PERFORMANCE AND SURFACE WATER QUALITY IN  
EFFLUENT DISCHARGED AREA AT SAVAR TANNERY ESTATE IN  
BANGLADESH**



**Ph.D. Thesis**

**Submitted by**

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**Reg: 2112586506, ID No. 20106**

**Session: 2020 - 2021**

**Institute of Environmental Science**

**University of Rajshahi**

**Rajshahi-6205, Bangladesh**

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***DEDICATED TO MY RESEARCH SUPERVISOR,  
BELOVED HUSBAND, PARENTS AND FAMILY  
MEMBERS***

## **DECLARATION**

It is now declared that the thesis entitled "**ASSESSMENT OF CENTRAL EFFLUENT TREATMENT PLANT (CETP) PERFORMANCE AND SURFACE WATER QUALITY IN EFFLUENT DISCHARGED AREA AT SAVAR TANNERY ESTATE IN BANGLADESH**" is written based on my research work. It has been carried out under the direct guidance and supervision of Dr. Md. Golam Mostafa, Professor, Institute of Environmental Science, and Professor Dr. Golam Sabbir Satter, Department of Geology and Mining, University of Rajshahi, Rajshahi 6205. This thesis is being humbly submitted to the Institute of Environmental Science at the University of Rajshahi, Rajshahi, Bangladesh for the degree of Doctor of Philosophy (Ph. D.) in Environmental Science.

I further declare that any part of this thesis has not been submitted to any other University or Institution for any other degree or diploma.

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## CERTIFICATE



This is to certify that the thesis entitled "**ASSESSMENT OF CENTRAL EFFLUENT TREATMENT PLANT (CETP) PERFORMANCE AND SURFACE WATER QUALITY IN EFFLUENT DISCHARGED AREA AT SAVAR TANNERY ESTATE IN BANGLADESH**" submitted by Umama Monira, ID: 20106, Reg. No. 2012586506, and Session: 2020-2021 is the outcome of his research work carried out at the Institute of Environmental Science, University of Rajshahi, Rajshahi 6205, Bangladesh under my supervision. Any part or whole of the dissertation has not been submitted elsewhere for any other degree or diploma.

We are all forwarding this dissertation to be examined for the degree of Doctor of Philosophy (Ph. D.) in the Institute of Environmental Science at the University of Rajshahi, Rajshahi, Bangladesh. The data presented in this dissertation are genuine and original. The candidate, Umama Monira has fulfilled all the requirements according to the rules and regulations of the University for submission of a dissertation for the degree of Ph. D. and made a distinct contribution to the field of Environmental Science.

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## PUBLICATIONS

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2. Monira U., Sattar G. S., & Mostafa M. G. (2023). Characterization of Tannery Effluent and Efficiency Assessment of Central Effluent Treatment Plant (CETP) at Savar in Bangladesh. *Asian Journal of Science and Applied Technology (AJSAT)*, 12(1):48-53.
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## ABSTRACT

An enormous amount of effluent that contains a number of harmful substances is produced by tannery industries. In Bangladesh, inadequately treated effluent discharge from the Central Effluent Treatment Plant (CETP) is a significant environmental and social issue. There is a Central Effluent Treatment Plant (CETP) at Savar Tannery Industrial Estate in Bangladesh to treat the composite tannery effluent, which consists of 132 tannery industries. The study is targeted to assess the performance of the Central Effluent Treatment Plant (CETP) and evaluate the surface water and groundwater quality in the effluent discharged area of the Savar tannery estate in Bangladesh. All the samples were collected three times (pre-monsoon, monsoon, and post-monsoon) in a year, from the monsoon of 2021 to the pre-monsoon of 2023. The composite effluent samples were collected before entering and discharging points of the CETP and analyzed for various physicochemical parameters to assess the performance of the CETP. There were five surface water samples collected from different locations, starting from the CETP discharge point and at different distances, i.e., 100, 500, 1000, and 2000 meters from the CETP discharge point, and the samples were named SW1, SW2, SW3, SW4, and SW5, respectively, as well as several groundwater samples collected around the CETP. The study results showed high values of EC, TSS, TDS, TH, BOD, COD,  $\text{NO}_3^-$ -N,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{Cl}^-$ , and metals (Na, Ca, Cr, Cu, Fe, Pb, and Zn) in the composite tannery influent and effluent collected from before entering and discharging points of the CETP tannery estate at Savar. The values of the physicochemical and anionic parameters were above the standard permissible limits of effluent discharge prescribed by the ISW-BDS-ECR (2023), DoE-BD (2023), and NEQS (2000). The higher values of TDS and TSS in the tannery effluent were due to the presence of various organic and inorganic substances. The pH values were 8.6 and 7.5 in the influent and effluent, respectively, indicating a neutral to slightly alkaline range. The average values of DO, BOD, and COD were 0.7, 573, and 1646 mg/L in the influent and 0.9, 96.7, and 337 mg/L in the effluent, respectively, causing serious surface water pollution in the areas. Higher COD and BOD levels indicate reduced oxygen concentration, or lower DO values, in the influent and effluent. The average EC was 11430  $\mu\text{S}/\text{cm}$  in the influent and 10190  $\mu\text{S}/\text{cm}$  in the

effluent, and the concentrations of anions, including  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{Cl}^-$ , were 60.18, 1900, 1200, 28.3, and 2417 mg/L in the influent and 4, 1850, 315, 7.2, and 1667 mg/L in the effluent, respectively. Higher values of these parameters are an indication of polluted water. Based on the above parameters, the study reported that the samples were heavily polluted and potentially harmful to the environment. The values of metal ions in the composite tannery influent and effluent were in the following order:  $\text{Na} > \text{Ca} > \text{Cr} > \text{Fe} > \text{Cu} > \text{Zn} > \text{Pb} > \text{Mn}$ . The study summarized that the overall efficiency of the CETP was 47.0%. Metal ions contained in the sludge were in the following order:  $\text{Na} > \text{Cr} > \text{Fe} > \text{Pb} > \text{K} > \text{Mn} > \text{Cu} > \text{Zn} > \text{Ni} > \text{Ca}$ . A similar organic functional group was found in influent and effluent by FTIR analysis, like alcohols, phenols, amides, ketones, quinone-conjugated carbonyls of lignin, alkanes, 1, 2, 4, – trisubstituted, alkyl halides, as well as aromatic and aliphatic amine functional groups, which again proved that the CETP was not working effectively.

Physicochemical characterization of the surface water and groundwater around the treated tannery effluent from the CETP discharge areas showed that the concentrations of BOD and COD were found to be higher at all sampling points, suggesting improving the biological treatment capacity of the CETP. Moreover, EC, Na, and  $\text{Cl}^-$  at the (CETP discharge point) SW1 point and TSS,  $\text{NO}_3^-$ -N, at the SW1 (CETP discharge area) and SW2 (500m downstream from the CETP discharge area) points exceeded the surface water standard, whereas the DO level ranged from 1.60 to 5.5, found below the Environmental Conservation Rules (ECR), 2023 standard. Seasonal pollution levels for surface water were found in the following order: pre-monsoon > post-monsoon > monsoon. For groundwater, the following sequence was found: post-monsoon > monsoon > pre-monsoon.

However, at the SW1 sampling point, *CWQI*, *WWQI*, *MWQI*, and *IWQI* scores suggested that the surface water quality was not suitable for irrigation and aquatic biota. The *NPI* indicated that higher values of BOD, COD,  $\text{Cl}^-$ , Na, Zn, Pb, and Cr were responsible for polluting most of the sampling sites in surface and groundwater.

The analysis results of the heavy metals showed that four (4) metal ions, viz., Cu, Pb, Cr, and Zn in the surface water and five (5) metals like Mg, Fe, Zn, Pb, and Cr in the groundwater exceeded the concentration limits of the DoE-BD (2023) in most of the

water sampling sites, indicating severe human health hazards. It may occur due to the infiltration of tannery effluent from the surface water into groundwater. The values of  $I_t$  and  $CPI$  for these metals were very high, i.e., much greater than 1. The other metal concentrations were found within safe permissible ranges. The values of heavy metal pollution indices, viz.,  $MI$ ,  $HMPI$ ,  $HMEI$ , and  $C_d$ , showed a high degree of contamination at all the sampling sites. The  $NeI$  showed that most of the water samples were found to have medium to high levels of contamination in the study area. The values of the total carcinogenic and non-carcinogenic hazard index ( $HI_{total}$ ) in all sampling sites were found to be higher than 1, and thus, the water in the areas was not suitable for domestic purposes without treatment. However, each sampling site poses a low ecological risk. The multivariate statistical analyses, such as principal component, cluster analysis, and correlation matrix showed significant anthropogenic intrusions of Cr and Pb in surface and groundwater in the study area. A strong positive correlation between these parameters indicated their common origin, especially from industrial effluent, which is responsible for the enrichment of these variables as they move together in surface and groundwater. The analysis results revealed that SW1 and SW2 sampling points were at high risk due to the presence of heavy metals, and each index represented that the degree of pollution decreased with increasing distance.

The study suggested that surface and groundwater quality should be continually monitored, and tannery effluent must be appropriately treated before being released into the environment. Finally, a biological treatment process combined with the existing treatment facilities, considering the quality and quantity of the effluent, could be adopted. Further research should be considered for developing an efficient treatment plant to adequately treat the tannery effluent, aiming at sustainable surface water management for achieving Sustainable Development Goal 6 (Clean Water and Sanitation).

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## **List of Abbreviations**

AAS - Atomic Absorption Spectroscopy  
APHA - American Public Health Association  
BCIC - Bangladesh Chemical Industries Corporation  
BD - Bangladesh  
BDWS - Bangladesh Drinking Water Standard  
BGS - British Geological Survey  
BOD - Biological Oxygen Demand  
COD - Chemical Oxygen Demand  
 $C_d$  - Degree of Contamination  
CCME - Canadian Council of Ministers of the Environment  
CETP - Central Effluent Treatment Plant  
CBE - Charge Balance Error  
CDI - Chronic Daily Intake  
CPI - Compound Pollution Index  
CWQI - Canadian Water Quality Index  
DO - Dissolved Oxygen  
DoE - Department of Environment  
DPHE - Department of Public Health and Engineering  
DW - Distilled Water  
EBT - Eriochrom Black - T  
EC - Electrical Conductivity  
ECR - Environment Conservation Rules  
EDTA - Ethylene Di-amine Tetra-acetic acid  
EPA - Environmental Protection Agency  
EPN - Environmental Protection Network  
ERI - Ecological Risks measurement  
ETP - Effluent Treatment Plant  
EU - European Union  
FAO - Food and Agriculture Organization  
FTIR - Fourier-transform Infrared Spectroscopy

HCA - Hierarchical Cluster Analysis  
HRA - Health Risk Assessment  
HI - Total Hazard Index (Total)  
HQ - Health Quittance  
HMEI - Heavy Metal Evaluation Index  
HMPI - Heavy Metal Potential Index  
IES - Institute of Environmental Science  
IWQI - Irrigation Water Quality Index  
ILCR - Incremental Lifetime Cancer Risk  
IUPAC - International Union of Pure and Applied Chemistry  
KR - Kelly's Ratio  
MAC - Maximum Admissible Concentration  
MAR - Magnesium Adsorption Ratio  
MC - Magnesium Content  
MI - Metal Indices  
MR - Magnesium Ratio  
MWQI - Meireles water quality index  
NPI - Nemerow's Pollution Index  
NTU - Nephelometric Turbidity Unit  
PCA - Principal Component Analysis  
RU - Rajshahi University  
RSC - Residual Sodium Carbonate  
SAR - Sodium Adsorptions Ratio  
SSP - Soluble Sodium Percentage  
SD - Standard Deviation  
SWS - Surface Water Standard  
TDS - Total Dissolved Solids  
TSS - Total Suspended Solids  
TH - Total Hardness  
UN - United Nations  
US - United States  
WHO - World Health Organization  
WWQI - Weight Average Water Quality Index

# **CHAPTER 1**

## **Introduction**

# CHAPTER 1

## Introduction

### 1.1 Background of the study

Generally, a Common or Central effluent treatment plant (CETP) is designed to help industries in easier control of pollution and develop a step towards a cleaner environment and service to the industrial sector at a large scale. For, this reason, an efficient effluent treatment plant is necessary for its liquid waste management.

The target of industrial effluent treatment is to protect the environment and lowering production costs by reducing toxic chemicals. Because of the untreated or not fully treated release of toxic chemicals through effluent, has become a growing source of bother, causing potential threats to the environment and life. Industrial wastewater is generated by various processes, and the enormous amount of toxic wastewater released varies according to the specific or particular industrial process. However, industrial wastewater is frequently referred to as effluent. It is a liquid that runs away from a container. Wastewater is any water whose quality has been wounded by anthropogenic activities. Toxic metal pollution of the biosphere has increased exotically since the beginning of the Industrial Revolution. The increasing industrialization upraises the standard of living, resulting in a highly contaminated atmosphere as a result of drainage waste from these industries (Tiwari et al., 2008). Rapid industrialization contributes remarkably to environmental pollution and causes severe degradation in the hydrosphere and atmosphere. The widespread industrialization of urban areas has vastly reduced the amount of land available for waste disposal. The discharge of untreated industrial and domestic wastewater into the environment has an impact on the characteristics of both soil and water (surface and ground). Because of the introduction of various contaminants

such as heavy metals and various toxic chemicals into the soil and water resources, cause a potential risk to our environment (Azumi and Bichi, 2010). Industrial wastewater is discharged into open drains without concern has harmed valuable resources, eventually making its way into rivers. As a result, it becomes an emerging issue or difficulty not only for the environment but also for the social context of the country.

The biosphere is an important component of the environment. The biosphere is made up of all living things. It reclines from 10,000 meters below sea level to 6000 meters above sea level. To sustain life on Earth, the biotic and abiotic components of the biosphere interact in a well-ordered manner. Any adverse effect or disturbance caused by man can cause ecological imbalance, which can lead to unfavorable conditions for living organisms and mankind. Rapid industrialization is one of the main anthropogenic causes of ecological imbalance and pollution (Azumi and Bichi, 2010). Economic development is dependent on industrial development, but it also brings a lot of environmental issues. Different industries generate a wide range of waste materials in solid, liquid, and gaseous forms. The liquid waste materials discharged from industry or sewage is known as effluent. The main industrial pollutants are typically considered to be organic and inorganic compounds, heavy metals, acids, bases, suspended solids, pathogens, and so on. When untreated or inadequately treated effluent is released into the environment, it disrupts the ecological balance and interferes with the physiological activities of living organisms. Hence, the toxic chemicals must be removed before discharging into water bodies. For this, a modern and effective Effluent Treatment Plant (ETP) of combined treatment facilities should be adopted in the industries to reduce environmental pollution (Monira et al., 2022; Islam and Mostafa, 2021).

Industrial estates are being built to meet the needs of the growing population of the country. Industries not only manufacture useful products but also produce waste products in the form of solid, liquid, or gas, which causes hazards, pollution, and energy losses. Environmental pollution is becoming a universal issue, with industrial effluent being one of the major sources of water pollution. Industrial effluent is discharged into regular drainage or nearby soil or water bodies (Lokhande et al., 2011), posing a serious threat to human health and the routine functioning of ecosystems (Lakshmi et al., 2010;

Olajumoke et al., 2010). Textiles, leather industries, pulp and paper mills, fertilizer, industrial chemical production, and refineries are the most troublesome or tricky industries for the water sector (surface and groundwater). All of these industries typically release a complex mixture of hazardous chemicals, both organic and inorganic, into bodies of water without treatment or insufficient treatment. In nature, organic pollutants are both biodegradable and non-biodegradable. During decomposition, the biodegradable organic components degrade water quality by consuming dissolved oxygen. Organic non-biodegradable components go on in the water system for a long time and enter the food chain (Ahmed and Reazuddin, 2000). Metallic salts, acidic and basic compounds are the most general inorganic pollutants in the river system, these inorganic components interact or interchange chemically and biochemically, degrading water quality when samples from the outlets of the leather industries were collected, it was discovered that the wastewater contained high salinity, high organic loading, higher concentrations of total dissolved solids, chromium, chloride, ammonia, nitrate and sulfates, and specific pollutants such as Cd, Cr, and Pb, among others (Calheiros et al., 2008). Fish and other aquatic species cannot survive in receiving water, which could be a river, a city gutter, a lake, surface water, or even the ocean if chemical pollutants are present; the receiving water becomes unhealthy for human and animal consumption.

The leather industry is a dominant part of the Bangladeshi economy in terms of foreign exchange earnings, as it is the second-largest earner. This industry is firstly focused on exports. More than 95 percent of Bangladesh's leather and leather products are exported, primarily or firstly in the form of wet-blue, crust leather, finished leather, leather garments, and footwear. The Export Promotion Bureau estimates that leather and leather products, valued at \$941.67 million in the FY 2020–2021, will be Bangladesh's second-largest export category. Which, corresponds to around 2.43 percent of the nation's total export revenue (\$38.758 billion). The country now has over 132 modern tannery units in function (Monira et al., 2023).

This promising sector is plagued by a number of matters, including environmental pollution issues related to effluent treatment technology, management and infusion of advanced technology, and an innovative and integrative marketing strategy. Furthermore, the owners of tannery industries are not specifically concerned with human health or

environmental safety. As a result, the country's natural resources are depleting, and serious pollution threats appear. Environmental matters such as air pollution, water pollution (both surface and groundwater), and solid waste disposal have grown exponentially. Circulating waste and effluent into water bodies such as lakes, canals, and rivers is still common due to a lack of consciousness and the absence of strong punitive measures (Ahmed and Reazuddin, 2000).

The tannery industry is one of the most pollution-generating and environmentally unfriendly industries all over the world. Leather industrial effluent is one of the most polluting industrial wastes or effluent in all environments, and it is one of our vital health concerns in developing countries (Shen, 1999; Soyalsan and Karaguzel, 2007; Camargo et al., 2003; Rahman, 1997). Environmental pollution is becoming a global issue, and the tannery industry is one of the major sources of water contamination. The saga of the disastrous environmental impact of the Hazaribagh tanneries is well-known, especially how it has destroyed the Buriganga River with magpie poisonous waste being ditched into it. This led major global biddable brands to stop buying leather and leather goods from Bangladesh many times ago because of their environmental pollution, which urged the government to shift the tanneries to Savar. But without the Central Effluent Treatment Plant (CETP) fully completed, the tanneries are again jilting incompletely treated waste, resulting in pollution of the Dhaleshwari River killing its fish and other submarine life, and depriving fishers of their only livelihood (Mollic, 2022).

Generally, a Common effluent treatment plant (CETP) is designed to help industries in easier control of pollution and develop a step towards a cleaner environment and service to the industrial sector at a large scale. For, this reason, an efficient effluent treatment plant is necessary for its liquid waste management. The Central Treatment Plant (CETP) has been established in the Savar tannery estate as an alternative to Hazaribagh tanneries located in Dhaka City, aimed to reduce pollution in the nearby areas of the city (Monira et al., 2022). Full benefits of the CETP can be achieved by bringing some changes in solid and liquid waste operation, it added. Industry leaders said that the under-construction CETP was the largest in Asia. Bangladesh will be the third-largest country in the tannery and leather assiduity from the current seventh if the CETP can be utilized duly. The CETP appears to be an illusion, as it has caused dislocated tanneries to actually

wind up poisoning the Dhaleshwari swash with partially treated wastewater. In order to protect the environment, we need an effective and fully operational CETP plant, and the effectiveness of the CETP should be monitored regularly (Mollic, 2022).

According to Mollic (2022) old Hazaribagh tanneries were first seriously considered for relocation in the 1990s, and the Bangladeshi government then developed a policy for relocation in 2001. In 2012, the government floated a tender for the construction of a CETP, and a Chinese company that won the bidding started the work in 2014 for completion by 2017. However, the government's allocation of land for 155 tanneries in the Tannery Industrial Estate in Savar could potentially lead to the initiation of the relocation process in early 2014. However, the shifting or relocation has been delayed over the last decade due to the delay in establishing the Common Effluent Treatment Plant (CETP) for the proposed industrial zone. The owners' unwillingness is also a vital factor in the delay. When the government decided to cut off the utilities to their former establishments in Hazaribagh in April 2017, the majority of tanneries were forced to relocate their factories. According to a recent report by BSCIC (April 2019), out of the 155 industries, 123 have already begun processing the leather at the newly established tannery estates, while 18 are under construction (Islam and Mostafa, 2018).

Approximately 155 tannery industries have been transferred from Hazaribagh, Dhaka to the Savar tannery estate at Hemayetpur to save the Buriganga River from further pollution, and around 132 industries are active in the production of leather goods (BSCIC, 2019; Mollic, 2022). The industries discharge the effluent through a pipeline and they enter into the CETP for treatment after treatment they release from the CETP and fall into the Dhaleshwari River. According to Hasan et al (2020), the Central Effluent Treatment Plant (CETP), which has a daily capacity to handle 30,000 m<sup>3</sup> of effluent, is the project's lifeline. Concerns about the efficient operation of the CETP and other supporting elements like the dumping yard and chrome recovery unit in ensuring environmental compliance have consequently developed as a 'teething problem' of the relocation process. Mollic (2020) reported that the current central effluent treatment plant at the Savar estate, according to Department of Environment sources, has the capacity to process about 25,000 cubic meters of liquid waste per day. But 40,000 cubic meters of waste are

produced by the tanners inside the estate. The warning, which asserts that 15,000 cubic meters of untreated waste are currently being dumped into the nearby Dhaleshwari River, is quite depressing. Heavy metals and chromium, which are also discharged into the river, cannot be treated in the exclusive tannery zone because there is no existing structure for that purpose. All of these things combine to make the Hemayetpur section of the river a source of open pollution. So, the efficiency of the Savar CETP is questionable. The assessment of the effectiveness of the Central Effluent treatment plant (CETP) is essential to compare their performance. The study was executed at Saver Tannery Estate to determine the effectiveness of the effluent treatment plant and the pollution level of surface and groundwater quality by testing different physicochemical parameters and using various indexing models. The aim of this study is to characterize the influent and effluent of the CETP, assess its performance of the CETP and determination of pollution level of surface and groundwater by various indexing methods to find its suitability for irrigation and drinking purposes.

## **1.2 Statement of the Problems**

Tanneries are generally characterized as pollutants generated diligence which produce wide kinds of high-strength poisonous chemicals and large amounts of water are used in the tanning process of which 90% of water is released as wastewater (Sinha et al., 2002) which are always characterized by its strong color (sanguine dull brown, black and any type of dark color), high pH, EC, organic and inorganic substances, Ca, COD, dissolved and suspended solids, ammonia, nitrate, nitrite and total Kjeldahl nitrogen (TKN) and specific high poisonous adulterants (sulfide, chromium, cadmium, lead, chloride, sodium, and other swab remainders) and heavy metals (Cooman et al., 2003; Chaudry et al., 1997; Tariq et al., 2005; Apte et al., 2005; Leghouichi et al., 2009; Ajmal et al., 1998a). All over 20- 30 L wastewater is discharged per kilogram of skins/ hides reused, and in the case of finishing units, this volume is about 35- 40 L kg skins/ hides (Nariagu and Pacyna, 1988; Nandy et al., 2001; Colak et al., 2005; Tudunwada et al., 2006. According to ImamulHuq (1998), colorful chemicals are used during soaking, liming, unhairing, deliming, bating, pickling, tanning, and post-tanning of hides and skins. The main chemicals are used sodium sulfite and chromium sulfate including ionic wetting down

agents, bactericides, soda ash, CaO, ammonium sulfide, ammonium chloride, enzymes, sodium bisulfate, NaCl, H<sub>2</sub>SO<sub>4</sub>, formic acid, different type of fat, sodium bicarbonate, vegetable tannins, resins, polyurethane, colors, binders and different type of waterproofing agent (Tudunwada et al., 2007). Azom et al., 2012 reported that about 40 heavy metals are used for recycling raw hides. Detergents and auxiliary materials come in a variety of colors for finishing procedures (ImamulHuq, 1998). Only around 20 % of the numerous chemicals employed in the tanning process are known to be absorbed by the leather, and the rest of the chemicals are released as wastes. The vast quantum of unutilized process chemicals is discharged from tannery industries directly or laterally throughout the public sewer lines and these adulterants are eventually linked to the gutters. The pickled pelt reacts with roughly 40–60 of the applied chromium granules during the chrome tanning process, and the remaining 6040 particles are typically released in the final wastewater (Heshem et al., 2010) causing serious trouble to the land (Van Groenestijn et al., 2002; Leghouichi et al., 2009, and Owlad et al., 2008).

Researchers have drawn attention to the problem of drains carrying untreated industrial effluent in developing nations (Amano et al., 2020; Onwuka et al., 2004; Rashid et al., 2018). Poor management of these results in effluent infiltration into the surrounding soil which severely affects the ground-water quality (Rashid et al., 2018). Industrial waste management is one of the major challenges affecting surface and groundwater quality (Amano et al., 2020). The tannery (leather) industry is one such industry that could pollute surface and groundwater. In order to treat animal skins, tanneries use a lot of water as well as a variety of harmful chemicals. Tannery wastes are strongly colored, have high BOD and pH levels, and have significant TDS concentrations. The tanning process makes substantial use of chromium, which is regarded as a major contaminant (Sajil Kumar & James, 2019). Most of the regions in and surrounding tanneries are believed to have extremely high levels of surface and groundwater pollution (Mondal and Singh, 2005; Sajil Kumar, 2014).

Exposure to chromium, pentachlorophenol, and other poisonous substances increases the threat of dermatitis, ulcer nasal septum perforation, and lung cancer (Carlos et al., 2002, Barnhart et al., 1997; Barceloux et al., 1999, Bajza and Vrcek, 2001; Kornhauser et al., 2002 and Stoyanova et al., 2004). The wastewater from tanneries is also contaminated with

high concentrations of Cu, Zn, Mn, and Ni, which when ingested, poses major health risks (Salt et al., 1995; Lakshmi et al., 2011). The major chemical components of the wastes from the post-tanning and finishing steps are different types of fat liquor, different types of coloring materials, colors, cationic fat, binders, etc. These chemicals mixed with water are released from the tanneries and defiled the groundwater permanently and making it unfit for drinking, irrigation, and general consumption. Above the discussion, pollution is described in colorful ways. It is seen as the human discharge of unwanted substances into the topography in quantities that threaten either the health of the resource or the resource itself (Tripathi et al., 2007).

According to the assessment of the literature, the Central Effluent Treatment Plant in the study area is not adequately treating the effluent produced by the tannery industries, which is causing a significant environmental hazard. Several, daily papers have already published reports concerning the harm that effluent from tannery companies has caused to agriculture, human health effects, and fish deaths in ponds, lakes, and rivers. So, tannery effluent should be treated properly. CETP is the treatment plant where tannery wastes are treated. However reports show that CETP is not fully operational. That means its efficiency is questionable. So, we need to assess the performance of the CETP.

The literature reports on the performance of the CETP and the areas where the discharge effluent of the leather industries concerns environmental pollution. No detailed scientific study has been conducted yet on the assessment of the CETP performance and areas where the discharge effluent of the leather industries concern environmental pollution. Not only the aim of this paper is to characterize the influent, effluent of the CETP, and assess its performance of the CETP but also to characterize surface and groundwater quality and determination of pollution labels by various indexing methods to determine its acceptability for irrigation and drinking purposes.

### **1.3 Scope of the Study**

#### **Research Gap:**

As far now no work has been done about the performance of the CETP at Savar near the Dhaleshwari River and no detailed study (indexing-based) has been conducted yet regarding the toxic effluent discharged by these tannery industries into surface water

bodies. In this context, this study is the pioneer in assessing the performance of CETP and surface and groundwater quality in the effluent discharge area.

So, the scope of these studies is:

- ❖ Characterization of influent and effluent
- ❖ Efficiency analysis of the CETP
- ❖ Characterization of surface and groundwater quality
- ❖ Identification of toxic elements
- ❖ Assessment of pollution level
- ❖ Recommendations for remedial measures

## 1.4 Objectives of the Study

Nowadays, environmental contamination is a major problem on a global scale. In Bangladesh, one of the most concerning environmental issues is water (surface and ground) pollution. Many factories and industries indiscriminately discharge their untreated or inadequately treated effluent into neighboring surface water bodies, having negative effects on both the environment and human health. Effluent must be properly treated before being discharged into water bodies. For this, we need an effective effluent treatment plant. In the study area tannery industry discharges improperly treated effluent into the Dhaleshwari River which has the potential to cause water pollution. To ensure sustainable water resource management, it is very necessary to assess the performance of the CETP and water (surface and ground) quality in the study area.

**The main objective is to assess the (Central Effluent Treatment Plant) CETP performance and surface water quality in the effluent discharged area.**

### Specific Objectives

1. To characterize influent, effluent, surface water, groundwater, and sediments quality
2. To Assess the performance of the CETP
3. To determine the pollution level by various indexing models like *CCME*, *WWQI*, *MWQI*, *IWQI*, *NPI*, *I<sub>t</sub>*, *CPI*, *MI*, *HMPI*, *HMEI*, *C<sub>d</sub>*, *ERI*, and *HRA*.

# **CHAPTER 2**

## **LITERATURE REVIEW**

# CHAPTER 2

## LITERATURE REVIEW

A critical analysis of the collection of information on a particular subject, including theories, criticisms, procedures, research findings, assessments, and evaluations, is known as a literature review. It involves comparing and contrasting the work with previously published work in a critical evaluation. It reviews what has already been determined and written about a subject. Thus, one can create an original or revolutionary idea and concept for use in future studies based on the available knowledge. A detailed and comprehensive literature analysis is required for performing qualitative research. It is a fundamental assignment that is completed in every research study. To understand the current situation of leather industrial effluent, this literature review was conducted. The pollution level was then determined using indexing models to evaluate its suitability for irrigation and drinking purposes. The study conducted the literature review based on many papers, books, the internet, and peer-reviewed national and international journals with high impact factors published within the last 30 years.

The present study used a variety of search engines, including Google Scholar (<http://www.Scholar.google.Com>), Web of Science ([www.Webofknowledge.Com](http://www.Webofknowledge.Com)), Wikipedia (<http://www.Wikipedia.Org>), Science Direct (<https://www.Sciencedirect.Com/>), PubMed Scopus (<http://www.Scopus.Com>), Research Gate (<https://www.Researchgate.Net>), etc., to understand the present status and explore research gaps in this study. The Boolean operators "and" and "or" were used to analyze the following phrases: (a) characterization of influent and effluent, (b) assessment of the performance of CETP, (c) surface and groundwater quality parameters, (d) water quality indices, (e) assessment of irrigation water quality, (f) evaluation of drinking water quality, etc.

Industrial wastewater is any wastewater, whether treated or not, that leaves a treatment facility or industrial outfall, also known as effluent. Prior to being released into any bodies of water, wastewater must be treated. Among many other industries, the tannery industry directly has ecological consequences that need to be considered. For numerous production processes like soaking, liming, deliming, tanning, retaining, fat-liquoring, and finishing, tanneries use a lot of water. As a result, the leather industry releases large amounts of effluent containing several harmful contaminants. These effluents, which are produced in several phases, frequently exceed the standard limit for a number of physicochemical criteria, making them very contaminated and hazardous to both human health and the aquatic ecosystem. A brief review of research information on the characteristics of the leather industries' effluent, surface and groundwater quality parameters, water quality indices, evaluation of drinking water quality, evaluation of irrigation water quality, and their detrimental effects on the environment has been attempted in this chapter.

## **2.1 Characterization of the leather industrial effluent**

One of the most polluting industrial sectors is the tanning industry. In comparison to other manufacturing sectors, the tanning industry has been identified as one of the most polluting industries. The high concentrations of chloride, ammonia, sulfate, and other organic and inorganic pollutants found in tannery wastewater are responsible for the wastewater's high pollution load. The composite tannery effluent (wastewater) is thus characterized by a high load of organic matter, strong color, turbidity, foul-smelling, high pH, dissolved and suspended particles, organic nitrogen, and ammonia originating from the hides as well as from the added chemicals (Cooman et al., 2003; World Bank, 1998; Boshoff et al., 2004; UNIDO, 2000). The effluents released from tanneries are thick and colorful and contain hazardous chemicals, physiologically oxidizable elements, toxic metallic compounds, and a significant amount of putrefying suspended particles. The land surface and water bodies that receive the tannery effluents suffer damage to their normal lifespans (ETPI, 1998; GATT, 1994; Khan et al., 1999).

Many studies revealed that the primary factor affecting pH is the chemicals used at various phases (Boshoff et al., 2004; UNIDO, 2000). Tannery effluents have extremely

high electrical conductivity values, which show that cations and anions are present in the effluents. The higher conductivity changes the chelating characteristics of water bodies and unbalances the availability of free metals for flora and fauna. The electrical conductivity, pH, chloride, sulfides, biological oxygen demand, and chemical oxygen demand in tannery effluent were reportedly substantially greater than the tolerance limits for industrial effluent discharged into the land surface, according to several sources (Vajpayee et al., 1999; Tunay et al., 1994; Tripathi et al., 1996). According to Kannan et al. (2008), tanneries' effluents have higher levels of total dissolved solids (TDS), which are mostly caused by carbonates, bicarbonates, chlorides, sulfates, phosphates, nitrates, nitrogen, calcium, sodium, potassium, and iron. Higher amounts of BOD, COD, and TSS were also found in tannery effluent, according to Akan et al. (2007, 2008).

Due to the great characteristics that chrome tanning imparts to the leather and its simplicity of use, nearly 90% of the tannery sector in Bangladesh uses this method. The nature of the tanning process employed, the amount of water utilized at various tanning stages, and the tanning processing capacity all have a significant impact on the properties of tannery wastewater. Nearly all of the tanning process is a wet one that uses a lot of water and emits roughly 90% of that water as waste (World Bank, 1998; IFC, 2007). Based on the processes involved, the raw materials used, and the finished products, different tanneries use different amounts of water, and as a result, produce different amounts of wastewater or effluent (Wiegant et al., 1999; UNIDO, 2000). The pre-tanning stages often use the most water, but the post-tanning operations also need a significant amount of water (ETPI, 1998). With each ton of raw, salted, animal hides that are typically handled batch-wise, the tanning industry produces between 50 and 60 m<sup>3</sup> of wastewater (Khan et al., 1999).

Conventional pre-tanning, tanning, and post-tanning methods discharge effluent (many unused process chemicals like Cr, sodium chloride dye-stuffs, different types of re-tanning materials, acids, and different types of fats, etc.), which contain enormous amounts of pollutants together with effluent. (ETPI, 1998; UNEP, 1991).

Pre-tanning operations are responsible for over 70% of the emission loads of biological oxygen demand (BOD), chemical oxygen demand (COD), and total dissolved solids

(TDS). There is a lot of organic matter released into the environment by tannery wastewater. Polyphenolic compounds, acrylic acid condensates, aliphatic ethoxylates, fatty acids, colors, proteins, and soluble carbohydrates belong to the organic substances found in these wastes (Szpryokowicz et al., 1995; Naumczyk et al., 1996). Industrial effluents contain both organic and inorganic materials that use dissolved oxygen, leading to oxygen depletion (Cooman et al., 2003). Oxygen has the ability to oxidize organic substances found in water bodies. Thus, organic materials consume oxygen when released into a water body, leaving the system in an oxygen-deprived state. These anoxic circumstances result in an environment with low electric potential and can alter the system's chemical composition. Several aquatic creatures, including fish, are stressed by the loss of oxygen (UNEP, 1999; Nicholas, 1996; Pittier and Chudoba, 1990; Nicholson, 1998). Tannery effluents from the processing of the beam house and related rinsing process may contain hidden compounds, dirt, blood, or drug residues and consequently have substantial loads of organic matter and total suspended solids. Sulfides, ammonium salts, and calcium salts are present in tannery effluents from deliming, bating, and tannery processes and are potential sources of odor. Biological decomposition of organic matter from leather industrial effluents and sulfide emissions (also owing to bacterial reduction of sulfate) were shown to be the causes of the unfavorable odors in tannery sites, according to reports (Balasubramanian et al., 2000; Dorman et al., 2000). The effluent is also marginally alkaline. According to several reports, the effluents from beam house processing have significant levels of chromium, sulfate, sulfide, total solids, and chloride (Cooman et al., 2002; Gupta, 2003; Junior et al., 2006).

This stage of the tanning process is the most polluting stage, making up roughly 50–55 percent of the industry's overall pollution burden. The pickling and chrome tanning effluents contained sulfates, sodium bicarbonate, chlorides, and chrome (UNIDO, 2000). Chrome salts, dyestuff residues, fat liquoring agents, syntans, and other organic debris, which are commonly assessed by COD, are the main post-tanning contaminants (Bajza and Vrcek, 2001; UNIDO, 2000). Chromium is extremely hazardous to a wide range of life forms (Cooman et al., 2003; ETPI, 1998). When discharged, tannery effluents harm the receiving water bodies and the land surface's capacity to sustain its normal life. The problem of pollution brought on by the tanning industry has been made worse by a lack

of effective legislative control, inefficient processing procedures, and the use of crude conventional methods to process leather. Additionally, it demonstrates that areas with high levels of toxic substances, especially heavy metals, are frequently harmful and persistent, having an impact on both human health and the ecosystem.

In summary, it is now understood that indirect exposure to chemicals used in the production of leather might possibly result in human impairment, sickness (toxigenic/carcinogenic), and even death. So, tannery effluents must be properly treated before being discharged into water bodies. For this, an effective treatment plant is essential.

Vapors from solvents used in degreasing and finishing can expose people. The improper and unsafe handling of insecticides, tanning agents, and processed hides and skins can also pose hazardous risks to human health. Moreover, the tanning industry is known to have visual effects, excessive noise, and air pollution. It is regrettable that the amount and types of hazardous waste produced in the majority of developing countries are not accurate estimates. There aren't many reports on composite and manufacturing unit-specific tannery effluents in Bangladesh. Due to increasing salt levels and the presence of several harmful compounds, including heavy metals, in tannery effluents, there is increasing environmental pressure against the production of leather today (Saravanabhavan et al., 2005; Bernel et al., 2006).

## **2.2 Characteristics and environmental impact of leather industrial effluent**

The general characteristics of effluents in assessing the potential for water pollution are high pH, EC, BOD, COD, suspended solids, total nitrogen, lead, sulfate, chromium, chloride, etc. (Jeved et al., 2005). Moreover, there are a lot of sediments in the wastewater. These parameters' values vary between tanneries due to various methods and the use of different raw materials. Because of wastewater's high contamination level, its release into the environment without taking any precautions has very negative environmental effects. The physical, chemical, and biological properties of surface and groundwater can quickly deteriorate in the presence of untreated or improperly treated tannery effluent.

The wastewater discharged by the tannery industry is often unpleasant and dark in color. Both biodegradable and non-biodegradable high molecular weight organic molecules, as well as a significant number of chemicals employed during processing, may be responsible for the effluent's color and bad odor.

When evaluating the potential for water pollution, pH is a crucial factor (UNIDO, 2000). Low-pH water corrodes water-carrying systems and, under the actual conflict, can lead to heavy metals dissolving in the effluent (Balasubramanian et al., 2000; Dorman et al., 2000). The employment of acids in various tannery operations results in wastewater with a low pH. On the other hand, lime is responsible for the high pH in tannery effluent because it is utilized excessively, which results in sewer scaling. The aquatic habitat is stressed by a significant pH change, which could lead to the extinction of several species there. A pH value in the range of 6 to 9 is advised by the NEQS (Chowdhury et al., 2013, 2015).

Due to the excess sulfuric acid added during pickling and the unhairing process, it is then oxidized to sulfate before being discharged into the sewer. At a pH level of less than 8.5, hydrogen sulfide is generated. Even in trace amounts, this gas has a disagreeable smell and is extremely poisonous to many types of life (Balasubramanian et al., 2000; Dorman et al., 2000). Fish mortality may happen in higher concentrations at a sulfide concentration of 10 mg/L (Chowdhury et al., 2013, 2015).

An essential component of the optical property known as turbidity allows light to scatter and absorb rather than pass through the sample without changing direction (APHA, 2005). The high amounts of salt, carbonate, bicarbonate, chloride, calcium, and magnesium used in the tanning industry may have been released and caused the effluent to become turbid (Chakrapani, 2005). Minimal light penetration and a resulting decline in photosynthesis as a result of the water's increased turbidity are two other indirect effects. The wastewater's higher electrical conductivity value indicates that more chemicals, such as cations and anions, were discharged in the effluent. The increased conductivity changes the chelating characteristics of water bodies and unbalances the availability of free ions for aquatic life (Akan et al., 2007). Venkatesh et al. (2008) noted that tannery

wastewater's electrical conductivity was significantly higher than the tolerance limits for industrial effluent released into aquatic bodies.

Apart from being a nuisance to civilization, total suspended solids primarily affect the environment when they settle. The natural fauna, which is a reservoir of aquatic life, is covered by the layer that has formed on the bottom of the watercourse. This may cause a significant reduction in the amount of oxygen present in the bottom waters. Total dissolved solids are mostly generated by calcium, sodium, potassium, carbonates, bicarbonates, chlorides, sulfates, phosphates, nitrogen, and iron (Kannan et al., 2005). Protein, hair, skin, and emulsified fats are taken from the hides during the liming stage of tanning. These materials are then discharged into the effluent, increasing the total dissolved solids (Bhalli and Khan, 2006). The greatest single ingredient group in the effluent is substantial amounts of proteins and their degradation derivatives. They have an impact on the environment, which is quantified by the biological oxygen demand (BOD) and the chemical oxygen demand (COD). BOD is a measurement indicating how effectively organic matter in water can consume oxygen. Organic matter doesn't directly disrupt the aquatic ecosystem by itself, but it does so indirectly by lowering the water's oxygen levels. An important indicator of the quality of the water is the oxygen content, and its reduction stresses the environment. An extreme case would be the ultimate extinction of all natural species in a region due to a complete lack of dissolved oxygen brought on by high BOD. The Chemical Oxygen Demand (COD) is the amount of oxygen required to oxidize the part of organic matter in a sample. It is an important, quickly measured parameter for studies of industrial waste as well as for the management of wastewater treatment facilities. Chromium, salts, dyestuff residues, fat liquoring agents, syntans, and other organic debris are the main post-tanning contaminants, which are commonly measured by COD (Bajza and Vrcek, 2001; UNIDO, 2000). It is the volume of oxygen needed to completely oxidize inorganic material when using a strong chemical oxidant. To assess the level of contamination in the effluent samples, COD is analyzed (Bhalli and Khan, 2006; Awan, 2004). According to Cooman et al. (2002), the COD values in the effluent were discovered to be 12 times higher than the tolerance limits. According to some sources, the COD value of tanneries' combined wastewater ranges from 2000 to 43,000 mg/L (UNEP, 1999; ETPI, 1998; FAO, 1996). Whereas a COD

value of 450 mg/L has been suggested by the NEQS in BDS. Hence, the COD value of untreated effluent from a composite tannery is 5 to 95 times greater than the permitted limits (UNEP, 1999; ETPI, 1998; FAO, 1996).

When sodium chloride (salts) concentrations in streams or lakes reach extremely high levels, it can definitely affect aquatic life in freshwater bodies. Sodium chloride used in the tanning industry has no effect when the effluents are dumped into estuaries or the sea (Chowdhury et al., 2013, 2015). On the other hand, plants are harmed by the high chloride concentrations found in water (Chowdhury et al., 2013, 2015). Removing salt from the wastewater is an economically ineffective method.

Sulfate is one of the most prevalent dissolved anions among those that exist in natural water. Natural surface and ground waters typically contain sulfate. To meet the demands of plants, the normal levels of sulfate are more than considerable. Sulfate is frequently employed as an electron acceptor for the breakdown of organic matter to form  $H_2S$  and causes a rotten egg smell (Welch, 1980).

According to Chowdhury et al. (2013, 2015) Nitrogen is present as a part of the chemical structure of various tannery effluent components. Ammonia (from deliming) and protein-aqueous materials (from liming/unhairing operations) are the most common chemicals. These nitrogen sources provide two particular concerns. First off, while nitrogen is necessary for plants to grow, the high levels released by substances containing nitrogen actively encourage growth. Too much growth of aquatic plants and algae causes blocked streams and decreased flow. An excessively large amount of organic matter needs to be decomposed as the plants die. To decompose organic matter oxygen is necessary. If the load exceeds the river's natural capacity to provide oxygen, vegetation, fish, and aerobic microorganisms die, and ultimately anaerobic conditions arise. Second, nitrogen is released as ammonia as a result of protein breakdown. Bacteria have the ability to transform ammonia to nitrogen gas through a number of processes into the water, which is then released into the atmosphere. Although none of these breakdown products is hazardous, a lot of oxygen is required for the process. If oxygen demand exceeds the amount of oxygen naturally provided by the watercourse, poisonous and anaerobic conditions may quickly arise.

In the leather industry, two types of tanning techniques are usually employed. One is chromium-free vegetable tanning, and another is the most popular chrome tanning, which uses a lot of 33% basic chrome powder and liquor (Sreeram et al., 2003; Islam et al., 2011). In the chrome tanning procedure, the collagen components of the skins combine with chromium to generate complexes that transform into leather. The most popular tanning agents are chromium salts, especially chromium sulfate, and chromium salt-tanned hides have good mechanical resistance (Chowdhury et al., 2013, 2015).

During the chrome tanning process, trivalent chromium is released. Compared to hexavalent chromium, it is substantially less toxic. All living things require the trace element chromium (Cr). It is required for the proper functioning of insulin and the metabolism of fat and glucose (Thacker et al., 2007). Trivalent chromium is difficult to dissolve and 100 times less toxic than hexavalent chromium. Poultry feed manufacturers use materials of tanneries due to the high protein content of the solid wastes e.g., fleshing, raw trimming, chrome shaving, buffing dust, etc. Rafiquallah et al. (2008) showed that poultry feed is made using solid wastes (chrome shaving dust) which contain hexavalent forms of chromium in our country. It seems that during the feed preparation, the transition of trivalent chromium to hexavalent chromium takes place, which poses a serious threat to human health (Javed, 2005). The potency of hexavalent chromium to cause mutations, irritation, and corrosion of the skin and respiratory tract in most microorganisms, as well as lung cancer in humans, has led to its identification as one of the most harmful environmental pollutants (Liu et al., 2005; Bhinde et al., 1996). Around 2% of all effluent is contributed by the chrome tanning process. Digestive tract cancer in people has been linked to long-term exposure to hexavalent chromium salts (2 to 26 years). Regional incidences of stomach cancer have been linked to soils with high levels of chromium. These metals decreased net photosynthesis and reduced the growth of plants (Tripathi, 1996; Chain et al., 1987, Chadderton, 2003).

The beam house, the tanyard, and the post-tanning processes are the sections in which the majority of the wastewater is released. Although gaseous emissions may occur in any section of the tannery, the dry-finishing procedures are the main source of air releases. The main sources of solid waste come from cutting, splitting, and fleshing (Buljan et al., 1994)

Azodyes, Cadmium compounds, Cobalt, Copper, Antimony, Barium, Lead, Selenium, Mercury, Zinc, Arsenic, Polychlorinated Biphenyls (PCB), Nickel, formaldehyde resins, and pesticide residues are some other pollutants related to tannery industry waste. It is critical to analyze the toxic character of such wastewater in order to fully understand its environmental effects and find suitable remediation techniques because tannery effluent comprises a variety of pollutants, including various heavy metals and chlorinated phenols, as previously mentioned. Also, strict rules are in place for the environmental control of pollutants such as heavy metals, whose discharge from tanneries may be subject to legislative limits, such as lead, aluminum, cadmium, and cadmium. These metals have various toxicities depending on the chemical species, which are significantly influenced by the presence of inorganic and organic matter, complex agents, and water pH. The growth of green algae is known to be inhibited by aluminum in particular, and crustaceans are sensitive to low concentrations. The following section discusses the other compounds discovered in tannery effluents:

An anthropogenic activity such as industrial effluent, sewage sludge, fertilizers, and pesticides cause the non-essential trace element cadmium to enter the environment (DWAF, 1996). Strongly cadmium adsorbs sediments and organic matter (Sanders et al., 1999). Cadmium has a variety of adverse physiological impacts on organisms, including reduced growth and harm to embryonic development (Newman and McIntosh, 1991). Cadmium, which is occasionally used in yellow pigments, is regarded to be extremely hazardous. It accumulates over time and affects a variety of organisms repeatedly. It can cause brittle bones if it's in drinking water (Brierley et al., 1986, 1993).

The non-essential trace element is lead. Lead toxicity depends on the organism's life stage, the presence of organic material, and changes in the pH of the water (Hellawell, 1986). In the aquatic environment lead is risky to live in since aquatic species use lead as food, which frequently holds onto roughly 1% of the ingested lead that might be consumed by people through the food chain (Ewers and Schlipkoter, 1991). Lead is considered to be carcinogenic and can harm the neurological system and the kidneys (Radojevic and Bashkin, 1999). Children are especially at risk when exposed to high lead levels. Akhan et al. (2009) stated that the amounts of lead in the wastewater and sediment samples under analysis above the US-EPA's limiting standards of 0.01 mg/L and 40

mg/g, respectively, indicating contamination of river water and potentially posing a risk to aquatic life.

Copper is a common natural metal that is necessary for cellular metabolism but can be extremely poisonous to fish in high concentrations (Grosell et al., 1997). Although copper is essential to human life, excessive amounts can harm the kidneys, liver, and stomach as well as cause anemia (Turnland, 1988). Typically, an acid-base ion exchange or oxidation mechanism is used to remobilize copper (Gomez et al., 2000). Copper consumption over an extended period of time may damage the kidneys and liver (EPA, 1999).

In the human diet, zinc is also a crucial component. Zn deficiency in the diet could be more harmful to human health than excessive consumption of it (ATSDR, 1994). However, for a number of aquatic organisms in aquatic ecosystems, Zn is extremely hazardous. In spite of the fact that Zn is not human carcinogenic, consuming huge dosages can be deadly (ATSDR, 1994). Moreover, zinc acts as the active site for a number of metalloenzymes, making it a necessary micronutrient for all living things (DWAF, 1996). Vomiting, dehydration, abdominal pain, nausea, drowsiness, and dizziness may result from consuming too much zinc (ATSDR, 1994).

### **2.3 Effluent discharge and water pollution**

Rapid and unplanned urbanization, as well as the growth of neighboring industries including the chemical, dye, tannery, and textile industries, are the most obvious causes of surface and groundwater contamination (Chen, 2017; Reza and Singh, 2010; Singh et al., 2005). Because of the intrusion of dangerous chemicals into the industrial areas, the quality of surface and groundwater has significantly deteriorated. Toxic chemicals can severely disrupt biological systems when they accumulate in the environment and food chains (Gupta, 1998). Effluents harm the biological ecosystem of rivers, which actually serve as sinks. Hence, they threaten human health, produce significant environmental hazards, and negatively impact aquatic life (Ahmed and Reazuddin, 2000). Chromium, cadmium, lead, sulfides, ammonia, chlorides, and other salts are among the harmful substances found in industrial effluents, which are released into the air, water, and soil and then enter the food chain. Water (surface and groundwater) can get contaminated

with leather industrial pollutants such as chromium, lead, cadmium, iron, copper, and organic waste that is released from tannery industries (Chen, 2017).

Because of the substantial employment, growth, and export potential of the leather industry, Bangladesh's economy depends on it (Tinni et al., 2014). In addition, it seriously negatively influences the environment by dumping solid waste and liquid effluent into nearby low-lying areas (Tinni et al., 2014). Tanneries and dyeing industries are considered "red category" industries under the Environment Conservation Act, 1995 (Amendment 2010), and are required to set up and maintain an ETP.

Leather industrial effluents are urgently needed for effective treatment because there is a high correlation between chrome tanning and its adverse environmental impacts. Concerns about water quality involve not only the quality of the water itself but also the threat of hazardous compounds spreading to adjacent ecosystems. Hazardous compounds may bioaccumulate in the water-dependent food chain, affecting the aquatic environment for living things (DoE-BD, 1997). The process, of bioaccumulation, may adversely affect water quality and the survival of certain species (Al-Salem et al., 2017; Schwarzenbach et al., 2010; Yadav, 2015). More importantly, the bioaccumulation of metals in edible aquatic species like fish, crabs, and other animals may cause health problems to enter the food chain. Also, this could damage rivers' natural purification system, as well as their water aeration system. Additionally, the process of eutrophication, which occurs when excess nutrients, particularly N and P, are absorbed by water bodies beyond their capacity to act as buffers, results in an increase in species mortality, modifications to species collections, and a loss of the diversity of aquatic flora and fauna (Chowdhury et al., 2013, 2015).

Due to Buriganga's poor condition, which was brought on by the tanneries' discharge of untreated chemical waste into the river, the High Court ordered the government to shift the tanneries from Hazaribagh to Savar in 2001. In Bangladesh, Savar is one of the main industrial areas close to Dhaka. Akter et al., 2019 stated that the Savar-based Dhaka Export Processing Zone (DEPZ) is an industrial area with roughly 86 existing industries (BEPZA, 2006). These industries produce a significant amount of wastewater each day, which they release into the nearby irrigation channels and wetlands, where it eventually

flows into the nearby river. As a result, the Bangladeshi government attempted to move the tanneries from the Hazaribagh to a suggested location outside of Dhaka (Savar, Baliapore) and provided US \$1.4 million in compensation for the move. A study by the Asian Development Bank estimated that US \$18.4 million would be required to construct a region with waste treatment facilities (Roy and Alam, 2012). However, the relocation plan was abandoned for lack of funds. Instead, the government decided to establish a single effluent treatment plant for the roughly 200 tanneries in Hazaribagh with the help of the United Nations Industrial Development Organization (UNIDO). However, such a large treatment facility would pose various problems and would not be a practical method for managing tannery effluents. Hence, an individual treatment plant for each and every tannery industry would have to be installed to save from further environmental degradation of the area. 220 tannery industrial units in Hazaribagh were shut down by the government in April 2017 and shifted to Savar. In the year 2017, the process of transferring tanneries from the city's Hazaribaghto the neighborhood of Savarwas finished. The 200-acre tannery estate's infrastructural installation is now complete. At the Savar tannery estate, about 72 factories have already begun operations; the other facilities are now undergoing construction and will soon be able to begin operations. Now, there are 132 active tannery industries at Savar (Monira et al., 2022, 2023). There were approximately 220 tanneries in Hazaribagh, and each day they discharged 88 tons of solid waste and 21,600 cubic meters of liquid waste, threatening the livelihood of 100,000 people and leading some to believe that the area is on the edge of requiring environmental digesters (DOE, BD) (Bhuiyan et al., 2011; Paul et al., 2013). So, it doesn't take much more time to imagine what the future of the Hemeyetpur and the river Dhaleshwari will be. The relocated tanning industry was restricted from the beginning by numerous infrastructure problems (Karn and Harada, 2001; McArthur et al., 2001; Talukder et al., 2016). In the beginning, the central effluent treatment plant (CETP) remained essentially a pipe dream. When it was finally declared operational, tanners found that it wasn't entirely working. The CEPT in Savar has the ability to treat, if fully functional, 2500 cubic meters of waste, but during this significant religious holidays, the tannery industries create more than double that amount (Ghosh&Hossain, 2019). Furthermore, not all tanneries participate in the CETP. Many researchers stated that

pollution could spread to the nearby Dhaleswari River if such a large wastewater treatment plant is not functioning correctly (Chowdhury, 2010; Saha and Hossain, 2011). A significant industrial region of Dhaka is Savar where, now a vital part of the tannery industry of our country relocated there. In fact, the Savarupazila of Dhaka City's quality scenarios along the nearby rivers may no longer be considered a source of water supply for human consumption (DoE-BD, 2023). We selected the Dhaleshwari River near Savar, Dhaka, for this reason. Previously, untreated and hazardous waste materials from the Hazaribagh tanneries were dumped into the adjacent canals and eventually flowed into the Buriganga River, causing havoc on a densely populated, vast area. The rural community next to the Savar Estate is about to suffer a dreadful experience if the practice continues.

The quality of water can be described by its physicochemical and microbiological characteristics; hence many researchers examined the physicochemical parameters of river water (Sinha, 1986; Trivedi et al., 2009; Sinha et al., 2000; Vinod et al., 2003; Yadav et al., 2011). Leather industrial effluents emitted greater levels of metal, particularly chromium (Ghosh&Hossain, 2019). Because of the accumulation of chromium, these effluents are deposited into groundwater, released into rivers or canals, and both (Ghosh&Hossain, 2019). Tanneries significantly harm the environment. According to survey findings, the presence of a strong odor in the neighborhood had a 45% response rate, and 32% of respondents said there was a lack of fresh water in the area (Tinni et al., 2014). People were using the adjacent river's water, which was contaminated with wastewater and was causing them to get sick. 90% of tannery workers die before the age of 50, and more than 8,000 of them have gastrointestinal, dermatological, and other illnesses (Human Rights Watch, 2012). Heavy metals, hazardous compounds, chlorides, lime with highly dissolved and suspended salts, and other pollutants in wastewater pose serious problems (Uberai, 2003). Around 90% of the final trimming wastes are utilized by local shoemakers, according to Imamul Huq (1998). Tanneries produce wastewater in the range of 30-35 L/Kg skin/hide (Nandy et al., 1999).

Water contamination has terrible impacts not only on people but also animals, birds, and fish. Moreover, treatment of effluents or wastes as well as accidental releases, spills, and leaks of specific agents may result in contamination of soil and groundwater. The

possible risk to human health and the environment from handling, storing, transporting, and packing chemicals should also be taken into consideration in all tanneries. The majority of wastes and effluents are decomposed naturally in the environment, which poses substantial pollution issues for land, water, air, and human life.

## **2.4 Water Quality Indices (*WQI*)**

Several indexing techniques have been developed to provide a clear and more understandable summary of water quality. According to reports, it was an effective method that allowed for the evaluation of the quality of different water samples based on a single arithmetical value rather than the parameter values of each sample, (UNEP-GEMS/Water, 2007; Dade et al., 2013; and Paun et al., 2016). However, Islam and Mostafa (2021) showed that no widely used water quality index model has yet been created. A small number of indexing models were created for groundwater, while maximum *WQIs* were constructed for surface water, particularly for river water. Horton (1965) was the first to deliver an index model that was meticulously established to measure water quality using the 10 most frequently used water parameters. This method was widely utilized and accepted in countries throughout Europe, Asia, and Africa. This method includes calculating the sub-indexes as well as the water quality index (*WQI*) using the arithmetic weighted average technique.

One benefit of this method is that fewer parameters are needed to compare water quality for a variety of uses (Tyagi et al., 2013). After that, this model was modified by Brown et al. (1972). A new water quality index, the Canadian Council of Ministers of Environment Water Quality Index (*CCEM-WQI*), was developed in the middle of the 1990s and may be recognized as the Canadian Water Quality Index (*CWQI*) in 2001 (Khan et al., 2003; Lumb et al., 2011a). Based on the frequency of sample variables, failed variables, and variation from the standard values, the *WQI* was assessed in this model. Eventually, the United Nations Environmental Program approved the *CWQI* model as a suitable methodology for evaluating the quality of drinking water around the world (Sarkar and Abbasi, 2006; Bharti and Katyal, 2011). For the protection of aquatic life, the *CWQI* was then used for the Canadian water quality guidelines (CCME, 2001). This indexing technique has also been used to assess the quality of irrigation water (Majeed, 2018).

Then, by altering some input variables and the number of sample stations and sampling periods, the Canadian *WQI*'s sensitivity test was carried out (CCME, 2006; UNEP-GEMS Water, 2007). In addition to the previously mentioned two techniques, the study area's irrigation water quality was also evaluated using the highly regarded Meireles water quality index (*MWQI*) model (Meireles et al., 2010).

The normalizing dataset of water parameters determines the maximum water quality indexing approach. Parameters are often then weighted according to their apparent importance to complete water quality and the index is calculated as the weighted average of all observations of interest (Pesce and Wunderlin, 2000; Liou et al., 2004; Tsegaye et al., 2006; Lumb et al., 2011a, b). The variations of water quality indices were addressed in literature over the past five decades (Horton, 1965; Brown et al., 1972; Bhargava, 1985; Dunette, 1979; Smith, 1990; Schultz, 2001, Said et al., 2004, Nasirian, 2007; Saeedi et al., 2010; Dade et al., 2013; Majeed, 2018; Banda and Kumarasamy, 2020). There is a crucial need to develop a widely accepted *WQI* model that will be flexible enough to represent drinking or irrigation or both purposes of water suitability for worldwide users. A recent innovation was the use of the index to assess the quality of the water (Sarkar and Abbasi, 2006; Semiromi et al., 2011; Sutadian et al., 2016; Othman, 2019; Mukate et al., 2019; Tripathi, 2019; Zhang et al., 2019; Pham et al., 2010).

#### **2.4.1 Drinking water quality indices**

The presence of heavy metals in the surface and groundwater of Bangladesh has been the subject of numerous studies. Some reporters assessed the excess lead (Pb) in groundwater in the northwest region of the country (Sarkar et al., 2003; Saha and Zaman, 2013; Mostafa et al., 2017). The largest environmental concern for nearly the whole country is increasing concentrations of iron (Fe) in potable and irrigation water (above 5 mg/L), with the exception of coastal areas (Nahar et al., 2014; Islam et al., 2017a; Islam et al., 2017b; Islam and Mostafa, 2021a). In the surface and groundwater of the selected location, greater than recommended amounts of other trace elements, such as manganese (Mn) and arsenic (As), were found (BGS, 2001; Seddique et al., 2004; Islam et al., 2015; Tahera et al., 2016; WB Group, 2019). With the exception of those, the quantity of other trace metals in the nation's surface and groundwater was almost within safe limits

(Hasan et al., 2019; WB Group, 2019). For the evaluation of water quality taking into account trace metal elements, a number of water quality indices have been proposed, including a Single Factor Pollution Index ( $I_t$ ), Compound Pollution Index ( $CPI$ ), Metal Index ( $MI$ ), Heavy Metal Evaluation Index ( $HMEI$ ), Degree of Contamination ( $C_d$ ), and Heavy Metal Pollution Index ( $HMPI$ ) (Bodrud-Doza et al., 2016; Chaturvedi et al., 2019; Rezaei et al., 2019; Islam and Mostafa, 2021a). Several indices were taken into account in this study as supporting evidence for the evaluation of the surface and groundwater's health risk assessment (HRA).

#### **2.4.2 Irrigation water quality indices**

Over 80% of Bangladesh's irrigation water originates from groundwater, although its quality is questionable (Islam and Mostafa, 2022). Some studies assumed that the country's surface and groundwater gradually deteriorated as a consequence of regular industrial discharge, geochemical variation, excessive water use, severe arsenic poisoning, the surface and groundwater's saltwater interface, and the deposition of agrochemicals on the soil (Mondal et al., 2010; Zahid 2015). The quality of irrigation water has improved in the coastal regions, where salinity is a serious issue (Mirza et al., 2012; Islam et al., 2022 a, c; Ahmed et al., 2018; Islam; Mostafa, 2021 b). The main problems in the upper Ganges River basin areas are calcium hardness and excessive trace metal loading in the surface and groundwater (Islam and Mostafa, 2021 b).

Several reports stated that the assessment of irrigation water quality is a difficult process since it depends on the physical and chemical characteristics of the soil, the local climate, the type of irrigation practice, land management, and the variety of plants (Simsek and Gunduz, 2007; Islam and Mostafa, 2021 b). It is very difficult to assess accurately the irrigation or drinking quality of that water through a single index model. Several studies recognized numerous irrigation water quality indices and standards for the proper justification of irrigation water suitability on a global scale (Ayers and Westcot, 1985; Simsek and Gunduz, 2007; Meireles et al., 2010; Ashraf et al., 2011; Bauder et al., 2011; Hussain et al., 2010, 2018; Bozdog, 2016; Arslan, 2017; Zaman et al., 2018). To assess the irrigation water quality in the Simav Plain, Turkey, researchers developed a GIS-based irrigation water quality ( $IWQ$ ) index by combining five geochemical hazards that

are predictable (salinity hazard, permeability hazard, ion toxicity, trace metal toxicity, and miscellaneous) (Simsek and Gunduz, 2007). Meireles et al. (2010) proposed a new approach for evaluating the quality of irrigation water using some water parameters. Ashraf et al. (2011) created an *IWQ* index by computing the Sodium Adsorption Ratio (*SAR*), Saturated Sodium Percentage (*SSP*), and Residual Sodium Carbonate (*RSC*), along with other parameters, using a geographic information system (GIS). Later, Romanelli et al. (2012) in order to determine the suitability of surface and groundwater for agriculture in Argentina's Wet Pampa Plain, the *IWQ* index was combined with measurements of water geochemistry, topographical characteristics, and other factors, including electrical conductivity (EC), hydraulic conductivity, aquifer size, percent sodium (*Na%*), *SSP*, *SAR*, and *RSC*. Hence, working together with GIS, Bozdog (2016) utilized an Analytical Hierarchy Process (AHP) to assess the adequacy of irrigation water in central Anatolia, Turkey. Although each of the several approaches to measuring water quality in irrigated agriculture has some degree of applicability, none is completely sufficient because of the wide variations in agricultural conditions and products. However, those systems use a small number of characteristics and hazard classes, as well as conventional and out-of-date methods for grading, scoring, and weighting the parameters.

Before designing a research project, a systematic review is required because it helps the investigator to investigate advanced research understanding of the subject, identify research gaps for additional exploration, and find research questions based on the findings from multiple prior studies.

# **CHAPTER 3**

## **MATERIALS AND METHODS**

# CHAPTER 3

## MATERIALS AND METHODS

This chapter discusses the materials employed in the current investigation as well as the procedures used to carry out the experimental work. The investigation was conducted using experimental work. The critical components of this research are sample collection, sample preparation, sample characterization, data analysis, and assessment of irrigation and drinking water quality.

At first, the influent and effluent which means treated and untreated effluent were collected, prepared, and analyzed in the laboratory. After that, samples of the groundwater and surface water were collected, processed, and examined in a lab. Water quality standards were used to compare the analysis results. The Water Resource Lab at the Institute of Environmental Science (IES) at the University of Rajshahi in Bangladesh was used as the location for this research. Bangladesh's Central Science Laboratory, University of Rajshahi, BCSIR Lab of Rajshahi, and Dhaka examined a few physicochemical characteristics of the samples. Each experiment was carefully carried out three times using the standard techniques of analysis. Titrimetric, gravimetric, colorimetric, and spectrophotometric techniques were used in the study to characterize the samples. This chapter discusses the materials and methods used in the current study to conduct the experimental work.

### 3.1 Study Area

The study area is located in the recently (2017) shifted tannery industrial zone in Savar Upazila, situated in the northwest part of Dhaka City, Bangladesh. It is located at 23°51'30"N 90°16'00"E / 23.8583°N 90.2667°E / 23.8583; 90.2667. **Table 3.1, Figures 3.2 and 3.3** represent the geographic coordinates, location map, and methodology of the study area.

**Table 3.1 Geographic coordinates of the study area**

| Location                              | Geographic coordinates                      |
|---------------------------------------|---------------------------------------------|
| Influent                              | 23.774945136443336 "N, 90.24008972419973"E  |
| Effluent                              | 23.775054984703193 "N, 90.23925096981657 "E |
| Mixing Point                          | 23.77520285008732 "N, 90.2383024296214 "E   |
| 100m downstream from the mixing point | 23.77562790171136 "N, 90.23841480868357 "E  |
| 500m downstream from the mixing point | 23.776138667555337 "N, 90.23839556382808 "E |
| 1km downstream from the mixing point  | 23.777295732812455 "N, 90.2384967794618 "E  |
| 2km downstream from the mixing point  | 23.778789653289735 "N, 90.23878183044707 "E |

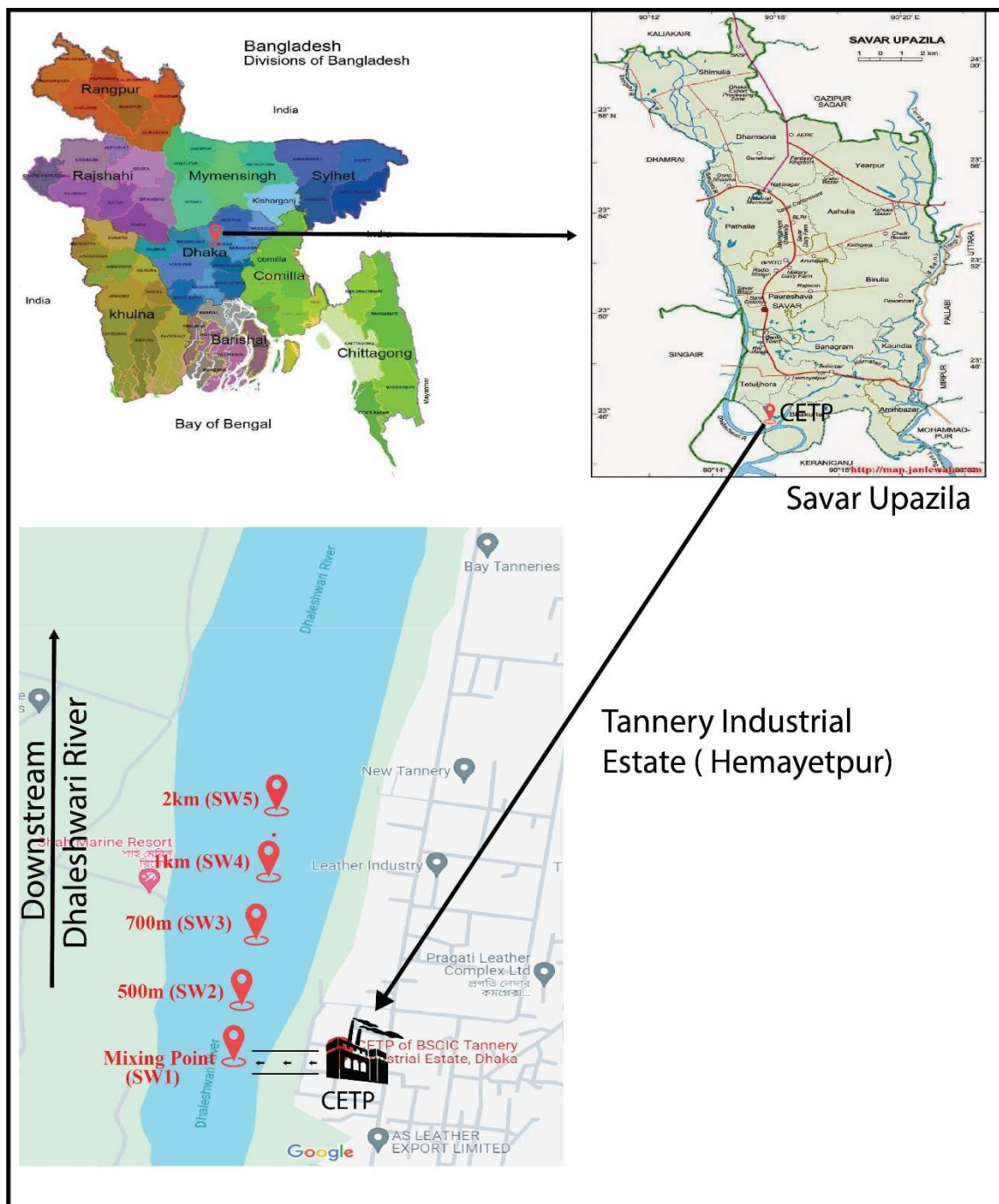


Figure 3.1 Study area and sample location map

### 3.2 Sample collection

The study was conducted from September 2021 to April 2023, and the samples were collected six times (Pre-monsoon, Monsoon, and Post-monsoon) during this period. The sample was collected from the input and output of the CETP and five different sites of the Dhaleshwari River i.e., CETP discharge point (SW1), 100 meters downstream (SW2), 500 meters downstream (SW3), 1km downstream (SW4), and 2km downstream (SW5) of the Dhaleshwari River from the CETP discharge point. Groundwater samples were also collected from the tube wells located inside the CETP plant (GW1), 500 meters downstream (GW2), 700 meters downstream (GW3), 1km downstream (GW4), and 2km downstream (GW5) of the Dhaleshwari River from the CETP discharge areas. The total numbers of influent, effluent, and surface and groundwater samples were 6, 6, 30, and 30 respectively.

Clean plastic bottles were used to collect the samples. The samples were acidified with  $\text{HNO}_3$  and brought to a pH of less than 2 in preparation for trace metal analysis. Samples were carefully labeled, sealed, and transported to the research laboratory and carefully stored in a refrigerator at a temperature of about 4 degrees Celsius until the analyses were completed.

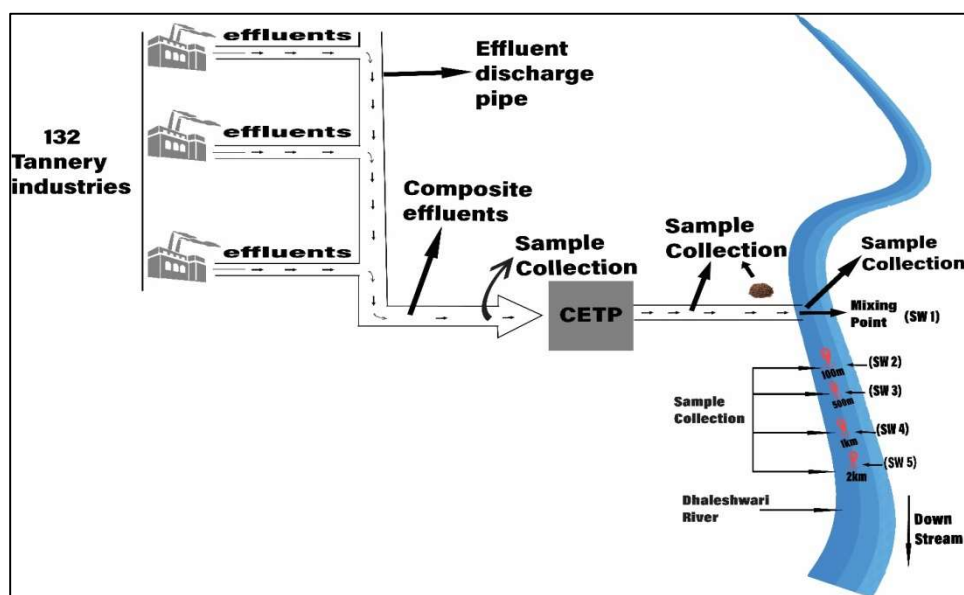


Figure 3.2 The sampling site of the present study

### 3.3 Analytical procedure

The study collected data on various physicochemical parameters, including temperature, pH, Electrical Conductivity (EC), Total Suspended Solids (TSS), Total Dissolved Solids (TDS), Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), turbidity, Dissolved Oxygen (DO), Total Hardness (TH),  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{HCO}_3^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , Fe, Mn, Pb, Cr, Ni, Cd, Cu, and Zn. The portable multi-meters were used to measure the pH, EC, DO, turbidity, and TDS immediately. The titrimetric method was used to assess BOD, COD, calcium ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ), bicarbonate ( $\text{HCO}_3^-$ ), and Total Hardness (TH). A flame photometer was used to determine the amounts of sodium (Na) and potassium (K). The UV spectrophotometer was used to measure the concentrations of chloride ( $\text{Cl}^-$ ), sulfate ( $\text{SO}_4^{2-}$ ), nitrate ( $\text{NO}_3^-$ ), and phosphate ( $\text{PO}_4^{3-}$ ) using the corresponding standard solutions. The accepted approach was used for assessing trace metals, including iron (Fe), manganese (Mn), lead (Pb), chromium (Cr), cobalt (Co), cadmium (Cd), nickel (Ni), copper (Cu), and zinc (Zn), using a Perkin-Elmer Atomic Absorption Spectrophotometer (AAS: Model 3110) (US-APHA, 2005).

The following processes are used to measure all detected water parameters:

### 3.4 Physicochemical Analysis

Various physicochemical parameters, including temperature, EC, turbidity, pH, DO, TDS, BOD, TSS, COD, TH,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{HCO}_3^-$ , Cr, Fe, Mn, Cu, Zn, Ni, Pb, and Cd were taken into consideration. To ensure accuracy and precision, each experiment was performed in triplicate, and all of the substances utilized in this investigation were of analytical quality. Below are descriptions of the analytical techniques.

#### 3.4.1 Temperature, EC, pH, DO, and turbidity

The temperature, EC, pH, DO, and turbidity were measured by a portable thermometer, EC meter (EC-210, HANNA, Italy), pH meter (Adwa AD 110), DO meter (Lutron YK-22DO), and turbidity meter (Lutron TU-2016) respectively, at the sampling sites immediately after sample collection.

### 3.4.2 Total Suspended Solids (TSS)

A Whatman 42 filter paper was first dried for 24 hours at  $103 \pm 2^{\circ}\text{C}$  in an oven, then it was allowed to cool and weighed. The filter paper was then used to filter a 100 mL sample, and it was dried in an oven at  $105^{\circ}\text{C}$  for 24 hours. After cooling, the filter paper was weighed. Up until a constant weight was achieved, the cooling and heating process was repeated.

$$\text{Total Suspended Solids (TSS, mg/L)} = \frac{(M - N) \times 1000000}{V_o}$$

Where,

$M$  = the final weight of the filter paper in grams (after filtration)

$N$  = initial weight of filter paper in grams (before filtration)

$V_o$  = water sample volume (in mL) = 100 mL

### 3.4.3 Total Dissolved Solids (TDS)

First, a 150 mL Pyrex beaker was used, and it was dried in an oven for 24 hours at  $105^{\circ}\text{C}$ . Once that, it was weighed after cooling. The above beaker was filled with 100 mL of sample, which was then filtered through oven-dried Whatman 42 filter paper and evaporated to dry at  $105^{\circ}\text{C}$  for 24 hours. After the beaker was cool down, its weight was noted. As long as a constant weight was achieved, the heating and cooling process was repeated.

$$\text{Total Dissolved Solids (TDS, mg/L)} = \frac{(M - N) \times 1000000}{V_o}$$

Where,

$M$  = final weight of the beaker in grams (after filtering)

$N$  = the initial weight of the beaker in grams (before filtration).

$V_o$  = water sample volume (in mL) = 100 mL

### 3.4.4 Total Hardness (TH)

The EDTA titration method at pH 10 was used to determine the total hardness of water samples. A conical flask was filled with 100 ml of water, 1 ml of ammonia buffer, and 2 drops of the Eriochrome Black T indicator. Standard EDTA solution was used to titrate the solution until the wine-red color turned blue.

$$\text{Total hardness, } \left(\frac{\text{mg}}{\text{L}}\right) = \frac{\text{volume of EDTA (ml)} \times 1000}{\text{volume of sample (ml)}}$$

### 3.4.5 Biological Oxygen Demand (BOD)

The traditional and most popular technique to determine the amount of organic matter in wastewater, surface, and groundwater samples is known as the BOD test. BOD is based on the idea that aerobic biological decomposition (i.e., stabilization of organic waste) by microorganisms will continue as long as there is sufficient oxygen to do so. Since the BOD test is based on an accurate measurement of DO at the start and end of a five-day period during which the sample is kept in dark, incubated conditions (i.e., 20°C or 68°F), it is also referred to as the "BOD" test.

#### Apparatus and Reagent:

1. Glass-stoppered bottles, or BOD bottles
2. BOD incubator with a 20 °C temperature control
3. Phosphate buffer: Prepare a 100 mL solution by dissolving 0.85 g  $\text{KH}_2\text{PO}_4$ , 2.17 g  $\text{K}_2\text{HPO}_4$ , 3.34 g  $\text{Na}_2\text{HPO}_4$ , and 0.17 g  $\text{NH}_4\text{Cl}$  in distilled water.
4. Magnesium sulfate solution: 8.25 g  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ /100 mL
5. For every 100 mL of calcium chloride solution, 2.75g of anhydrous  $\text{CaCl}_2$  is used.
6. Solution of ferric chloride: 0.025g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ /100 mL.

#### Procedure:

- i. Dilution water is produced by 30 minutes of bubbling compressed air in distilled water.
- ii. Mix well 1 cc of each of the following solutions: phosphate buffer,  $\text{MgSO}_4$ ,  $\text{CaCl}_2$ , and  $\text{FeCl}_3$  solution in a liter of dilution water.
- iii. Neutralize the water sample's pH level to 7.
- iv. The sample is mixed with a known volume of dilution water that is high in oxygen because it may not have enough dissolved oxygen to allow biologically degradable organic matter to oxidize.
- v. Conduct the dilution in a big bucket or trough, and stir it well.
- vi. BOD bottles of sets I and II should be filled.
- vii. As soon as possible, measure the dissolved oxygen in the sample bottles of set I.

- viii. After maintaining the bottles in a BOD incubator at 20 C for 5 days, measure the dissolved oxygen content of the sample bottles from Set II.

**Calculation:**

$$BOD, \left( \frac{mg}{L} \right) = (D_0 - D_5) \times \text{dilution factor}$$

Where,

$D_0$  = the sample's dissolved oxygen concentration.

$D_5$  = concentration of dissolved oxygen after five days of incubation.

### 3.4.6 Chemical Oxygen Demand (COD)

The term "Chemical Oxygen Demand" (COD) refers to the volume of oxygen needed for the complete oxidation of oxidizable organic matter by an effective oxidizing agent. Typically, potassium dichromate is used as an oxidizing agent for COD identification in the presence of  $H_2SO_4$ .  $HgSO_4$  and  $Ag_2SO_4$  (catalysts) are used to reflux  $K_2Cr_2O_7$  and concentrate  $H_2SO_4$  into the water sample. Using ferroin as an indicator, the remaining dichromate is titrated back with a standard solution of ferrous ammonium sulfate.

**Reagents:**

- 6.125g of dry  $K_2Cr_2O_7$  was dissolved in distilled water to make 500 ml or 0.25 N  $K_2Cr_2O_7$
- Standard  $K_2Cr_2O_7$  solution was used to standardize the 0.1N ferrous ammonium sulfate solution.
- 1.485 grams of 1,10-phenanthroline and 0.695 grams of ferrous sulfate were dissolved in distilled water and diluted to form a 100 ml solution for the ferroin indicator.
- $H_2SO_4$  in concentrated form (1.84 sp. gr.).
- $HgSO_4$  with  $Ag_2SO_4$  in solid form.

**Procedure:**

- 20 mL of the water sample should be added to a 250 mL round-bottom flask with a ground glass junction for attaching a reflux condenser.
- Add 20 mL of  $H_2SO_4$ , 10 mL of 0.25 N  $K_2Cr_2O_7$ , a small amount of  $HgSO_4$ , and  $Ag_2SO_4$ . 2-3 hours of reflux.

- (iii) Using ferroin as an indicator, cool, dilute, and titrate with 0.1N ferrous ammonium sulfate solution until the color changes from blue to red.
- (iv) Also, run a blank.

**Calculation:**

$$COD, (mg/L) = \frac{(M - N) \times X \times 1000 \times 8}{V_o}$$

Where,

$M$  = Volume (mL) of ferrous ammonium sulfate for the blank

$N$  = Volume (mL) of ferrous ammonium sulfate for the sample

$X$  = normality of the used ferrous ammonium sulfate

$V_o$  = volume (mL) of the sample taken

### 3.4.7 Chloride ion (Cl<sup>-</sup>)

Using the AgNO<sub>3</sub> titration method, the chloride ion (Cl<sup>-</sup>) in the samples was identified as follows:

**Reagents:** 0.0141N AgNO<sub>3</sub> and K<sub>2</sub>CrO<sub>4</sub> indicator.

**Preparation of 5% K<sub>2</sub>CrO<sub>4</sub> indicator:** 50 mL of distilled water was added to 5g of K<sub>2</sub>CrO<sub>4</sub> in a 100 mL volumetric flask to dissolve it. Then, 0.0141N AgNO<sub>3</sub> was gradually added to the volumetric flask containing K<sub>2</sub>CrO<sub>4</sub> until the first permanent red precipitate appeared. The solution was filtered, gradually diluted with distilled water, and then brought up to the mark.

**Preparation of 0.0141N AgNO<sub>3</sub>:** Weighing out 2.397g of AgNO<sub>3</sub>, transferring it to a 1000 mL volumetric flask, and gradually adding distilled water to the required level. The solution was 0.0141 N as a consequence. The prepared solution was standardized against the NaCl. Reagent-grade the NaCl was carefully dried overnight and then, cooled at room temperature. NaCl fragments of 0.25 g each were weighed into Erlenmeyer flasks, and distilled water was used to dissolve the salt. Finally, distilled water was used to dilute it to the 100 mL mark. Small amounts of NaHCO<sub>3</sub> were added to the solutions until the bubbling stopped in order to change the pH. After adding around 2 mL of K<sub>2</sub>CrO<sub>4</sub>, the mixture was titrated until the first K<sub>2</sub>CrO<sub>4</sub> red appeared permanently.

**Procedure:**

A 250 mL conical flask was initially filled with 100 mL of filtered sample. The flask was filled with 1 mL of  $K_2CrO_4$  indicator, and it was gently shaken. The solution was gradually diluted with distilled water and then brought up to the mark. After that, the sample was titrated with 0.0141 N  $AgNO_3$  until the brick red, color occurred. It was noted the quantity of 0.0141N  $AgNO_3$  was utilized for titration.

**Calculation:**

$$Chloride (Cl^-, mg/L) = \frac{(M \times N)}{V_o} \times 35450$$

Where,

$M$  = 0.0141N  $AgNO_3$  in mL from a burette was used for titration

$N$  =  $AgNO_3$  normality = 0.0141N

$V_o$  = the volume of the water sample taken = 100 mL.

**3.4.8 Sulfate ion ( $SO_4^{2-}$ )**

In order to measure the sulfate ion ( $SO_4^{2-}$ ) in the samples, a UV spectrophotometric method was used.

**Apparatus:** UV-Spectrophotometer (wavelength at 420 nm silt).

**Reagent:**

**Buffer solution:** In a 1000 mL volumetric flask, the buffer solution was made by adding approximately 30g of  $MgCl_2 \cdot 6H_2O$ , 5g of sodium acetate ( $CH_3COONa \cdot 3H_2O$ ), 0.111g of sodium sulfate ( $Na_2SO_4$ ), and 20 mL of acetic acid. It was then well shaken and dissolved in the distilled water. With distilled water, it was finally brought up to the mark.

**Barium chloride:** To create homogeneous turbidity, 20 to 30 meshes of  $BaCl_2$  crystal were used.

**Standard sulfate solution:** The standard sulfate solution was made by measuring out approximately 0.1479g of anhydrous  $Na_2SO_4$  and transferring it into a volumetric flask with a 1000 mL capacity. Then it was thoroughly shaken while being dissolved in distilled water. Finally, distilled water was used to bring it up to the required level, with 1 mL equaling 100 g of sulfate ( $SO_4^{2-}$ ).

**Procedure:**

**Formation of barium sulfate turbidity:** In a 250 mL Erlenmeyer flask, 100 mL of sample was collected, and 20 mL of buffer solution was added and stirred. A teaspoon of  $\text{BaCl}_2$  crystals was added at the time of stirring, and the mixture was stirred for 1 minute. With distilled water, it was finally brought up to the mark.

**Measurement of turbidity:** Within five minutes of pouring the solution into the absorption cell after stirring, the turbidity was measured.

**Preparation of standard curve:** In five separate 1000 mL volumetric flasks,  $\text{Na}_2\text{SO}_4$  solutions in proportions of 2, 4, 6, 8, and 10 mg/L were collected. Distilled water was then gradually added, carefully shaken, and made up to the mark with distilled water. Using a UV Spectrophotometer, the absorbance of the water samples was determined. The absorbance against the concentration was plotted to create a standard curve.

**Calculation:**

Sulfate ( $\text{SO}_4^{2-}$ , in mg/L) = from the standard curve  $\text{SO}_4^{2-}$  concentration in mg/L  $\times$  dilution factor.

**3.4.9 Nitrate nitrogen ( $\text{NO}_3^-$ )**

In order to measure the nitrate ion ( $\text{NO}_3^-$ ) in the samples, a UV spectrophotometric method was used.

**Apparatus:** UV-Spectrophotometer (wavelength at 220 and 275 nm silt) with matching 1 cm silica cells.

**Reagents:**

**Nitrate-free water:** All solutions and dilutions were made with double-distilled water.

**Stock nitrate solution:** For 24 hours, potassium nitrate ( $\text{KNO}_3$ ) was dried in an oven at  $105^\circ\text{C}$ . Weighting out 0.7218 g of  $\text{KNO}_3$ , it was then transferred to a 1000 mL volumetric flask and gradually filled with distilled water, where 1 mL = 100 g of  $\text{NO}_3^-$ -N.

**Intermediate nitrate solution:** In a 1000 mL volumetric flask, 100 mL of stock nitrate solution was introduced. Distilled water was then gradually added until the volume reached the mark where 1 mL equaled 10 g  $\text{NO}_3^-$ -N. To keep the solution stable for at least six months, 2 mL  $\text{CHCl}_3$  was employed per solution.

**1N Hydrochloric acid (HCl) solution:** Concentrated HCl in the amount of 83 mL was measured, transferred to a 1000 mL volumetric flask, and then gradually filled to the mark with distilled water.

**Procedure:**

**Treatment of sample:** 50 mL of clear sample was carefully mixed with 1 mL of 1 N HCl solution before filtering.

**Preparation of standard curve:** In three separate 1000 mL volumetric flasks, the proportions of 0.50, 1.0, and 2.0 mL intermediate nitrate solutions were taken, and distilled water was gradually added while being vigorously shaken until the required quantity was reached by distilled water. With the use of a UV Spectrophotometer, the absorbance of the water samples was assessed. The absorbance against the concentration was plotted to create a standard curve

**Spectrophotometric measurement:** The absorbance was measured against the zero absorbance set for distilled water.  $\text{NO}_3^-$ -N readings were obtained using a 220 nm wavelength and interference from dissolved organic matter was assessed using a 275 nm wavelength.

**Calculation:**

Two wavelengths, 275 and 220 nm, of a UV-Spectrophotometer were used to estimate  $\text{NO}_3^-$ -N. Both samples and standard solutions had their absorbance measured at two different wavelengths. For each sample and standard solution, the reading at 275 nm was subtracted from the reading at 220 nm.

$$\text{Nitrate} - \text{Nitrogen (NO}_3^- \text{ - N mg/L)} = \frac{\text{NO}_3 (\mu\text{g}) - \text{N from the standard curve}}{\text{Volume Vo(mL) of the sample taken}}$$

$$\text{Nitrate N-NO}_3^- \text{ (mg/L)} = (\text{NO}_3^- \text{-N}) \times (4.429)$$

### **3.4.10 Phosphate ( $\text{PO}_4^{3-}$ )**

To measure the phosphate ion ( $\text{PO}_4^{3-}$ ) in the samples, a UV spectrophotometric method was used

**Reagent:**

**Ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ) solution:** 20 mL of pure  $\text{HNO}_3$  was introduced to a 1000 mL volumetric flask that contained 2.5 g of sample. After filtration, the mixture was diluted with distilled water to bring it up to the required mark.

**Ammonium heptamolibdate solution:**

A 100 mL volumetric flask containing 5g of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  was filled to the required level with distilled water.

**Sulfuric Acid:** The prepared 1:6  $\text{H}_2\text{SO}_4$  was stored in a glass bottle.

**Standard phosphate solution:** Approximately 0.4391g  $\text{KH}_2\text{PO}_4$  was taken in a clean 100 mL volumetric flask. Then dissolved it in distilled water through continuous shaking and finally made up to the mark by using distilled water. 10 mL of this prepared solution was carefully transferred to a clean 100 mL volumetric flask and finally made up to the mark with distilled water (Appendix II).

Here, 1 (mL) solution = 100 mg  $\text{PO}_4^{3-}$ .

**Standard curve:**

In five different 100 mL volumetric flasks, portions of 0.5, 1, 2, 4, and 8 mL intermediate phosphate solutions were collected. The flasks were gradually filled with distilled water, carefully agitated, and then filled to the proper level. In a 50 mL volumetric flask, 2 mL of the reference sample, 5 mL of  $\text{NH}_4\text{VO}_3$ , 5 mL of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  solution, and 5 mL of  $\text{H}_2\text{SO}_4$  were added. The absorbance was measured against previously set zero absorbance distilled water. The absorbance of  $\text{PO}_4^{3-}$  ions was measured at a wavelength of 450 nm. The absorbance against the concentration was plotted to create a standard curve

**Calculation:**

Phosphate ( $\text{PO}_4^{3-}$ ) in mg/L = from the standard curve the concentration of  $\text{PO}_4^{3-}$  (mg/L)  $\times$  dilution factor.

**3.4.11 Bicarbonate ion ( $\text{HCO}_3^-$ )**

Using the titration method, which is detailed below, the bicarbonate ion ( $\text{HCO}_3^-$ ) in the samples, was determined.

**Reagents:** Phenolphthalein indicator, 0.1N HCl, and methyl orange indicator.

**Procedure:**

Two drops of methyl orange indicator were applied to the sample and progressively shaken in a 250 mL conical flask and then gradually filled to the mark with distilled water. The sample was then titrated with 0.1N HCl until the endpoint was reached (color

turned orange). The amount of acid (mL) from the burette used for the titration was recorded.

**Calculation:**

$$\text{Bicarbonate ion (HCO}_3^-), \text{ in mg/L} = \left( \frac{M \times N \times 1000 \times 50}{V_o} \right)$$

Where,

$M$  = HCl (mL) used for titration

$N$  = 0.1N HCl = normality of HCl

$V_o$  = 100 mL = volume of the water sample

### 3.4.12 Sodium ion (Na<sup>+</sup>)

The atomic absorption method, which is explained as follows, is used for determining the sodium ion in wastewater, surface water, and groundwater samples.

**Apparatus:** AAS (wavelength at 330.2 nm with 0.7 nm slit).

**Reagent:**

**1000 mg/L standard solution:** The exact amount of 2.540 g of analytically pure 99% sodium chloride was placed in a 1000 ml volumetric flask, to which distilled water was slowly added while being thoroughly shaken, to produce the standard solution of sodium ion.

**Suppressing agents:**

**0.1% potassium:** In a 100 ml volumetric flask, 0.52 g of potassium chloride was dissolved, and the required volume was slowly filled with distilled water. Then, 100 ml of potassium ion solution was diluted with 1000 ml of distilled water to produce the final concentration of 0.1% potassium. To reduce the percentage of relative standard deviation (RDS), two drops of a 0.1% potassium solution were added to each standard and sample.

**Procedure:**

**Sample preparation:** 2 ml concentrated HNO<sub>3</sub> and 3 ml concentrated HCl were introduced to a 100 ml sample of water in a beaker. The beaker was heated on a hot plate at 90 to 95°C until the water level reached 10 to 15 ml. As soon as that was done, it was taken off the hot plate and left to cool. After that, samples were filtered through a membrane filter with a 0.45 micrometer pore size. Finally, distilled water was added to

bring the volume up to 100 ml. The preparation of the samples for K, Fe, Cu, Zn, Mn, Pb, Cr, and Cd followed the same procedure.

**Standard curve:** In four separate 1000 ml volumetric flasks, the ratios of 2, 5, 8, and 10 ml sodium ion-containing standard solution were collected. Distilled water was then gradually added, properly shaken, and then made up to the required level. An AAS was used to calculate the water samples' absorbance. The absorbance against the concentration was plotted to create a standard curve.

**Calculation:** Sodium (Na) in mg/L = from the standard curve the concentration of sodium (Na) in mg/L  $\times$  dilution factor

### 3.4.13 Potassium ion ( $K^+$ )

The atomic absorption method, which is explained as follows, is used for determining the potassium ion in wastewater, surface water, and groundwater samples.

**Apparatus:** AAS (wavelength at 766.49 nm with 0.7 nm slit).

**Reagent:**

**1000 mg/L standard solution:** The exact amount of 1.91 g of analytically pure 99% potassium chloride was placed in a 1000 ml volumetric flask, to which distilled water was slowly added while being thoroughly shaken, to produce the standard solution of potassium ion.

**Suppressing agent:**

**0.1% potassium:** In a 100 ml volumetric flask, 0.1 g of potassium chloride was dissolved, and the required volume was slowly filled with distilled water. The final concentration of 0.1% potassium was then obtained by diluting 100 ml of a 1% potassium ion solution with 1000 ml of distilled water. To reduce the percentage of relative standard deviation (RDS), two drops of a 0.1% potassium solution were added to each standard and sample.

**Sample preparation:** As mentioned in section 3.5.13

**Standard curve:** In four separate 1000 ml volumetric flasks, the ratios of 2, 5, 8, and 10 ml potassium ion-containing standard solution were collected. Distilled water was then gradually added, properly shaken, and then made up to the required level. An AAS was used to calculate the water samples' absorbance. The absorbance against the concentration was plotted to create a standard curve.

**Calculation:** Potassium (K) in mg/L = from the standard curve the concentration of potassium (K) in mg/L  $\times$  dilution factor.

### 3.4.14 Calcium ion ( $\text{Ca}^{2+}$ )

**Method:** Calcium hardness or EDTA titrimetric method

**Instrument:** Titrating apparatus

**Reagents:** i) 37.225 g EDTA + 1000 ml DW in 0.01 (M) EDTA solution

ii) 40g NaOH + 1000 ml DW for 1 N NaOH

iii) Murexide indicator: 100 ml ethylene glycol and 150 mg Murexide.

**Procedure:** A 25 ml sample was taken to titrate a 0.01 (M) EDTA solution by adding 1 ml of a 1 (N) NaOH solution and 1 drop of a Murexide indicator. The endpoint changed from pink to purple.

$$\text{Ca hardness } \left(\frac{\text{mg}}{\text{L}}\right) = \frac{M \times N \times 1000}{V_o}$$

Where,  $M$  = Volume of EDTA (mL)

$N$  = 1ml of EDTA contains milligrams of  $\text{CaCO}_3$

$V_o$  = (mL) of sample

Ca in the sample (mg/L) = (0.4) (calcium hardness)

### 3.4.15 Magnesium ion ( $\text{Mg}^{2+}$ )

**Method:** EDTA titrimetric procedure

**Instrument:** Titrating apparatus

**Reagents:** i) EBT indicator ii) 1 (N) NaOH iii) 0.01 (M) EDTA iv) Murexide indicator

**Procedure:** i) Total hardness was assessed using a 25 ml sample and 0.01 (M) EDTA and EBT indicator

ii) Utilizing 0.01 (M) EDTA and Murexide as indicators, calcium hardness was determined as described above

iii) The basic of two titre values was used to determine the amount of Mg as

Magnesium hardness (mg/L) = (Total hardness – Calcium hardness)

The concentration of Magnesium (mg/L) = (Mg hardness)  $\times$  (0.244)

### 3.4.16 Iron (Fe)

**Apparatus:** AAS (wavelength at 248.3 nm with 0.7 nm slit).

**Reagent:**

The exact amount of 4.980 g of analytically pure (99%)  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was placed in a 1000 mL volumetric flask. Distilled water was then gently added while the mixture was shaken, and finally made the desired level of distilled water.

**Sample preparation:** As mentioned in section 3.5.13

**Standard curve:**

In three separate 1000 ml volumetric flasks, the ratios of 0.5, 1.0, and 2.0 mL Fe ion - containing standard solution were collected. Distilled water was then gradually added, properly shaken, and then made up to the required level. An AAS was used to calculate the water samples' absorbance. The absorbance against the concentration was plotted to create a standard curve (Appendix II).

**Calculation:**

Iron (Fe), in mg/L = from the standard curve the concentration of Fe (mg/L)  $\times$  dilution factor.

**3.4.17 Copper (Cu)**

**Apparatus:** AAS (wavelength at 324.75 nm with 0.7 nm slit).

**Reagent:**

The exact amount of 3.93 g of analytically pure (99%)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  was placed in a 1000 mL volumetric flask. Distilled water was then gently added while the mixture was shaken, and finally made the desired level of distilled water.

**Sample preparation:** As mentioned in section 3.5.13.

**Standard curve:**

In three separate 1000 ml volumetric flasks, the ratios of 0.5, 1.0, and 2.0 mL Cu ion - containing standard solution were collected. Distilled water was then gradually added, properly shaken, and then made up to the required level. An AAS was used to calculate the water samples' absorbance. The absorbance against the concentration was plotted to create a standard curve (Appendix II).

**Calculation**

Copper (Cu), in mg/L = from the standard curve the concentration of Cu (mg/L)  $\times$  dilution factor.

### 3.4.18 Zinc (Zn)

**Apparatus:** AAS (wavelength at 213.86 nm with 0.7 nm slit).

**Reagent:**

The exact amount of 4.980 g of analytically pure (99%)  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  was placed in a 1000 mL volumetric flask. Distilled water was then gently added while the mixture was shaken, and finally made the desired level of distilled water.

**Sample preparation:** As mentioned in section 3.5.13.

**Standard curve:**

In three separate 1000 ml volumetric flasks, the ratios of 0.1, 0.2, and 0.4, mL Zn ion - containing standard solution were collected. Distilled water was then gradually added, properly shaken, and then made up to the required level. An AAS was used to calculate the water samples' absorbance. The absorbance against the concentration was plotted to create a standard curve (Appendix II).

**Calculation:**

Zinc (Zn), in mg/L = from the standard curve the concentration of Zn (mg/L)  $\times$  dilution factor.

### 3.4.19 Manganese (Mn)

**Apparatus:** AAS (wavelength at 279.48 nm with 0.2 nm slit).

**Reagent:**

The exact amount of 3.070 g of analytically pure (99%)  $\text{MnSO}_4 \cdot 10\text{H}_2\text{O}$  was placed in a 1000 mL volumetric flask. Distilled water was then gently added while the mixture was shaken, and finally made the desired level of distilled water.

**Suppressing agent:**

To produce the 2% calcium solution, 3 mL of 1M HCl was added to exactly 2 g of  $\text{CaCO}_3$  in a 100 mL volumetric flask. Distilled water was then gently added while the mixture was shaken, and finally made the desired level of distilled water. Then, in order to attain the final concentration of 0.2%  $\text{CaCO}_3$ , 10 mL of the 2%  $\text{CaCO}_3$  solution was diluted to 100 mL with distilled water. Every standard and sample maintenance were carried out using this solution.

**Sample preparation:** As mentioned in section 3.5.13.

**Standard curve:**

In three separate 1000 ml volumetric flasks, the ratios of 1.0, 3.0, and 5.0 mL Mn ion - containing standard solution were collected. Distilled water was then gradually added, properly shaken, and then made up to the required level. An AAS was used to calculate the water samples' absorbance. The absorbance against the concentration was plotted to create a standard curve (Appendix II).

**Calculation:**

Manganese (Mn), in mg/L = from the standard curve the concentration of Mn (mg/L)  $\times$  dilution factor.

**3.4.20 Lead (Pb)**

**Apparatus:** AAS (wavelength at 283.31 nm with 0.7 nm slit).

**Reagent:**

The exact amount of 1.599 g of analytically pure (99%) Pb (NO<sub>3</sub>)<sub>2</sub> was placed in a 1000 mL volumetric flask. Distilled water was then gently added while the mixture was shaken, and finally made the desired level of distilled water.

**Sample preparation:** As mentioned in section 3.5.13.

**Standard curve:**

In three separate 1000 ml volumetric flasks, the ratios of 2.5, 5, and 10 mL Pb ion - containing standard solution were collected. Distilled water was then gradually added, properly shaken, and then made up to the required level. An AAS was used to calculate the water samples' absorbance. The absorbance against the concentration was plotted to create a standard curve (Appendix II).

**D. Calculation**

Lead (Pb), in mg/L = from the standard curve the concentration of Pb (mg/L)  $\times$  dilution factor.

**3.4.21 Chromium (Cr)**

**Apparatus:** AAS (wavelength at 248.3 nm with 0.7 nm slit).

**Reagents:****(i) Standard solution (1000 mg/L)**

The exact amount of 2.8290 g of analytically pure potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) was placed in a 1000 mL volumetric flask to produce the standard solution for chromium ion.

Then 5 ml of sulfuric acid was added to it, then distilled was added gradually, shaken well, and then made up to the required level with distilled water.

**(ii) Standard solution for chromium containing 10 mg/L of chromium**

A 1000 ml volumetric flask was filled with 10 ml of the chromium stock solution using a pipette. Nitric acid (20 ml) was added, then water (to the mark), and proper mixing was done.

**(iii) Chromium standard solution (corresponding to 0.4 mg/L of chromium)**

Using a pipette, 20 ml of the chromium standard solution was transferred into a 500 ml volumetric flask. Nitric acid (10 ml) was added, then water (to the mark), and thorough mixing was performed to make the solution.

**Sample preparation:** As mentioned in section 3.5.13.

**Standard curve:**

In three separate 1000 ml volumetric flasks, the ratios of 0.5, 1.0, and 2.0 mL Cr - containing standard solution were collected. Distilled water was then gradually added, properly shaken, and then made up to the required level. An AAS was used to calculate the water samples' absorbance. The absorbance against the concentration was plotted to create a standard curve (Appendix II).

**Calculation:**

Chromium (Cr), in mg/L = from the standard curve the concentration of Cr (mg/L) × dilution factor.

### **3.4.22 Cadmium (Cd)**

**Apparatus:** AAS (wavelength at 228.80 nm with 0.7 nm slit).

**Reagent:**

The exact amount of 2.282 g of analytically pure (99%)  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$  was placed in a 1000 mL volumetric flask. Distilled water was then gently added while the mixture was shaken, and finally made the desired level of distilled water.

**Sample preparation:** As mentioned in section 3.5.13.

**Standard curve:**

In three separate 1000 ml volumetric flasks, the ratios of 0.1, 0.2, and 0.4 mL Cd - containing standard solution were collected. Distilled water was then gradually added, properly shaken, and then made up to the required level. An AAS was used to calculate

the water samples' absorbance. The absorbance against the concentration was plotted to create a standard curve (Appendix II).

**Calculation:**

Cadmium (Cd), in mg/L = from the standard curve the concentration of Cd (mg/L) × dilution factor.

### **3.4.23 FTIR analysis**

The samples' organic functional groups were identified using FTIR analysis. This study made use of a PerkinElmer Spectrum 100 FTIR Spectrometer.

### **3.4.24 Sediments Collection**

For the assessment of sediment quality, surface sediments are most commonly collected. Generally, 1 kg of sediment should be sufficient for analyses of most contaminants. All samples should be stored using equipment and techniques appropriate for the desired analysis (US-EPA, 2001). Sample containers and sampling devices should be cleaned thoroughly before use by soaking plastic containers and devices in 10% nitric acid (for metals) or rinsing glass containers or devices with acetone for organics (ASTM, 2008; US-EPA, 2001). Before sample retrieval, and between each sampling event, the outside of the sampling device should be rinsed clean with water from the sampling station. For some assessments, more rigorous between samples cleaning of the sampler might be required.

## **3.5 Evolution of irrigation water quality**

Originally in Germany in 1848, measurements of water quality levels were kept according to the level of contamination (Lumb et al., 2011a, b). Since then, more than a hundred water quality indexing models with local and global bases have been discovered. Here, five (5) different *WQI* methods—Canadian *WQI* (*CWQI*), Weighted Average *WQI* (*WWQI*), and Meireles *WQI* (*MWQI*), Irrigation Water Quality Index (*IWQI*), Nemerow's Pollution Index (*NPI*) —were used for the chosen parameters of water quality in order to facilitate the analysis of the datasets. Here are three research papers that helped choose the models mentioned above: (Meireles et al., 2010, Lumb et al., 2011a, b; and Banda and Kumarasamy, 2020. These indexing models are discussed below:

### **3.5.1 Water Quality Index (*WQI*)**

A useful method for communicating water quality data is the water quality index (*WQI*) (Islam and Mostafa, 2021b). One of the best methods for determining the level of water pollution is the water quality index (*WQI*), which is universally recognized and used (Islam and Mostafa, 2021c; Alobaidy et al., 2010; Shakil and Mostafa, 2021b; Lumb et al., 2011). *WQI*, a unit less 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 and Mostafa, 2021c; Rai et al., 2012).

### 3.5.1.1 Canadian Council of Ministers of the Environment (CCME)

The Canadian Council of Ministers of the Environment (CCME) Water Quality Index (*WQI*) was used to assess the water quality in the study area. A total of twenty-two (22) water quality parameters (Temperature, pH, DO, EC, TSS, TDS, BOD, COD,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ -N,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , Ni, Fe, Cu, Zn, Mn, Pb, Cr, and Cd) were considered to calculate the *WQI* score of surface water because turbidity,  $\text{PO}_4^{3-}$ , total hardness,  $\text{HCO}_3^-$ , and  $\text{Mg}^{2+}$  have no surface water standard in Bangladesh.

The CCME *WQI* comprises three factors to calculate i.e., Scope (*F1*), frequency (*F2*), and amplitude (*F3*) (CCME, 1999). *F1* is the percentage of parameters (failed parameters) that did not achieve their goals at least once throughout the period (Equation 1). *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 below:

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

Where,

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

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

$$\text{Amplitude } F3 = \frac{nse}{0.01nse + 0.01} \quad (4)$$

$$\text{Normalized Sum of Excursions (nse)} = \frac{\sum \text{Excursion}}{\text{total number of tests}} \quad (5)$$

$$\text{excursion} = \frac{\text{failed tests test}}{\text{standard value}} - 1 \quad (6)$$

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).

### 3.5.1.2 Weight Average Water Quality Index (*WWQI*)

Equation 9 was used to obtain the index value of the weighted average *WQI* technique. The weighted arithmetic/average *WQI* approach, proposed by Horton (1965), was used to calculate the *WWQI*. It was then developed by Brown et al., 1970 and Cude, 2007. With the following three equations (Equations (7) – (9)), water quality parameters are multiplied by a weighting factor and merged simply:

$$Wi = \frac{K}{Si} = \frac{1}{\sum(\frac{1}{Si})} \div Si \quad (7)$$

$$Qi = \frac{(Vn - Vo)}{(Si - Vo)} \times 100 \quad (8)$$

$$WWQI = \sum_{i=1}^n \frac{Wi Qi}{\sum_{i=1}^n Wi} \quad (9)$$

Where  $V_n$  is the experience value of the parameter,  $V_o$  is the ideal value of the parameter, and  $S_i$  is the standard value of the  $i^{th}$  parameter.  $W_i$  is the unit weightage of the  $i^{th}$  parameter.  $Q_i$  is the  $i^{th}$  parameter's sub-index. The ideal value for pH = 7, DO = 14.6 mg/L, and other parameters, is generally equal to zero for most parameters (Tripaty & Sahu, 2005; Chowdhury et al., 2012).

That is,

$$QpH = \frac{(VpH - 7)}{8.5 - 7} \times 100 \quad (10)$$

Each parameter's weighting unit ( $W_i$ ) produced a value that is inversely proportionate to the World Health Organization standard ( $S_i$ ) (WHO, 2011).

This index value was calculated using a simple Excel tool. **Tables 4.7, 4.8, 4.9, and 4.10** include the average observed value ( $V_n$ ). 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, the Equation (9) is used to determine the final index (*WWQI*).

### 3.5.1.3 Meireles Water Quality Index (*MWQI*)

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.

The Sodium Adsorption Ratio (*SAR*), EC,  $Na^+$ ,  $Cl^-$ , and  $HCO_3^-$  were five parameters that were specified in this approach.

It was recognized that accumulated weights ( $w_i$ ) and water quality measurement limitations ( $Q_i$ ) were classified. The parameters for irrigation water quality recommended by the UCCC (1974) and Ayers & Westcot (1985) were taken into consideration while determining the values of  $Q_i$ , which are listed in **Table 3.2**.

**Table 3.2 Parameter limiting values for quality measurement ( $q_i$ ) calculation**

| $Q_i$                     | SAR<br>(mEq/L) <sup>1/2</sup> | Cl <sup>-</sup> (mEq/L) | HCO <sub>3</sub> <sup>-</sup><br>(mEq/L)          | Na <sup>+</sup><br>(mEq/L) | EC (ds cm <sup>-1</sup> )   |
|---------------------------|-------------------------------|-------------------------|---------------------------------------------------|----------------------------|-----------------------------|
| 85-100 or<br>85 ≤ 100     | 2 ≤ SAR < 3                   | 1 ≤ Cl < 4              | 1 ≤<br>HCO <sub>3</sub> < 1.5                     | 2 ≤ Na < 3                 | 0.20 ≤ EC<br>< 0.75         |
| 60-85 or<br>60 ≤ 85       | 3 ≤ SAR < 6                   | 4 ≤ Cl < 7              | 1.5 ≤<br>HCO <sub>3</sub> < 4.5                   | 3 ≤ Na < 6                 | 0.75 ≤ EC<br>< 1.5          |
| 35-60 or<br>35 ≤ 60       | 6 ≤ SAR < 12                  | 7 ≤ Cl < 10             | 4.5 ≤<br>HCO <sub>3</sub> < 8.5                   | 6 ≤ Na < 9                 | 1.5 ≤ EC <<br>3.0           |
| 0-35 or<br>0 ≤ 35         | SAR ≥ 12 or<br>SAR < 2        | Cl ≥ 10 or<br>Cl < 1    | HCO <sub>3</sub> < 1 or<br>HCO <sub>3</sub> ≥ 8.5 | Na < 2 or<br>Na ≥ 9        | EC < 0.20<br>or<br>EC ≥ 3.0 |
| Weight value<br>( $w_i$ ) | 0.189                         | 0.194                   | 0.202                                             | 0.204                      | 0.211                       |

According to Richards (1968), the  $SAR$  value of the water sample calculates the relative proportion of Na<sup>+</sup> to Ca<sup>2+</sup> and Mg<sup>2+</sup>.  $SAR$  was determined by the following equation:

$$SAR = \frac{Na+}{\sqrt{\frac{(Ca2+ + Mg2+)}{2}}} (meq/L) \quad (11)$$

**Table 3.3 Water quality parameters for irrigation applications**

| Index method | FAO'94 standard | Category                                                                                                       | References                                       |
|--------------|-----------------|----------------------------------------------------------------------------------------------------------------|--------------------------------------------------|
| <i>SSP</i>   | -               | <20 Excellent<br>20-40 Good<br>40-80 Fair<br>> 80 Poor                                                         | Islam et al., 2017                               |
| <i>% Na</i>  | -               | < 40 Recommended<br>> 40 Not Recommended                                                                       | US SL, 1954                                      |
| <i>SAR</i>   | 15              | < 10 Excellent<br>10-18 Good<br>18-26 Fair<br>>26 Poor                                                         | Ayers and Westcot, 1985; Simsek and Gunduz, 2007 |
| <i>KR</i>    | -               | < 1 Excellent<br>>1 bad water, high level of Na <sup>+</sup><br>>3 unsuitable Excess levels of Na <sup>+</sup> | Shammi et al., 2016; Kelly, 1940; Kelly, 1951    |
| <i>MAR</i>   | -               | <50 Excellent<br>>50 harmful to soil and aquatic life                                                          | Ayers and Westcot, 1985; Simsek and Gunduz, 1987 |

The values of  $q_i$  were obtained by applying the following equation:

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

Where  $X_{ij}$  is the measured value of the parameter,  $X_{inf}$  is the lower value of the parameter to which the class belongs,  $Q_{iamp}$  is class capacity, and  $X_{amp}$  is the class capacity to which the parameter belongs.  $Q_{i \max}$  is the highest value of  $Q_i$  for the related class.

The highest value obtained from the physicochemical analysis of the water samples was taken into consideration as the upper limit to determine  $X_{amp}$  in the case of the last class of each parameter. Each parameter's weight used to calculate the  $MWQI$  was normalized so that their combined value is one. The weights of the  $WQI$  parameters are shown in **Table 3.2**. Finally,  $MWQI$  was determined as follows using Equation (13):

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

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 result of water quality analysis (**Tables 4.7, 4.8, 4.9, and 4.10**) and the tolerance limits shown in (**Table 3.2**). Also, the weight of each parameter used in the  $MWQI$  is shown in the same table. The water quality is rated as  $85 \leq 100$  (No - restriction),  $70 \leq 85$  (Low-restriction),  $55 \leq 70$  (Moderate -restriction),  $40 \leq 55$  (High - restriction), and  $0 \leq 40$  (severe restriction).

### 3.5.1.4 Irrigation Water Quality Index Parameters

In addition to  $IWQI$ , in this study, several parameters were selected to assess the acceptability of the Dhaleshwari River water for irrigation applications. The parameters include Magnesium Adsorption Ratio ( $MAR$ ), Percentage Sodium ( $\% Na$ ), Sodium Adsorption Ratio ( $SAR$ ), Soluble Sodium Percentage ( $SSP$ ), and Kelly's Ratio ( $KR$ ). The recommended standard values for irrigation water of these  $IWQI$  parameters are presented in (**Table 3.3**). Their significance and calculations are described in the following sections.

#### 3.5.1.4.1 Magnesium Adsorption Ratio ( $MAR$ )

One of the most crucial qualitative factors in establishing the quality of water for irrigation is the magnesium adsorption ratio ( $MAR$ ), also known as Magnesium Content ( $MC$ ) or Magnesium Ratio ( $MR$ ), which measures the relative concentration of calcium and magnesium in water (Joshi et al., 2009). In general, calcium and magnesium keep the pH of water at equilibrium, and more magnesium makes the soil more alkaline, which is bad for crop yields (Nishanthiny et al., 2010). The following formula is used to compute this ratio (Paliwal, 1972):

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

#### 3.5.1.4.2 Sodium Adsorptions Ratio (SAR)

When determining whether water is suitable for irrigation, the sodium content as the sodium adsorption ratio (SAR) must be evaluated because it has an impact on the soil's salinity, hardness, and penetration rate (Subramani et al., 2005; Todd, 1980). The SAR increases when Na concentrations in relation to Ca and Mg increase (Vyas and Jethoo, 2015). This sodium hazard is also connected to a number of elements, including soil types, salinity, etc. For example, sandy soils may be more able to withstand high SAR water (Vasanthavigar, 2010). The SAR is expressed as follows (Raghunath, 1987; Richards, 1954) :

$$SAR = \frac{Na+}{\sqrt{\frac{(Ca^{2+} + Mg^{2+})}{2}}} \text{ (mEq/L)} \quad (15)$$

#### 3.5.1.4.3 The Soluble Sodium Percentage (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; Todd, 1980):

$$SSP = \frac{(Na + K) \times 100}{(Ca + Mg + Na + K)} \text{ (Ions are expressed in mEq/L)} \quad (16)$$

#### 3.5.1.4.4 Percentage Sodium (% Na)

Percentage Sodium is another crucial consideration when determining whether water is suitable for irrigation because the high percentage of sodium in the water inhibits plant growth and lowers soil permeability (Mishra, 2005). It is computed as displayed below (Islam et al., 2017; Todd, 1980):

$$\% Na = \frac{(Na) \times 100}{(Ca + Mg + Na + K)} \text{ (ions are expressed in mEq/L)} \quad (17)$$

#### 3.5.1.4.5 Kelly's Ratio (*KR*)

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

$$KR = \frac{(Na) \times 100}{(Ca + Mg)} \quad (\text{ions are expressed in mEq/L}) \quad (18)$$

#### 3.5.1.5 Nemerow's Pollution Index (*NPI*):

Nemerow's Pollution Index (*NPI*) is expressed by the following equation:

$$NPI = \frac{C_n}{S_n} \quad (19)$$

Where,

$C_n$  = Concentration of the  $n^{th}$  parameter.

$S_n$  = Prescribed standard limits of the  $n^{th}$  parameter.

**The result of the *NPI* Calculation will be:**

*NPI* values  $\leq 1$

*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.

### 3.6 Assessment of Drinking Water Quality

Various methods were considered to evaluate the surface and groundwater quality for use in drinking purposes. For this reason, Health Risk Assessment (*HRA*) for trace metals was considered. Here, the computing procedures are explained in more detail.

#### 3.6.1 Risk calculation of heavy metal pollution

The degree of trace heavy metal pollution (**Table 3.5**) in the research area's surface and groundwater was evaluated using two different risk assessment techniques, as shown below:

##### 3.6.1.1 Single-Factor Pollution Index ( $I_i$ )

The single-factor pollution index ( $I_i$ ) is used to assess how a single heavy metal pollutes surface and groundwater at a sampling station:

$$I_t = \frac{C_t}{S_t} \quad (1)$$

Where  $C_t$  is the amount of contaminant  $t$  that has been measured in surface and groundwater (mg/L) and  $S_t$  is the standard value (**Table 3.4**). Here, we followed the WHO recommended value (2011). When it is greater than 1, the amount of that heavy metal is above the standard (Wang et al., 2011).

**Table 3.4 Standard values ( $S_t$ ), Ideal values ( $I_t$ ), and Max. Permissible Concentration ( $MPC$ ) (all are in mg/L) for the analyzed metals**

| Metal | $I_t$ | $W_i$          | $S_t$ or $S_i$ | $MPC$ |
|-------|-------|----------------|----------------|-------|
| Mn    | 0.1   | 0.005958       | 0.3            | 0.3   |
| Pb    | 0     | 0.202634       | 0.01           | 0.01  |
| Ni    | 0.07  | 0.022053       | 0.1            | 0.1   |
| As    | 0     | 0.005260       | 0.01           | 0.01  |
| Cu    | 0.5   | 0.001023       | 2.0            | 2.0   |
| B     | 1.0   | 0.000852       | 2.4            | 2.4   |
| Cr    | 0     | 0.039977       | 0.05           | 0.05  |
| Co    | 0     | 0.045677       | 0.05           | 0.05  |
| Cd    | 0     | 0.674379       | 0.003          | 0.003 |
| Zn    | 0.5   | 0.000682       | 3.0            | 3.0   |
| Fe    | 0.3   | 0.001855       | 1.0            | 1.0   |
|       |       | $\sum W_i = 1$ |                |       |

### 3.6.1.2 Compound Pollution Index ( $CPI$ )

The heavy trace metal contamination in water was assessed using the compound pollution index ( $CPI$ ), which is given as the following equation (2):

$$CPI = \sum_{t=1}^n \frac{I_t}{n} \quad (2)$$

Where  $I_t$  is a single-factor index and  $n$  is the total number of heavy metals.  $CPI < 1$  shows that water samples are free of heavy metal pollution;  $CPI \geq 1$  shows that water samples are not free of heavy metal pollution (Zhong et al., 2015).

### 3.6.2 Pollution indices

#### 3.6.2.1 Metal Indices (*MI*)

The heavy trace metal contamination in water was assessed using the metal index (*MI*), which is given as the following equation (3):

$$(MI) = \sum_{i=1}^n \left( \frac{Ci}{MPCi} \right) \quad (3)$$

Where,

$Ci$  = Concentration (mean values) of the  $i^{th}$  heavy metals in the samples analyzed.

$MPC$  = Maximum Allowed Concentration of the  $i^{th}$  heavy metals.

#### 3.6.2.2 Heavy Metal Pollution Index (*HMPI*)

The heavy trace metal pollution index (*HMPI*) model has been identified by choosing the surface and groundwater parameters on which the index must be based and allocating weights ( $W_i$ ) for certain parameters. It can be described as being inversely proportional to each parameter's suggested standard ( $S_i$ ) (Mohan et al., 1996; Bhuiyan et al., 2016). The concentration limits were taken from the WHO standard (2011). Equation (4), which calculates the heavy metal pollution index (*HMPI*), was used to determine the weightage ( $W_i$ ) for each specific parameter (Mohan et al., 1996).

$$HMPI = \frac{\sum_{i=1}^n W_i Q_i}{\sum_{i=1}^n W_i} \quad (4)$$

Where  $W_i$  is the parameter's unit weight,  $Q_i$  is its sub-index, and  $n$  is the total number of parameters. The sub-index  $Q_i$  is calculated by,

$$Q_i = \sum_{t=1}^n \frac{|Mt - I|}{(St - It)} \quad (5)$$

Where,  $M_t$ ,  $I_t$ , and  $S_t$  each contribute to the  $t^{th}$  parameter's "monitored value," "ideal value," and "standard values," respectively (**Table 3.4**). Ignoring the algebraic sign, the negative sign (-) represents a numerical difference between the two values.

**Table 3.5 Degree of pollution classification of each index**

| Parameter                  | Degree of pollution                                                                                                                                                         |
|----------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <i>MI</i>                  | Very poor: $< 0.3$<br>Pure: $(0.3-1)$<br>Slightly Affected: $(1-2)$<br>Moderately Affected: $(2-4)$<br>Strongly Affected: $(4-6)$<br>Seriously Affected: $> 6$              |
| <i>HMEI</i>                | $10 <:$ Low<br>$10-20$ : Medium<br>$> 20$ : High                                                                                                                            |
| <i>HMPI</i>                | $< 45$ : Low<br>$45-90$ : Medium<br>$> 90$ : High                                                                                                                           |
| <i>C<sub>d</sub></i>       | $< 10$ : Low<br>$10-20$ : Medium<br>$> 20$ : High                                                                                                                           |
| <i>CPI</i>                 | $< 1$ : no heavy metal contamination<br>$\geq 1$ : heavy metal contamination                                                                                                |
| <i>ERI</i>                 | $< 110$ : Low risk<br>$110 \leq ERI < 400$ : Moderate risk<br>$200 \leq ERI < 400$ : Considerable risk<br>$ERI \geq 400$ : Very high risk                                   |
| <i>NeI</i>                 | $NeI < 1$ : insignificant contaminated<br>$1 \leq NeI < 2.5$ : slightly contaminated<br>$2.5 \leq NeI < 7$ : moderately contaminated<br>$NeI \geq 7$ : heavily contaminated |
| <i>(a) HI (nc)</i>         | $< 1$ = non-carcinogenic are not predictable to occur from any metal<br>$> 1$ = may be a concern for the potential non-carcinogenic impact                                  |
| <i>(b) HI (ca)</i>         | $< 1$ = carcinogenic are not predictable to occur from any metal<br>$> 1$ = may be a concern for the potential carcinogenic impact                                          |
| <i>I<sub>t</sub> Value</i> | $< 1$ : no heavy metal contamination<br>$\geq 1$ : heavy metal contamination                                                                                                |

### 3.6.2.3 Heavy Metal Evaluation Index (*HMEI*)

The following equation (6) was used to calculate the heavy metal evaluation index (*HMEI*), which is consistent with the *HMPI* approach and provides information on the general quality of surface and groundwater with respect to heavy trace metals (Prasad et al., 2001; Edet et al., 2002).

$$HMEI = \sum_{i=1}^n \frac{Hc}{H_{mpc}} \quad (6)$$

Where  $H_c$  is the value being monitored and  $H_{mpc}$  is the maximum allowable concentration of the parameters.

#### 3.6.2.4 The Degree of Contamination ( $C_d$ )

The degree of contamination ( $C_d$ ) is recognized by (Backman et al., 1997), and the Equation (7) was used to calculate  $C_d$ :

$$Cd = \sum_{i=1}^n Cfi \quad (7)$$

Where  $C_{fi} = (C_{ai}/C_{ni}) - 1$  and the contamination factor is  $C_{fi}$ , the analytical value is  $C_{ai}$ , the upper acceptability concentration is  $C_{ni}$  or ( $S_i$ ) and the normative value is represented by  $n$ .  $C_{ni}$  is used in this circumstance as the maximum allowable concentration (MPC) (Table 3.4).

#### 3.6.2.5 Nemerow Index ( $Nel$ )

The index is calculated using the following equation (8) in this multifactorial and integrated assessment method (Liu et al., 2015).

$$Nel = [\{(M_t / I_t)^2_{mean} + (M_t / I_t)^2_{max}\} / n]^{1/2} \quad (8)$$

Where  $(M_t/I_t)$  mean is the average value of a surface and groundwater sample and  $(M_t/I_t)$  max is the maximum value of  $(M_t/I_t)$  among all target heavy metals detected in the water sample.

#### 3.6.2.6 Ecological Risks Measurement ( $ERI$ )

We used the Ecological Risk Index ( $ERI$ ) (Sharif et al., 2016; Wen et al., 2019) to assess any potential environmental risks brought on by the presence of heavy toxic metals in surface and groundwater. The ecological risk index was derived as follows:

$$ERI = \sum_{i=0}^n [Ti \times (\frac{Mi}{Ii})] \quad (9)$$

Where  $T_i$  is the  $i^{th}$  target heavy metal's biological toxicity factor. Trace metals' toxic-response factors are as follows: Cd = 30, Cu, Pb = 5, Cr = 2, and Zn, Mn = 1 (Wang et al., 2018, Hakanson, 1980).

#### 3.6.2.7 Health Risk Assessment ( $HRA$ ) for Humans:

Human health risk assessment is a multi-step procedure that includes data collection and evaluation, exposure evaluation, toxicity estimation, and risk classification.

**Table 3.6 Key factors for calculating the health hazards caused by oral and dermal routes**

| Symbol      | Value                            | Exposure Route/ Exposure Factor         | Reference/Source          |
|-------------|----------------------------------|-----------------------------------------|---------------------------|
| $IRW_c$     | 1 L/day                          | Water ingestion rate for child          | Harries and harper, 2004  |
| $IRW_{adj}$ | 2.229 L-year/kg-day              | Age-adjusted water ingestion rate       | Eqn. 12                   |
| $IRW_a$     | 2 L/day                          | Water ingestion rate for adult          | Rani et al., 2013         |
| $EF$        | 365 days/year                    | Exposure frequency                      | Duggal et al., 2013       |
| $ED_a$      | 70 years                         | Exposure duration for adult             | Harries and Harper, 2004  |
| $C_w$       | (mg/L)                           | Contaminant conc. of each metal         | -                         |
| $ED_c$      | 6 years                          | Exposure duration for child             | Harries and Harper, 2004  |
| $BW_c$      | 15 kg                            | Bodyweight for child                    | Harries and Harper, 2004  |
| $BW_a$      | 70 kg                            | Bodyweight for adult                    | Rani et al., 2013         |
| $ET_a$      | 0.58 hour/day                    | Absorbed dose per event                 | Eqn. 11                   |
| $AT_a$      | 25550 days                       | Average time for adult                  | $AT = EF \times ED$       |
| $ET_c$      | 1 hour/day                       | Exposure time for a child               | US-EPA, 2004              |
| $ET_{adj}$  | 0.616 hour/day                   | Age-adjusted exposure time              | Eqn. 13                   |
| $AT_c$      | 2190 days                        | Average time for a child                | $AT = EF \times ED$       |
| $SA_c$      | 6600 cm <sup>2</sup>             | Skin surface area for child             | US-EPA, 2004              |
| $CF$        | 0.001 L/cm <sup>3</sup>          | Conversion factor                       | 1L = 1000 cm <sup>3</sup> |
| $K_p$       | COPC-specified (see Table 2)     | Permeability coefficient for each metal | US-DOE, 2011              |
| $SA_{adj}$  | 19097 cm <sup>2</sup> -yr/kg-day | Age-adjusted skin surface area          | Eqn. 13                   |
| $SA_a$      | 18000 cm <sup>2</sup>            | Skin surface area for adult             | US-EPA, 2004              |
| $EV_c$      | 1 event/day                      | Event frequently for child              | US-EPA, 2004              |
| $EV_a$      | 1 event/day                      | Event frequently for adult              | US-EPA, 2004              |

**Table 3.7 Values for the studied metals'  $RfD_{oral}$ ,  $CSF_{oral}$  and  $GI_{ABS}$  (US-DOE, 2011; US-EPA, 1989)**

| Element | $RfD_{oral}$<br>(mg/kg/day) | $CSF_{oral}$<br>(mg/kg/day) | $K_p$<br>(cm/hour) | Gastro-intestinal absorption<br>factor ( $GI_{ABS}$ ) |
|---------|-----------------------------|-----------------------------|--------------------|-------------------------------------------------------|
| Fe      | 7.00E-01                    | -                           | 0.005              | 1                                                     |
| Cr      | 1.50                        | -                           | 0.002              | 1.3E-02                                               |
| Co      | 3.00E-04                    | -                           | 0.001              | 1                                                     |
| B       | 2.00E-01                    | -                           | 0.002              | 1                                                     |
| Mn      | 4.60E-02                    | -                           | 0.003              | 4.00E-02                                              |
| Pb      | 3.50E-03                    | 8.50E-03                    | 0.001              | 1                                                     |
| Cd      | 5.00E-04                    | 6.10E-03                    | 0.001              | 5.00E-02                                              |
| Ni      | 2.00E-02                    | 8.60E-04                    | 0.002              | 4.00E-02                                              |
| Zn      | 3.00E-01                    | -                           | 0.006              | 1                                                     |
| Cu      | 4.00E-02                    | -                           | 0.001              | 1                                                     |
| As      | 3.00E-04                    | -                           | 0.002              | 5.00E-01                                              |

The unique carcinogenic and non-carcinogenic risks through the oral and dermal channels were assessed in this investigation. The US-DOE Risk Assessment Information System (Equations 10-13) was used to calculate the dose acknowledged (chronic daily intake,  $CDI_{inc-ca}$ ) (US-DOE, 2011) and (US-EPA, 1997, 2001) for two sub-resident groups of adults and children. Here, we avoided using any previously published descriptions or formulae and only provided the calculated forms of the relevant equations.

For calculating non-carcinogenic ( $nc$ ) risk;

$$CDI_{oral} - nc = \frac{C_w \times ED \times IRW \times EF}{AT \times BW}$$

$$= C_w \times \text{Factor } A_{adult/child} \text{ mg/k/day} \quad (10)$$

The derived values of Factor  $A_{adult}$  and Factor  $A_{child}$  are 0.2048 and 0.0667, respectively.

$$CDI_{derm} - nc = \frac{K_p \times ETa \times SA \times C_w \times CF \times ED \times EV \times EF}{AT \times BW}$$

$$= Cw \times K_p \times \text{Factor } B_{adult/child} \text{ mg/kg/day} \quad (11)$$

Where, the predicted values of Factors  $B_{adult}$  and  $B_{child}$  are, respectively, 0.000149 and 0.00044 (**Table 3.6**). In **Table 3.7**, the  $K_p$ , values of each metal are listed.

For carcinogenic (*ca*) risk calculation;

$$CDI_{oral} - nc = \frac{Cw \times EF \times IRW_{adj}}{AT}$$

$$= Cw \times \text{Factor } C_{adult/child} \text{ mg/k/day} \quad (12)$$

Where, the age-adjusted water ingestion rate ( $IRW_{adj}$ ) is 2229 L (yr/kg) per day and the computed values of Factors  $C_{adult}$  and  $C_{child}$  are 0.0318 and 0.2048, respectively, for adults and kids (calculated by **Table 3.6**).

$$CDI_{derm} - nc = \frac{K_p \times ET_{adj} \times SA_{adj} \times Cw \times CF \times EF}{AT}$$

$$= Cw \times K_p \times \text{Factor } D_{adult/child} \text{ mg/kg/day} \quad (13)$$

Where exposure time,  $ET_{adj}$ , is 0.615 hr. day<sup>-1</sup> and skin surface area (age-adjusted),  $SA_{adj}$ , is 19097.2 cm<sup>2</sup>.day.yr/kg. Factor  $D_{adult}$  and Factor  $D_{child}$  have computed values of 0.0002 and 0.002, respectively (calculated by **Table 3.6**). All factors/parameter values (Equations 10 to 13) are composed of the literature of Duggal et al., 2013, 2017; US-EPA, 2004; Harries and Harper, 2004; and Rani et al., 2013. The assessed  $CDIs$  for each metal were divided by their respective reference doses ( $RfD$ ) and  $RfD$  with gastrointestinal absorption factor ( $GI_{ABS}$ ), in order to obtain the  $HQ_{oral}$  and  $HQ_{derm}$  values (**Table 3.7**). The hazard index ( $HI$ ) (Equation 14) is represented below:

$$HI = \sum_{i=1}^n HQ_i \quad (14)$$

### 3.7 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 varimaxnormalized 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 (Islam and Mostafa, 2021c; Bhuiyan et al., 2010).

By using the above materials and methods the results were delivered with proper discussion in the next chapter.

# **CHAPTER 4**

## **Results and Discussion**

# CHAPTER 4

## Results and Discussion

There is a Central Effluent Treatment Plant (CETP) at Savar Tannery Industrial State in Bangladesh to treat the composite tannery effluent of 132 tannery industries. However, reports illustrated that the treatment plant is not effective enough which has a detrimental effect on the flora and fauna. So, the study was targeted to assess the performance of the CETP and surface water and groundwater quality in the effluent discharged area at Savar Tannery Estate in Bangladesh.

The samples were collected three times (pre-monsoon, monsoon, and post-monsoon) in a year, from the monsoon of 2021 to the pre-monsoon of 2023. The composite effluent samples were collected before entering and being discharged from the CETP and analyzed for various physicochemical parameters in order to assess the performance of the CETP. There were five surface water samples collected from different locations, starting from the CETP discharge point and at different distances, i.e., 100, 500, 1000, and 2000 meters from the CETP discharge point, and the samples were named SW1, SW2, SW3, SW4, and SW5, respectively, as well as several groundwater samples collected around the CETP. The characterization of treated and untreated tannery effluent, surface water, and groundwater in the effluent discharged area considering major physicochemical, anionic, and cationic parameters. Seasonal variation was performed to assess the seasonal pollution level sequence of surface and groundwater. Additionally, FTIR analysis was carried out to identify the functional groups of organic contaminants. Then various indexing models, like the Canadian Council of Ministers of the Environment (*CCME*), Meireles Water Quality Index (*MWQI*), Weight Average

Water Quality Index (*WWQI*), Irrigation Water Quality Index (*IWQI*), Nemerow's Pollution Index (*NPI*), Single-Factor Pollution Index (*I<sub>i</sub>*), Compound Pollution Index (*CPI*), Metal Index (*MI*), Heavy Metal Pollution Index (*HMPI*), Heavy Metal Evaluation Index (*HMEI*), Degree of Contamination (*C<sub>d</sub>*), Nemerow Index (*NeI*), Ecological Risk Measurement (*ERI*), and carcinogenic and non-carcinogenic Hazard Index (*HI<sub>total</sub>*), were used to determine the pollution level of surface water and groundwater in the study area. Several computer software were used for analyzing the experimental data. The previous chapter (Materials and Method) described all aspects of the analysis procedures in detail. Here, the chapter discusses the experiment results, the findings of the analysis, and their interpretation are given, together with pertinent references.

#### **4.1 Characterization of the CETP influent and effluent**

The influent (before treatment), and effluent (after treatment) of the Central Effluent Treatment Plant (CETP) of the Savar tannery industrial zone in the northwest of Bangladesh, Dhaka district were analyzed and stated below (detailed results in Appendix I).

##### **4.1.1 Physicochemical parameters of the CETP influent and effluent**

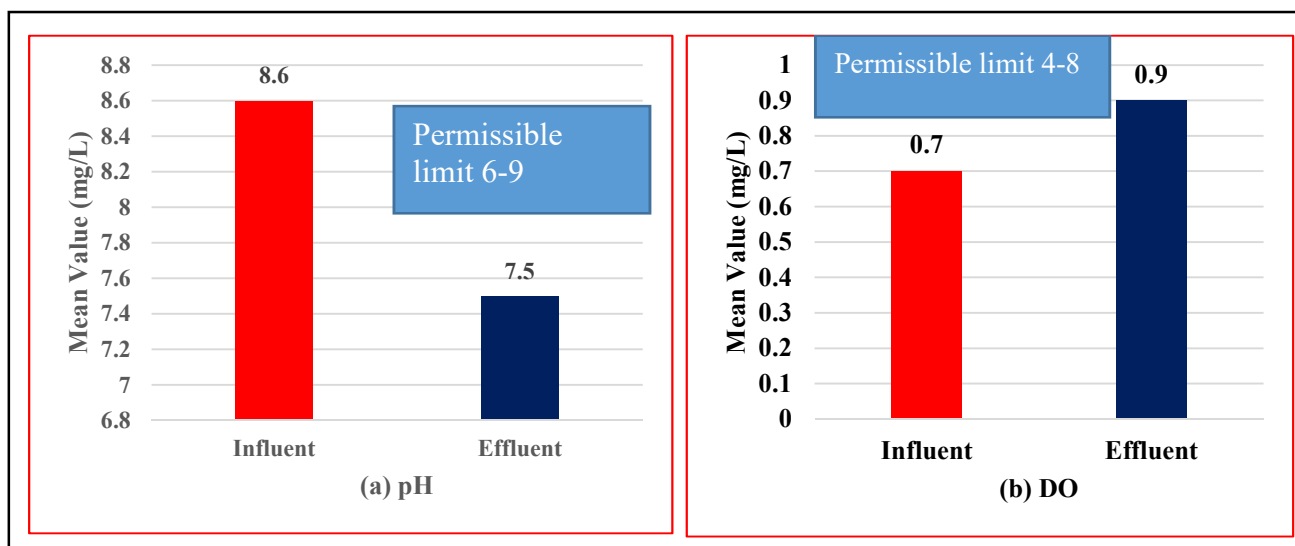
The influent (before treatment) and effluent (after treatment) of the Central Effluent Treatment Plant (CETP) were analyzed to find the major physicochemical parameters, including pH, DO, EC, TDS, TSS, BOD, COD, TH, etc. These parameters represent the pollution status of the sample. The physicochemical parameters of influent and effluent are described below:

###### **4.1.1.1 pH**

The pH is the most essential quality indicator for wastewater discharge in the manufacturing industry. The pH of the released effluent affects some chemical reactions, including solubility and metal toxicity (Yusuff and Sonicare, 2004; Shakil and Mostafa, 2021; Rouse, 1979; Balasubramanian et al., 2000; Dorman et al., 2000), which is a crucial factor (UNIDO, 2000). The pH values in untreated and treated composite tannery effluent ranged from 6.9 to 8.9 and 6.6 to 8.3, with a mean of 8.6 and 7.5, respectively (**Figure 4.1 (a)**) during the study period. The mean value of influent and effluent pH was

within the standard value (6-9) of the discharge limit of the Department of Environment, Bangladesh (DoE-BD, 2023). The alkaline nature of these composite tannery effluent was due to the use of lime,  $\text{Na}_2\text{CO}_3$ , and  $\text{Na}_2\text{S}$  during rawhide and skin processing. A similar observation was stated by various researchers, (Chowdhury et al., 2015; Ghosh and Hossain, 2019), which supported the present study.

In the present investigation, the pH was in the safe zone and pH was not responsible for contaminating the study area.



**Figure 4.1 (a) pH and (b) DO of the tannery influent and effluent**

#### 4.1.1.2 Dissolved Oxygen (DO)

The amount of gaseous  $\text{O}_2$  dissolved in an aqueous solution is measured by a Dissolved Oxygen (DO) meter (Islam and Mostafa, 2018, 2022). One of the crucial factors in determining the quality of the water is the measurement of DO (Shakil and Mostafa, 2021). The mean DO values were 0.7 mg/L in the influent and 0.9 mg/L in the effluent during the study period, which were far below the standard prescribed limits set by the DoE-BD (2003) (**Figure 4.1 (b)**). The DO value of the influent and effluent samples that were analyzed was less than the DoE standard for discharge, suggesting that the discharge effluent was unfit for aquatic life. For the aquatic environment, a DO concentration of 5-8 mg/L is considered fair, and less than 4 mg/L is considered a crucial

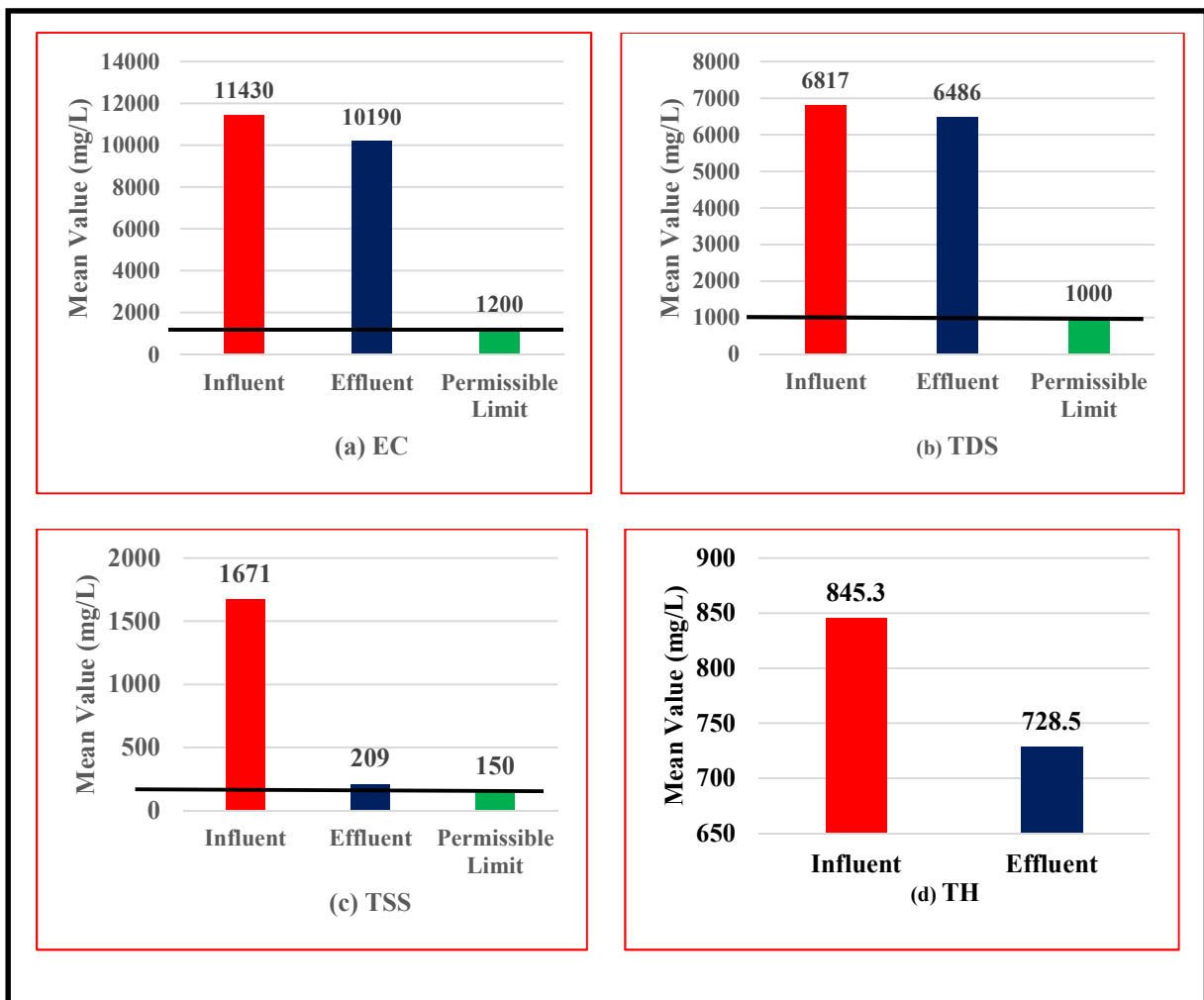
limit (Akan et al., 2007). The presence of significant amounts of organic pollutants in the effluent might be the cause of low DO levels (4 mg/L) in all sampled effluent. The DO value ( $>1$  mg/L) indicated that the discharged composite influent and effluent were heavily polluted and potentially harmful to aquatic life (Monira et al., 2023). A similar observation was illustrated by several research (Ghosh and Hossain, 2019; Chowdhury et al., 2013, 2015; Verma et al., 2008), which sustained the present findings.

All aquatic life, including the creatures responsible for the water's natural cleansing processes, depends on dissolved oxygen (Kant, 2012). The existence of a significant organic load in the water, which decreases oxygen, may be responsible for the lower DO level (Mohabansi et al., 2011). At DO values less than 4 mg/L, aquatic life must change its breathing habits or reduce its activity (Rahim and Mostafa, 2021). Low DO decreases the photosynthetic rate which is harmful to aquatic life (Tyagi & Mehra, 1990). In the recent investigation, it found a low concentration of DO as one of the main contaminants responsible for polluting the study area.

#### **4.1.1.3 Electrical Conductivity (EC)**

Electrical Conductivity (EC) is a measure of how well different ions can carry electric current (Islam and Mostafa, 2020, 2022). It is often used to estimate the quantity of total dissolved salts. Salinity is measured indirectly by electrical conductivity (Shakil and Mostafa, 2021). The electrical conductivity values of the composite influent and effluent samples ranged from 10270 to 14500  $\mu\text{S}/\text{cm}$  with a mean value of 11430  $\mu\text{S}/\text{cm}$  and 9300 to 12700  $\mu\text{S}/\text{cm}$  with a mean value of 10190  $\mu\text{S}/\text{cm}$  (**Figure 4.2 (a)**), respectively, in the study period and showed higher EC as compared to the prescribed standard limit (1200  $\mu\text{S}/\text{cm}$ , DoE-BD, 2023; NEQS, 2000; 288 mg/L). Kabir et al. (2007) reported that the EC values of the Hazaribagh tannery effluent area ranged from 9587 to 11000  $\mu\text{S}/\text{cm}$ , which showed some similarity with the results of the present research. The higher EC indicated the existence of an adequate amount of organic and inorganic compounds and salts, mostly sodium and chromium salts used during the pickling and tanning procedures, which may boost the electrical conductivity of the effluent samples. Chowdhury et al., 2013 made a similar observation. The average EC of all composite influent and effluent samples was far above the permissible limits, indicating a very poisonous environment for the aquatic biota (Monira et al., 2022). The higher electrical conductivity of the

effluent samples indicated that more chemicals containing cations and anions were discharged into the effluent. The increased conductivity changes the chelating characteristics of water bodies and unbalances the availability of free ions for aquatic life (Akan et al., 2007). Venkatesh et al. (2008) noted that the electrical conductivity of tannery effluent was significantly higher than the acceptable limits for industrial effluent released into aquatic bodies. Therefore, the higher EC values indicated that the discharge tannery effluent contained large amounts of pollutants, causing severe pollution around the discharge area.



**Figure 4.2 (a) EC, (b) TDS, (c) TSS, and (d) TH of the tannery influent and effluent**

#### 4.1.1.4 Total Dissolved Solids (TDS)

In tannery effluent, the Total Dissolved Solids (TDS) are composed of organic salts, phosphate, nitrates, chlorides, carbonates, bicarbonates, and sulfates of magnesium, calcium, sodium, iron, potassium, manganese, and other particles (Chowdhury et al., 2013). The study results showed that the concentration of TDS ranged from 6367 to 7378 mg/L with an average value of 6817 mg/L in the influent and 6405 to 6617 mg/L with an average value of 6486 mg/L in the effluent, respectively (**Figure 4.2 (b)**). The input and output samples of the CETP exceeded the standard permissible limits (1000 mg/L, DoE-BD, 2023), which was almost seven times higher compared to the standard permissible limit, set by the (DoE-BD, and ISW-BDS-ECR, 2023) indicating the presence of large amounts of dissolved solids. Higher levels of TDS are mostly caused by carbonates, bicarbonates, chlorides, sulfates, phosphates, nitrates, nitrogen, calcium, sodium, potassium, and iron. Protein, hair, skin, and emulsified fats are taken from the hides during the liming stage of tanning. These materials are then discharged into the effluent, increasing the total dissolved solids. A similar observation was given by various researchers (Kannan et al., 2008, 2005; Bhalli and Khan, 2006). Rouf et al. (2013) stated that the TDS concentration of the tannery effluent was 3455 mg/L from various points of the Hazaribagh tannery industrial zone, which was much lower than the TDS concentration of the present study. The findings indicated that the concentration of TDS was higher than predicted, indicating that they may be released with the potential to damage the quality of surface water and aquatic life. High TDS water is harmful to the environment and human health because it causes salinity issues (Hussian and Rao, 2013; Kolhe and Pawar, 2011). Based on TDS concentration we observed that the effluent must be properly treated before being discharged into the surface water bodies.

#### 4.1.1.5 Total Suspended Solids (TSS)

The suspended contaminants found in the effluent are known as Total Suspended Solids (TSS). TSS is an important consideration when evaluating water transparency. TSS is composed of clay, algae, bacteria, decomposed organic particles, and effluent (Monira et al., 2023; Casey, 1997). TSS were 1486 to 1918 mg/L in the influent and 82 to 322 mg/L

in the effluent with a mean value of 1671 mg/L and 209 mg/L, respectively (**Figure 4.2 (c)**) during the study period. These values exceeded the prescribed permissible limit set by the DoE-BD, 2023 (150 mg/L), indicating huge amounts of suspended solids present in the discharge influent and effluent. High TSS value was due to the use of raw materials in the leather manufacturing process. Tannery effluent from the processing of the beam house and related rinsing process may contain hidden compounds, dirt, blood, or drug residues and consequently have substantial loads of organic matter and total suspended solids. A similar observation was delivered by Rouf et al. (2013). According to several reports, the effluent from beam house processing has significant levels of chromium, sulfate, sulfide, total solids, and chloride (Cooman et al., 2002; Gupta, 2003; Junior et al., 2006). High TSS may block the sunlight required for photosynthesis (Langland and Cronin, 2003; Peavy et al., 1985; Davis and Cornwell, 1998). The higher value of TSS increased sedimentation rates and water turbidity levels and produced sludge, which consequently increased oxygen demand and decreased aquatic plant photosynthesis (Bash et al., 2001). It is responsible for pollution transportation and increases the level of contaminants and pathogens, thus disrupting the aquatic biota's food chain (Giller et al., 1998). According to TSS information, the effluent was extremely contaminated in the study present study.

The higher values of EC, TDS, and TSS in the tannery effluent were due to the presence of various organic and inorganic substances. The high levels of TDS and TSS in the influent and effluent indicated that the influent must be properly treated before discharging into the surface water bodies.

#### **4.1.1.6 Total Hardness (TH)**

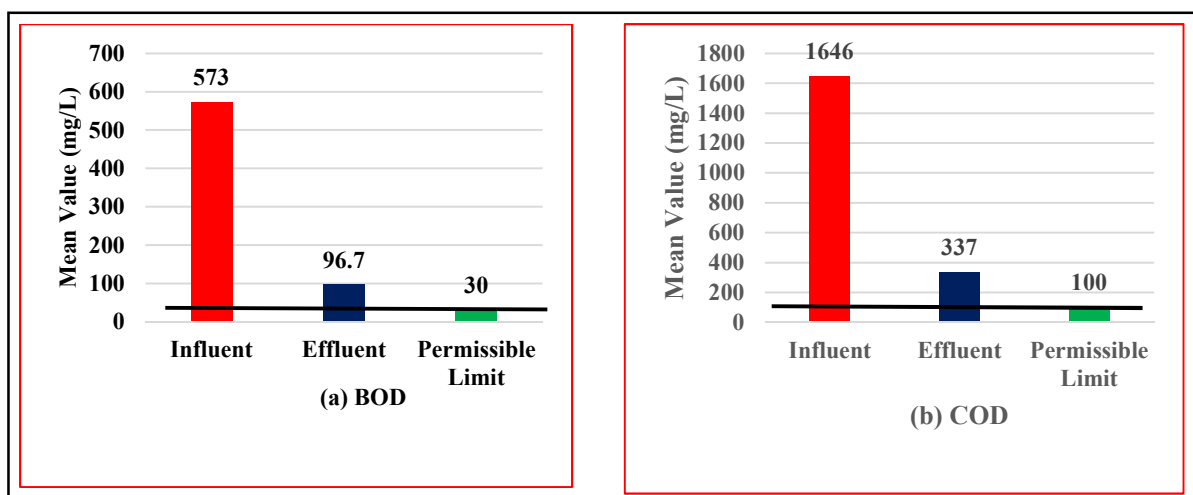
The Total Hardness (TH) is very substantial and significant for industrial, drinking, and irrigation purposes (Islam and Mostafa, 2022). TH is not caused by a single constituent by a diverse type of dissolved metal ions including the Ca and Mg cations, carbonate, and bicarbonate (WHO, 2011).

The total hardness of the study ranged from 350 to 1470 mg/L in the influent and 635 to 932 mg/L in the composite tannery effluent with an average value of 845.3 mg/L and 728.5 mg/L, respectively, during the study period (**Figure 4.2 (d)**). The highest total

hardness observed was 1470 mg/L in the discharge effluent. The study observed that the hardness value of influent and effluent was higher than that of the standard limit of the DoE-BD, 2023, and the sample was found very hard (Islam and Majumder, 2020; Islam and Mostafa, 2021a). Gosh and Hossain (2019) illustrated that the total hardness of the tannery influent and effluent was 602 mg/L and 510 mg/L, respectively which was very similar to the present study. The study observed that, the higher content of total hardness indicates the high content of carbonate and bicarbonate and specifies the existence of higher levels of liquified salts. This finding was consistent with the Bosnic et al. (2000) investigation. Soft water is commonly defined as having a  $\text{CaCO}_3$  (equivalent Value) concentration below 60 mg/L; moderately hard water is defined as having a concentration between 121 and 180 mg/L; and very hard water is defined as having a concentration over 180 mg/L (McGowan, 2000). Hard water has adverse effects on human health, including skin and hair, and the environment because hard water causes scale formation, diabetes, gastroenteritis, neural and cardiovascular disorders, and so on (Islam and Mostafa, 2021a). From the investigation, we got the study influent and effluent as very hard water.

#### **4.1.1.7 Biological Oxygen Demand (BOD)**

Biological Oxygen Demand (BOD) is a crucial indicator of water quality since it offers a biological index to evaluate the impact of effluent discharge on the ecosystem. It is critical to estimate the amount of oxygen that the organic matter in the effluent will consume (Islam and Mostafa, 2018).



**Figure 4.3 (a) BOD and (b) COD of the tannery influent and effluent**

In the present study, the values of BOD in the influent and effluent samples were in the range of 508- 630 mg/L and 53-137 mg/L, with a mean of 573 mg/L and 96.7 mg/L, respectively (**Figure 4.3 (a)**). A maximum of 630 mg/L of BOD was found in the influent of the Savar tannery industrial area. All the BOD values of the tannery effluent obtained were higher than the discharge standard of tannery effluent (30 mg/L, DoE-BD). The high value of BOD indicates the presence of a huge quantity of organic substances in the tannery effluent. The high content of organic ingredients consumes a huge quantity of O<sub>2</sub> and increases the level of BOD (Monira et al., 2022). A high BOD level signals a reduction in DO because bacteria are consuming the oxygen in the water, making fish and other aquatic animals survive in bodies of water (Islam and Mostafa, 2022). This finding was consistent with the Imtiazuddin et al. (2012) investigation. At the DEPZ industrial area, Savar, Dhaka, the BOD in the effluent was 12 to 18 times greater than the DoE standard (Momtaz et al., 2012). According to other researchers, the BOD in the industrial effluent of the Hayatabad industrial park in Peshawar, Pakistan, ranged from 97 to 615 mg/L (Tariq et al., 2006). Which was also consistent with the present investigation. In the present study, the results of BOD showed that the effluent was in very bad conditions indicating a highly polluted industrial area.

#### 4.1.1.8 Chemical Oxygen Demand (COD)

One of the most crucial factors for determining the amount of chemically oxidizing materials in water is the chemical oxygen demand (COD) (Islam and Mostafa, 2020). COD is a key indicator of the degradation of water quality caused by effluent discharge (Shakil and Mostafa, 2021). In the present study, an average value of COD observed was 1646 mg/L and 337 mg/L (**Figure 4.3 (b)**) in the composite mixture of the tannery influent and effluent, respectively which was fifteen to sixteen times higher than DoE-BD, 2023 discharge standard limits. The COD level commonly indicates the concentration of organic and inorganic matter in effluent that is not decomposed by microorganisms. It includes both biodegradable and non biodegradable components of a live bacterial attack, yet it can be oxidized by vigorous chemical oxidants. Some researchers delivered a similar observation (Islam et al., 2014; Abbasi, 1998; Jahan et al., 2014; Tan et al., 2000; Chiron et al., 2000). A study conducted by Gosh and Hossain (2019) illustrated that the COD of the tannery influent and effluent was 1628 and 430 mg/L, respectively. Which shows similarity with the present study. In Bangladesh, India, and Pakistan, the COD of untreated tannery effluent ranged from 2000 mg/L to 4000 mg/L, 2500 mg/L to 3000 mg/L, and 1000 mg/L to 2000 mg/L, respectively (Monira et al., 2023). Which were far higher than the present study which represents that pollution level in our country is less than neighboring countries. The presence of a large amount of physiologically resistant organic compounds and the toxicity of tannery effluent are both indicated by the high levels of COD, which put the environment in danger (McMullan et al., 1995; Yusuff et al., 2004; Geetha et al., 2008). During the present investigation, based on COD values we found it as the main contaminant.

A relationship exists between BOD, COD, and DO. The DO values were supported by the COD and BOD readings. Higher COD and BOD levels indicate reduced oxygen concentration, or lower DO values, in the effluent (Islam and Mostafa, 2018). Unproperly treated Effluent released into aquatic ecosystems decreases the DO and increases the BOD and COD (Monira et al., 2023). So, the tannery effluent should be properly treated before being released into surface water bodies.

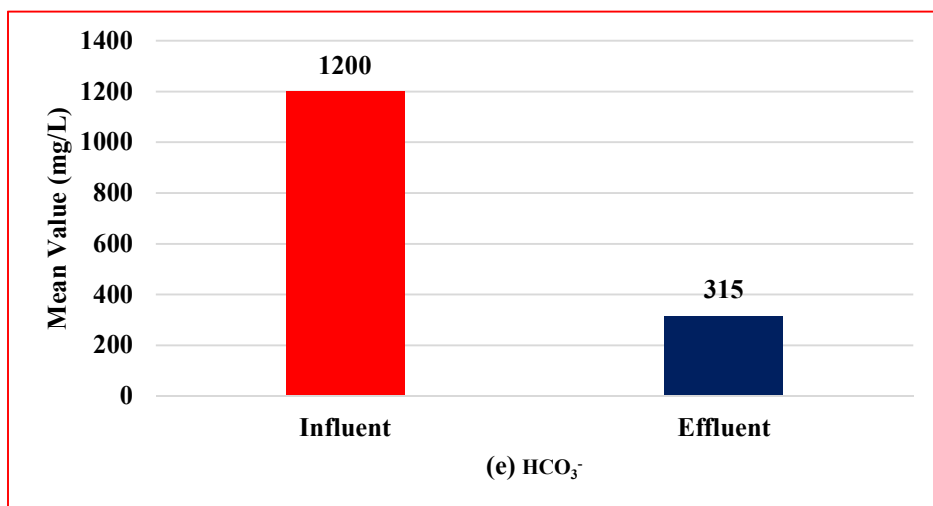
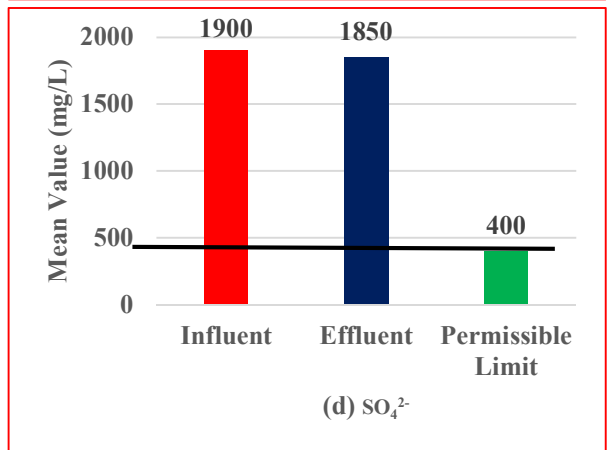
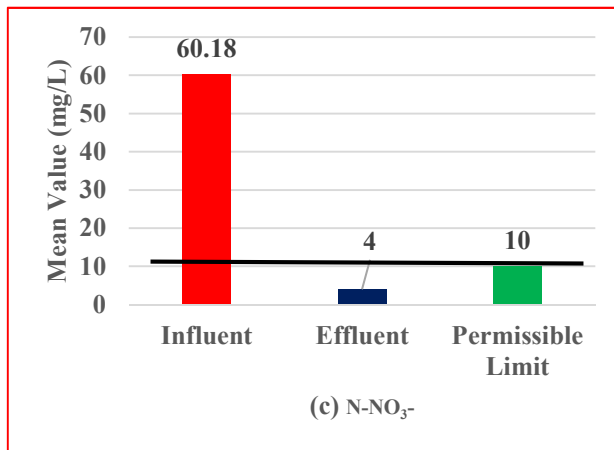
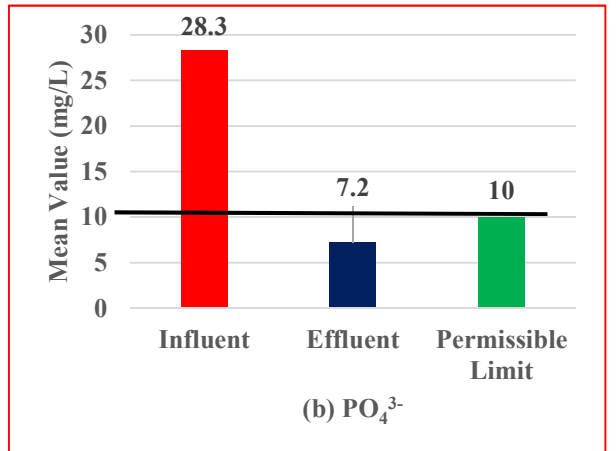
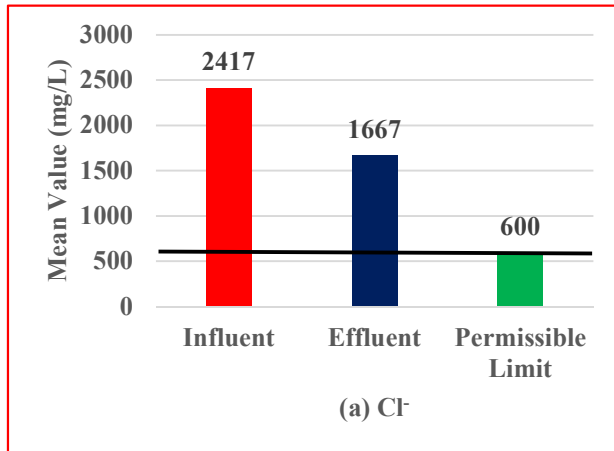
### 4.1.2 Anionic parameters of the CETP influent and effluent

In this research, the concentrations of five anions— $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{PO}_4^{3-}$  in the tannery influent, effluent, surface water, and groundwater samples were determined. The results of the analysis are presented below:

#### 4.1.2.1 Concentration of chloride ion ( $\text{Cl}^-$ )

Waters with chloride ( $\text{Cl}^-$ ) ions are almost always natural (Islam and Mostafa, 2022). According to EPA (2001) guidelines 250 mg/L of chloride is the recommended maximum content in water. Both the lower and higher permitted limits could be harmful to people. The average value of chloride ( $\text{Cl}^-$ ) concentration in the influent and effluent of the Savar tannery industrial estate was found to be 2417 and 1667 mg/L (**Figure 4.4 (a)**), respectively during the study period. These chloride values were greater than the ISW-BDS requirement of 600 mg/L for the discharge of tannery effluent into waterways in the studied areas (DoE-BD, and ISW-BDS-ECR, 2023). Ghosh and Hossain (2019) illustrated that the chloride concentration of the tannery influent and effluent was 4500 mg/L and 3800 mg/L, respectively which was almost double in the present study. The incidence of a higher amount of chloride content in tannery effluent was due to adding the surplus quantity of NaCl for the preservation, bleach liquor, which is extremely hazardous because it contains chloride ions, and pickling procedures of the raw skins and hides. A similar observation was delivered by several reports (Chowdhury et al., 2015; Bhatia, 2005, Bosnic et al., 2000).

Thus, it indicated a load on the surrounding environment (Islam and Mostafa, 2022). Hence, a higher value of chlorides in the composite effluent increased the chloride contamination of the adjacent water bodies (Monira et al., 2023). Aleem et al. (2016), stated that the most common toxicity of  $\text{Cl}^-$  is irrigation water. Since  $\text{Cl}^-$  is not absorbed by soils, it rapidly flows with the water in the soil. As a result, the crops absorb chlorides and store them in their leaves. Injury symptoms such as leaf burn or drying of the leaf tissue appear when the chloride content in the leaves is higher than what the crop can tolerate (Ayers and Westcot, 1985). The present study revealed significant  $\text{Cl}^-$  contamination in the studied area.



**Figure 4.4 Concentration of (a)  $\text{Cl}^-$ , (b)  $\text{PO}_4^{3-}$ , (c)  $\text{NO}_3^-$ , (d)  $\text{SO}_4^{2-}$ , and (e)  $\text{HCO}_3^-$  in the tannery influent and effluent**

#### 4.1.2.2 Concentration of Phosphate ion ( $\text{PO}_4^{3-}$ )

Phosphate ( $\text{PO}_4^{3-}$ ) is usually the restrictive nutrient for algal growth. Low concentrations of  $\text{PO}_4^{3-}$  ion are suggested because their presence in water bodies can lead to eutrophication (Zhang et al., 2011). The results of the present research showed that the concentration of  $\text{PO}_4^{3-}$  ions in the tannery influent and effluent ranged from 26.6 to 29.6 mg/L with an average value of 28.3 mg/L and 6.9 to 7.5 mg/L with an average value of 7.2 mg/L, respectively (**Figure 4.4 (b)**). Which was almost within the DoE-BD, 2023 discharge standard (10 mg/L) after treatment. Whitehead et al. (2021) illustrated that the mean concentration of phosphate in the untreated tannery effluent in Bangladesh was 27.6 mg/L, which shows some similarities with the present study results. However, a number of additives, such as wet and dry strength additives containing phosphorus compounds, water conditioners, defoamers, scale inhibitors, slimicides, biocides, dyes/pigments, and detergents, may increase the concentration. The municipal effluent discharges may also produce higher levels of  $\text{PO}_4^{3-}$ . A similar observation was delivered by various researchers (Islam and Mostafa, 2020; Shakil and Mostafa, 2021). Therefore, it can be concluded that the tannery effluent was free of  $\text{PO}_4^{3-}$  pollution based on the phosphate ion concentration.

#### 4.1.2.3 Concentration of nitrate ion ( $\text{NO}_3^-$ -N)

One of the crucial nutrients for algae growth is nitrate, which also contributes to eutrophication at high concentrations (Islam and Mostafa, 2022). The results of the present research showed that the concentration of nitrate ions in the tannery influent and effluent ranged from 56.2 to 64.25 mg/L and, 3.25 to 4.65 mg/L with a mean value of 60.18 mg/L and 4 mg/L, respectively (**Figure 4.7(c)**). According to DoE-BD (2023), 10 mg/L is the maximum permissible limit of nitrate and in the study present study, the nitrate concentration was higher than the maximum permissible standard before treatment but after treatment, the nitrate concentration was within the permissible range. In a study, Sultana et al. (2009) found that the average amount of nitrate ion for untreated effluent was 68.87 mg/L. According to another study, the average  $\text{NO}_3^-$  concentration in the treated samples ranged from 2.86 to 5.65 mg/L (Momtaz et al., 2012). Which shows some similarities with the present study. The concentration of nitrate was obtained due to

the use of excess ammonia in the deliming stage and due to the presence of aqueous protein materials which come from the liming stage. A similar observation was delivered by Chowdhury et al. (2013, 2015).

Nitrification of surface water and groundwater is caused by nitrate ions, which may have detrimental consequences on a person's health (Patel, 2016). Nitrate is a frequent contaminant of groundwater and surface water that can harm animals, including newborns, and cause eutrophication of aquatic environments (Fennessy and Cronk, 1997). Methemoglobinemia, which can result in neonatal death, can develop when bacteria convert the comparatively harmless nitrate ion to the nitrite ion (Winton et al., 1971). However, the  $\text{NO}_3^-$  ion concentrations of the effluent were lower than the permissible limit after treatment, indicating that the nitrate pollution in that area was simply moderate.

#### **4.1.2.4 Concentration of sulfate ion ( $\text{SO}_4^{2-}$ )**

Sulfate ( $\text{SO}_4^{2-}$ ) ion naturally exist in water, which are colorless and odorless. Sulfates are sulfur and oxygen compounds that remain in the water as dissolved salts. Sulfates are more concerning since they frequently occur in higher quantities (Islam and Mostafa, 2022). The results of the present research showed that the concentration of sulfate ions in the tannery influent and effluent ranged from 1890 to 1950 mg/L and, 1830 to 1870 mg/L with a mean value of 1900 mg/L and 1850 mg/L, respectively (**Figure 4.4 (d)**). According to DoE-BD (2023), 400 mg/L is the maximum permissible limit of sulfate and in the present study, the sulfate concentration was higher than the maximum permissible standard. Ghosh and Hossain (2019) illustrated a similar observation. Whitehead et al. (2021) illustrated that the mean concentration of sulfate of the untreated tannery effluent in Bangladesh was 1883.6 mg/L, which shows some similarities with the present study results. The higher content of sulfate in the composite tannery effluent samples may also be the result of many auxiliary chemicals used in the industry like the use of chrome tanning powders, sulfuric acid, or by-products containing a lot of sodium sulfate, which can be responsible for the high quantities of sulfate found there. According to Chowdhury et al. (2013, 2015) due to the massive amounts of sodium sulfide used in the liming and unhairing process to make lime pelt, the liming and unhairing effluent has a

very high content of sulfate (about 27000 mg/L). A similar observation was delivered by Bosnic et al. (2000).

Due to the excess sulfuric acid added during pickling and the unhairing process, it is then oxidized to sulfate before being discharged into the sewer. At a pH level of less than 8.5, hydrogen sulfide is generated. Even in trace amounts, this gas has a disagreeable smell and is extremely poisonous to many types of life (Balasubramanian et al., 2000; Dorman et al., 2000). Fish mortality may happen in higher concentrations at a sulfide concentration of 10 mg/L (Chowdhury et al., 2013, 2015). Agarwal (1996) stated that sulfate ion-containing effluent shouldn't be dumped into bodies of water because a higher concentration could alter the water's flavor. Sulfate ions often correlate with high levels of hardness and have a laxative impact on domestic animals and humans (Islam and Mostafa, 2022). Therefore, based on sulfate concentration, it is noticeable that the effluent of the current study area was not free of sulfate pollution.

#### **4.1.2.5 Concentration of bicarbonate ion ( $\text{HCO}_3^-$ )**

Bicarbonate ( $\text{HCO}_3^-$ ) ion plays a dominant role in electrical conductivity (Shakil and Mostafa, 2021). It is a simple one-carbon molecule and essential in a variety of biological functions (Dey and Islam, 2015). The results of the present research showed that the concentration of bicarbonate ions in the influent and effluent ranged from 1050 to 1250 mg/L and, 100 to 730 mg/L with a mean value of 1200 mg/L and 315 mg/L, respectively (**Figure 4.4(e)**). According to DoE-BD (2023), there is no permissible limit for bicarbonate but in the study present study, the bicarbonate concentration was high. Hussian et al. (2004) observed that tannery effluent had a greater concentration of bicarbonate ions, which is consistent with the current findings. A higher concentration of bicarbonate was obtained due to the use of various auxiliary chemicals during the processing of rawhide and skins. Various researchers illustrated similar observations (Whitehead et al. (2021) and Ghosh and Hossain, 2019). Lower concentrations of bicarbonate ions in water are not regarded as pollution, while higher concentrations lower the degree of water quality (Islam and Mostafa, 2018, 2020, and 2022).

The higher value of bicarbonate can harm aquatic organisms (Harper et al., 2014). Many macroinvertebrates, including chironomids, crayfish, and other species of fish, including

catfish, rainbow trout, and bluegill, are tolerant to bicarbonates (Bringolf et al., 2005). However, the effluent under the current investigation had greater concentrations of  $\text{HCO}_3^-$ , indicating a little more water contamination in the studied area.

### **4.1.3 Cationic Parameters of the CETP influent and effluent**

In this research, the concentrations of various cations like  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ , in the tannery influent, effluent surface water, and groundwater samples were determined (**Table 4.1**). The results of the analysis are presented below:

#### **4.1.3.1 Calcium ( $\text{Ca}^{2+}$ )**

The human body and the crust of the earth both contain large amounts of mineral calcium ( $\text{Ca}^{2+}$ ). The results show that the concentrations of sodium ions ranged from 206 to 232 mg/L in the influent and 85 to 115 mg/L in the effluent with the mean values of 225.3 and 98.3 mg/L, respectively during the research period (**Table 4.1**). Those values were much higher than the permissible limit (200 mg/L) set by (USEPA, 2004) before treatment but after treatment from the CETP, this value was within the permissible limit. Calcium concentration was found due to the use of various auxiliaries during the processing of raw hides and skins. A similar observation was made by various researchers (Monira et al., 2022, 2023; Chowdhury et al., 2013). Along with the descent of the testis, this ion is important for human cell function, heart disease, hormones, cancer, fluid balance inside the body, neurological illness, muscular contraction, etc. (Tandogan and Ulusu, 2005; Pravina et al., 2012). Although calcium is harmful to the brain, urinary tract, kidney, vascular disease, and constriction of bone regeneration, it is beneficial for bones and prevents osteoporosis (Nerbrand et al., 2003; Heaney et al., 1982). The current research shows that there is no environmental risk associated with the calcium concentration in the effluent.

#### **4.1.3.2 Sodium ( $\text{Na}^+$ )**

One of the most significant inorganic components of tannery effluent is sodium ( $\text{Na}^+$ ), which is typically present as salts such as chloride, bicarbonate, phosphate, nitrate, and sulfate (Whelton et al., 2007). It is an important electrolyte that helps maintain the balance of water or other fluids in the cells of the human body (He and MacGregor, 2008).

The results show that the concentrations of sodium ions ranged from 1960 to 2000 mg/L in the influent and 1647 to 1944 mg/L in the effluent with the mean values of 1884 and 1814 mg/L, respectively during the research period (**Table 4.1**). Those values were much higher than the permissible limit (200 mg/L) set by ISW in BDS. It may be caused due to the excess use of sodium chloride for primary preservation. A similar observation was made by various researcher (Monira et al., 2022; Chowdhury et al., 2013). The dark brown type soaking effluent was caused by the presence of blood, filth, vessels, and too much sodium chloride (Chowdhury et al., 2013, 2015).

Sodium ions also maintain healthy muscle and neuron function, blood acid-base balance, stable blood pressure, plasma osmotic pressure, and other functions (Caldwell et al., 2010). Hyponatremia is the medical term for a lack of sodium in the body. However, a high level of  $\text{Na}^+$  raises blood pressure as it causes the body to retain more fluid, which also raises the risk of heart disease, kidney disease, stomach cancer, osteoporosis, and stroke (Farquhar et al., 2015). High sodium concentrations revealed significant  $\text{Na}^+$  contamination in the studied area.

#### **4.1.3.3 Potassium ( $\text{K}^+$ )**

Potassium ( $\text{K}^+$ ) is naturally present in tannery effluent as salts such as chloride, bicarbonate, nitrate, and sulfate. The results show that the concentrations of  $\text{K}^+$  ranged from 1.3 to 2.1 mg/L in the influent and 1.0 to 1.8 mg/L in the effluent with the mean values of 1.6 and 1.3 mg/L, respectively during the research period (**Table 4.1**). Those values were much less although there are no established guidelines for  $\text{K}^+$  in Bangladesh. Potassium concentration was found due to the use of various auxiliaries during the processing of raw hides and skins. A similar observation was made by various researchers (Monira et al., 2023; Chowdhury et al., 2015).

Normally potassium ( $\text{K}^+$ ) concentration remains lower than that of other relevant cations in effluent (Whelton et al., 2007). That shows some similarity with the study present study. It is a crucial component of the human diet because, along with  $\text{Na}^+$ , it maintains the cell's normal osmotic pressure (Grollman, 1961; He and MacGregor, 2008). Additionally, it is essential for the release of insulin, muscle contraction, creatinine phosphorylation, carbohydrate digestion, protein disintegration, and nerve stimulation. It

also functions as a co-factor for other physiological enzymes (WHO, 2018). Increasing  $K^+$  and decreasing  $Na^+$  in human meals can help control hypertension and reduce the risk of cardiovascular disease and death (Aaron and Sanders, 2013).

However, the extra amount of  $K^+$  in the human body can lead to cardiac problems, depression, and muscle weakness (UKEVM, 2003; Gosselin et al., 1984). The current research shows that there is no environmental risk associated with the potassium concentration in the effluent.

**Table 4.1 Cationic parameters of tannery Influent and Effluent**

| Parameters |           | Periods                    |                        |                            |                 | Permissible limit |                       |                  |
|------------|-----------|----------------------------|------------------------|----------------------------|-----------------|-------------------|-----------------------|------------------|
|            |           | Sep-Oct<br>(2021-<br>2022) | Dec-Jan<br>(2021-2022) | March-April<br>(2022-2023) | Mean<br>±<br>SD | ISI-<br>2000      | NEQS<br>2004<br>USEPA | ISW<br>In<br>BDS |
| Na         | Influent  | 1991                       | 1960                   | 2000                       | 1884±132        | -                 | -                     | 200              |
|            | Effluent  | 1852                       | 1647                   | 1944                       | 1814±152        |                   |                       |                  |
| K          | Influent  | 2.1                        | 1.28                   | 1.3                        | 1.6±0.9         | -                 | -                     | -                |
|            | Effluent  | 1.8                        | 1.0                    | 1.0                        | 1.3±0.8         |                   |                       |                  |
| Ca         | Influent  | 206                        | 232                    | 238                        | 225.3±24.1      | -                 | 200                   | -                |
|            | Effluent  | 115                        | 85                     | 95                         | 98.3±27.3       |                   |                       |                  |
| Cu         | Influent  | 1.8                        | 1.7                    | 1.8                        | 1.8±0.1         | 2                 | 1.5                   | -                |
|            | Effluent  | 0.94                       | 0.95                   | 0.93                       | 0.94±0.03       |                   |                       |                  |
| Zn         | Influent  | 1.6                        | 1.7                    | 1.8                        | 1.7±0.1         | 5                 | 5                     | 5                |
|            | Effluents | 0.9                        | 0.95                   | 0.93                       | 0.93±0.02       |                   |                       |                  |
| Cr         | Influent  | 75.1                       | 85.8                   | 80.9                       | 79.2±5.2        | 0.1               | 0.05                  | 2                |
|            | Effluent  | 5.9                        | 6.3                    | 6.4                        | 6.1±0.3         |                   |                       |                  |
| Fe         | Influent  | 2.6                        | 2.7                    | 2.9                        | 2.7±0.2         | 2                 | -                     | -                |
|            | Effluent  | 1.8                        | 2.7                    | 1.9                        | 2.05±0.4        |                   |                       |                  |
| Pb         | Influent  | 0.30                       | 0.39                   | 0.39                       | 0.36±0.1        | 0.2               | 0.01                  | -                |
|            | Effluent  | 0.20                       | 0.29                   | 0.29                       | 0.26±0.1        |                   |                       |                  |
| Mn         | Influent  | 0.7                        | 0.5                    | 0.6                        | 0.6±0.1         | 0.2               | 0.05                  | -                |
|            | Effluent  | 0.2                        | 0.3                    | 0.2                        | 0.2±0.1         |                   |                       |                  |

#### **4.1.4 Heavy metals of the CETP influent and effluent**

The density, atomic weights, and atomic numbers of heavy metals remain relatively high. The hypothesis is that heavy metals, which are thought to be associated with toxicity and heaviness, can cause toxicity even at low exposure concentrations. Over the last few years, there has been an increasing pattern in environmental contamination brought on by trace metals that are linked to ecological and global public health. Additionally, due to their exponential increase in use across a variety of industrial, agricultural, household, and technological uses, human exposure has significantly increased (Bradl, 2002). Geogenic, industrial, agricultural, pharmaceutical, domestic waste, and atmospheric components are some of the sources of heavy metals in the environment that have been reported (Huq, 2005). In tannery effluent, metals progress from metal complex dyes and their derivatives through dye-baring agents, oxidizing agents, and finishers (Heinfling et al., 1997; Zeiner et al., 2007; Mountassir et al., 2013). Several heavy metals like Cr, Mn, Fe, Ni, Cu, Zn, Pb, and Cd were examined in the influent, effluent, surface water, and groundwater as part of this study. The results are shown in **Table 4.1**.

##### **4.1.4.1 Chromium (Cr)**

Chromium (Cr) is a transition metal. Leather industrial effluent emitted greater levels of metal, particularly chromium (Ghosh & Hossain, 2019). The results show that the concentrations of Cr 75.1 to 85.8 mg/L in the influent, and 5.9 to 6.4 mg/L in the effluent, with the mean value of 79.2 and 6.1 mg/L, respectively during the research period (**Table 4.1**). Those values were much higher than the permissible limit (2 mg/L) set by ISI-2000. Ghosh & Hossain (2019) illustrated the mean value of chromium concentration in the influent and effluent was 76.1 and 6.5 mg/L, respectively which was very similar to the present study. These results were obtained due to the chrome-tanning process because the tanning process makes substantial use of chromium, which is regarded as a major contaminant. A similar observation was stated by Sajil Kumar & James (2019). The present findings were higher than the reported values indicating high Cr poisoning in the study area.

Because of the accumulation of chromium, these effluents are deposited into groundwater, released into rivers or canals, and both (Ghosh & Hossain, 2019). Most of the regions in and surrounding tanneries are believed to have extremely high levels of surface and groundwater pollution (Mondal and Singh, 2005; Ram et al., 2012; Sajil Kumar, 2014). Exposure to chromium, pentachlorophenol, and other poisonous substances increases the threat of dermatitis, ulcer nasal septum perforation, and lung cancer (Carlos et al., 2002, Barnhart et al., 1997; Barceloux et al., 1999, Bajza and Vrcek, 2001; Kornhauser et al., 2002 and Stoyanva et al., 2004). According to several reports, the effluent from beam house processing has significant levels of chromium, sulfate, sulfide, total solids, and chloride (Cooman et al., 2002; Gupta, 2003; Junior et al., 2006). Chromium, salts, dyestuff residues, fat liquoring agents, syntans, and other organic debris are the main post-tanning contaminants (Bajza and Vrcek, 2001; UNIDO, 2000).

During the chrome tanning process, trivalent chromium is released. Compared to hexavalent chromium, it is substantially less toxic. All living things require the trace element chromium (Cr). It is required for the proper functioning of insulin and the metabolism of fat and glucose (Thacker et al., 2007). Trivalent chromium is difficult to dissolve and 100 times less toxic than hexavalent chromium. The potency of hexavalent chromium to cause mutations, irritation, and corrosion of the skin and respiratory tract in most microorganisms, as well as lung cancer in humans, has led to its identification as one of the most harmful environmental pollutants (Liu et al., 2005; Bhinde et al., 1996). Around 2% of all effluent is contributed by the chrome tanning process. Poultry feed manufacturers use materials of tanneries due to the high protein content of the solid effluent e.g., fleshing, raw trimming, chrome shaving, buffing dust, etc. Rafiquallah et al. (2008) showed that poultry feed is made using solid effluent (chrome shaving dust) which contain hexavalent forms of chromium in the study country. It seems that during the feed preparation, the transition of trivalent chromium to hexavalent chromium takes place, which poses a serious threat to human health (Javed, 2005). Therefore, based on Cr concentration, it is noticeable that the effluent of the current study area were not free of chromium pollution.

#### 4.1.4.2 Iron (Fe)

It is the third most common element in the crust of the earth and is still present as ferrous ( $\text{Fe}^{2+}$ ) and ferric ( $\text{Fe}^{3+}$ ) oxides, sulfides, hydroxides, and carbonates (Knepper, 1981; Elinder et al., 1986). Even though low concentrations of iron are necessary for human food and plant metabolism and cannot cause significant damage, they can stimulate the growth of harmful bacteria (iron bacteria) inside water supply systems, which leads to the deposition of a slushy coating on the piping system (CanDNHW, 1990).

The results show that the concentrations of iron ions ranged from 2.6 to 2.9 mg/L in the influent and 1.8 to 2.7 mg/L in the effluent with the mean values of 2.7 and 2.05 mg/L, respectively during the research period (**Table 4.1**). Those values were slightly higher than the permissible limit (2 mg/L) set by ISI-2000. Ahmed et al., (2019) stated that in Bangladesh the concentration of Fe varied from 2.5 to 3.0 mg/L. According to other researchers, the concentration of Fe in the effluent was similar to the current study and ranged from 2.1 to 2.9 mg/L (Joshi et al., 2015) and was approximately 2.8 mg/L (mean) (Ram et al., 2011). Which shows some similarity with the present study. Iron concentration was found due to the excess use of water, numerous types of dyes, and various auxiliaries during the processing of raw hides and skins. A similar observation was stated by various researchers (Monira et al., 2023; Chowdhury et al., 2015; Ahmed et al., 2019; Islam and Mostafa, 2018). Although most pathogenic organisms require iron for growth, the presence of high iron content may make them more dangerous. Fe poisoning can be dangerous and is an important contributor to the emergence of heart disorders (Sobana and Swaminath, 2007). Additionally, excessive iron levels (above 0.3 mg/L) can cause diabetes, hemochromatosis, stomach issues, nausea, and a tendency to vomit in patients (Bothwell, 1988; Swaminathan et al., 2007; Toyokuni, 2009).

Therefore, based on Fe concentration, it is noticeable that the effluent of the current study area was not free of iron pollution.

#### 4.1.4.3 Lead (Pb)

Another widely poisonous trace element that poses a serious threat to human health is lead (Pb) (WHO, 2011; Flora et al., 2012). One of the earliest metals used by humans was

lead.  $\text{Pb}^{2+}$  and lead hydroxy complexes are the most stable forms of lead. Lead is not a necessary element, but it is a well-known metal toxin whose effects have been studied more thoroughly than those of other heavy metals (Shakil and Mostafa, 2021).

The results show that the concentrations of lead ions ranged from 0.30 to 0.39 mg/L in the influent and 0.20 to 0.29 mg/L in the effluent with the mean value of 0.4 and 0.3 mg/L, respectively during the research period (**Table 4.1**). Those values were slightly higher than the permissible limit (0.2 mg/L) set by ISI-2000. Lead concentration was found due to the excess use of water and various auxiliaries during the processing of raw hides and skins. The results of the present investigation were partially verified by a study by Manekar et al. (2014) on the effluent of a tannery industry in western India, which found that the Pb concentration fluctuated between 0.21 and 0.28 mg/L. This might be because the relevant tannery industries employ colors and other chemicals that contain Pb. A similar observation was stated by various researchers (Monira et al., 2023; Islam and Mostafa, 2018; Chowdhury et al., 2015). Paints, solders, pipelines, construction materials, gasoline, and other products release lead into surface water (Wuana and Okieimen, 2011). Due to the widespread usage and distribution of tetraethyl lead (TEL) as a gasoline additive, the toxicants and environmental consequences of organo lead complexes are considerable (Wuana and Okieimen, 2011).

One naturally occurring element, lead, is harmful to the central and peripheral nerve systems and has an impact on the brain and behavior (WHO, 2006). It is typically poisonous and builds up in the skeleton; newborns, children, and pregnant women are particularly vulnerable to its negative health effects (Moore and Ramamoorthy, 1984). Absorption to lead for a long time can have a variety of biological impacts (Elom et al., 2014). These side effects may include adult blood pressure increases, altering the chemistry of red blood cells, delaying a child's normal physical and mental development, reducing a baby's capacity for hearing and learning, kidney illness, a lack of attention span, cancer, and stroke (Baldwin and Marshall, 1999; Moore, 1988; Ong and Lee, 1980). The hematological, renal, reproductive, and central neurological systems are adversely affected by lead exposure in a variety of ways, primarily through an increase in

oxidative stress (Flora et al., 2012). The study found that there is a significant risk of Pb poisoning in the study areas.

#### **4.1.4.4 Manganese (Mn)**

Manganese is a vital component of plant, animal, and human metabolism. It is necessary for the operation of various cellular enzymes. According to reports, it is necessary for biological activity in all kinds of animals (Islam and Mostafa, 2018, 2022).

The results show that the concentrations of manganese (Mn) ions ranged from 0.5 to 0.7 mg/L with a mean value of 0.6 mg/L in the influent and 0.2 to 0.3 mg/L with a mean value of 0.2 mg/L in the, respectively during the research period (**Table 4.1**). Those values were slightly higher than the permissible limit (0.2 mg/L). In the untreated wastewater, the Mn concentration ranged from 0.68 to 0.72 mg/L, according to a study report (Islam et al., 2016), which is similar to the findings of the current investigation. Manganese concentration was found due to the excess use of water, dye bath stuff, and various auxiliaries during the processing of raw hides and skins. A similar observation was found by Chowdhury et al. (2013). Mn overdose can also result in hallucinations, memory loss, disorientation, and emotional instability (Gupta and Gupta, 1998). Hydrolases, kinases, transferases, and decarboxylases can all be activated by it (IPCS, 2002). However, excessive use of Mn-rich water (>1.8 mg/L) may result in neurological symptoms like Parkinson's disease (Kondakis et al., 1989). It is shown that the current research's effluent contained significant Mn contamination.

#### **4.1.4.5 Zinc (Zn)**

Zn is a naturally occurring trace metal that is abundant and an essential component for human metabolism and growth, especially for infants and young children (Askary et al., 2011). One of the essential micronutrients, zinc contributes to physiological processes in plants and has favorable impacts on plant growth. However, water can get contaminated by significant amounts of Zn from industrial effluent (Islam and Mostafa, 2018, 2022).

The results show that the concentrations of zinc ions ranged from 1.6 to 0.95 mg/L in the influent and 1.6 to 1.8 mg/L in the effluent with the mean values of 1.7 and 0.93 mg/L, respectively during the research period (**Table 4.1**). Those values were within the permissible limit (5mg/L) set by ISI-2000.

According to studies by Jasim et al. (2009), the Zn concentration of the untreated effluent at DEPZ ranged from 0.49 to 1.69 mg/L. Momtaz et al. (2012) also presented a study result that the concentration of Zn in the untreated effluent was in the range of 0.90 to 1.5 mg/L, which is very similar to the current findings of the study. Due to the use of chemical impurities and the wet process of leather in industries, Zn content in effluent increases. A similar observation was stated by Hussain et al. (2004). Birth defects may result from a Zn deficiency (Wuana and Okieimen, 2011). Aquatic life is most negatively impacted by high Zn concentrations in the early stages of development (ImtiazUddin et al., 2014). Living in Zn-contaminated streams might cause some fish to accumulate Zn in their bodies. When Zn enters into these fish, it has the potential to biomagnify as it moves up the food chain (Wauna and Okieimen, 2011). The current research shows that there is no environmental risk associated with the Zn concentration in the effluent.

#### **4.1.4.6 Copper (Cu)**

Copper (Cu) plays a vital role in metabolism and is a necessary element for both plants and animals (Bremmer and Beattie, 1990). The results show that the concentrations of copper ions ranged from 1.7 to 1.8 mg/L with a mean value of 1.8 in the influent and 0.93 to 0.95 mg/L with a mean value of 0.94 mg/L in the effluent, respectively during the research period (**Table 4.1**). Those values were within the permissible limit (2 mg/L) set by ISI-2000. Copper concentration was found due to the excess use of water, various dyes, and various auxiliaries during the processing of raw hides and skins. Cu is widely used in pipes and fittings, and in an acidic environment, it may dissolve from water pipes. To control harmful algal growth, copper sulfate ( $\text{CuSO}_4$ ) salt is occasionally added to water supply tanks. Copper compounds have also been used extensively in agricultural insecticide treatments. Similar observations were found by several research (Monira et al., 2022, 2023; Chowdhury et al., 2013, 2015; Ahmed et al., 2019; Islam and Mostafa, 2018, 2022).

Copper participates in many metabolic processes found in all living things (Islam and Mostafa, 2018, 2020). Due to its ability to act as an electron donor or acceptor in metalloenzymes, copper is an essential component of human nutrition (Deepali and Gangwar, 2010). Although humans can tolerate a relatively high quantity of copper, too much metal can have serious negative effects on health (Baysal et al., 2013). However, it

may cause deliberate irritability, anemia, kidney and liver damage, gastrointestinal issues, and anemia in high quantities (Imtiazuddin et al., 2014). Cu concentrations below 1 mg/L are toxic to aquatic flora, whereas concentrations around this level can be hazardous to some fish (Nergis et al., 2005; Tuzen et al., 2008). Based on the Cu concentration in the current findings, the effluent was free from Cu contamination.

#### **4.1.5 Removal Efficiency**

The performance efficiency of the CETP is presented in the following **tables (4.2, 4.3, and 4.4) and figure (4.5)**. The efficiency of the CETP was calculated by considering EC, COD, BOD, TSS, TDS, Hardness,  $\text{HCO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{N-NO}_3^-$ , Na, Ca, Cu, Cr, Zn, Fe, Mn, K, and Pb of the inlet and outlet of the CETP. The percentage of reduction in TSS, BOD, and COD was 88%, 83.7%, and 79.5% respectively. The maximum reduction of 87.5 % was observed in TSS followed by BOD, COD, Hardness, EC, and TDS which were 83.1 %, 79.5 %, 36.7 %, 10.8 %, and 4.8 % respectively. The above reduction indicates that removal efficiency ranges between 4.8 % to 87.5 % with an average removal efficiency of 50.4 % (**Table 4.2**). Which was not enough for satisfaction.

**Table 4.2 Removal efficiency (%) for physicochemical parameters**

| <b>Parameters</b>                                                                                          | <b>Influent (Avg)</b> | <b>Effluent (Avg)</b> | <b>% Removal</b> | <b>DoE-BD, 2023</b> | <b>ISW-BDS-ECR</b> | <b>NEQS</b> |
|------------------------------------------------------------------------------------------------------------|-----------------------|-----------------------|------------------|---------------------|--------------------|-------------|
| pH                                                                                                         | 8.6                   | 7.5                   | -                | 6-9                 | 6-9                | 6-9         |
| DO                                                                                                         | 0.7                   | 0.9                   |                  | 4-6                 | 4.8-9              | 4-6         |
| EC (µS/cm)                                                                                                 | 11430                 | 10190                 | 10.8%            | 1200                | 1200               | 288         |
| TDS                                                                                                        | 6817                  | 6486                  | 4.8%             | 2100                | 2100               | 3500        |
| TSS                                                                                                        | 1671                  | 209                   | 87.5%            | 150                 | -                  | 150         |
| BOD                                                                                                        | 573                   | 96.7                  | 83.1%            | 50                  | -                  | 50          |
| COD                                                                                                        | 1646                  | 337                   | 79.5%            | 200                 | -                  | 200         |
| TH                                                                                                         | 1150                  | 728                   | 36.7%            | -                   | -                  | -           |
| <p>Overall efficiency (Physico-chemical parameters):</p> $[(10.8+4.8+87.5+83.1+79.5+41.3)/6]100\%= 50.4\%$ |                       |                       |                  |                     |                    |             |

**\*(Parameters are expressed in mg/L except pH and EC)**

The percentage of reduction in  $\text{N-NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{HCO}_3^-$ , was 93 %, 74.5 %, and 43.3 %, respectively. The maximum reduction of 93 % was observed in  $\text{N-NO}_3^-$ . The above reduction indicates that removal efficiency ranges between 2.6 % to 93 % and an average removal efficiency of 49 % (**Table 4.3**). Which was comparatively lower than the removal efficiency of physicochemical parameters.

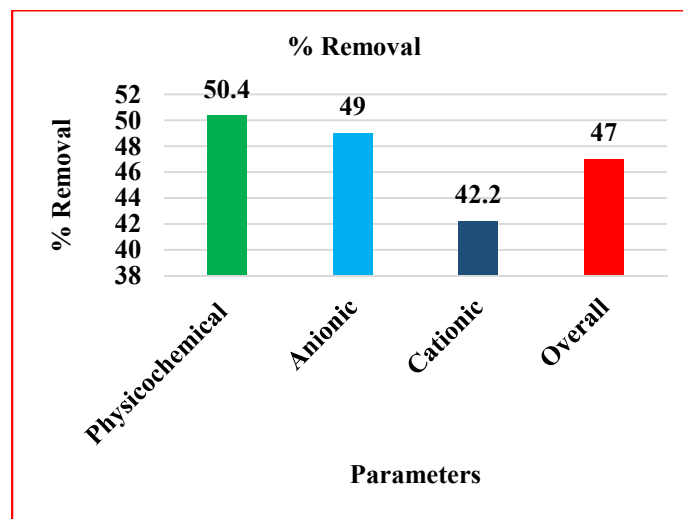
**Table 4.3 Removal efficiency (%) for Anionic parameters**

| <b>Parameters<br/>(mg/L)</b>                                                                                 | <b>Influent<br/>(Avg)</b> | <b>Effluent<br/>(Avg)</b> | <b>% Removal</b> | <b>DoE-BD, 2023</b> | <b>ISW-<br/>BDS-<br/>ECR</b> | <b>NEQS</b> |
|--------------------------------------------------------------------------------------------------------------|---------------------------|---------------------------|------------------|---------------------|------------------------------|-------------|
| HCO <sub>3</sub> <sup>-</sup>                                                                                | 1200                      | 680                       | 43.3%            | -                   | -                            | -           |
| PO <sub>4</sub> <sup>3-</sup>                                                                                | 28.3                      | 7.2                       | 74.5%            | 10                  | -                            | -           |
| SO <sub>4</sub> <sup>2-</sup>                                                                                | 1900                      | 1850                      | 2.63%            | 400                 | -                            | 5           |
| Cl <sup>-</sup>                                                                                              | 2417                      | 1667                      | 31%              | 600                 | -                            | 600         |
| N-NO <sub>3</sub> <sup>-</sup>                                                                               | 60.18                     | 4                         | 93%              | 10                  | -                            | 50          |
| <p>Overall efficiency (Anionic parameters):</p> $[(43.3\% + 74.5\% + 2.63\% + 31\% + 93\%) / 5]100\% = 49\%$ |                           |                           |                  |                     |                              |             |

The percentage reduction of cationic parameters in Cr, Ca, Zn, Cu, Pd, Fe, K, Mn, and Na was 92%, 53.6%, 46%, 48%, 29%, 24%, 17.6, 66.6, and 3.7%, respectively. A maximum reduction of 92 % was observed in Cr. The above reduction indicates that removal efficiency ranges between 3.7 % to 96 % with an average removal efficiency of 42 % (**Table 4.4**). Which was quite low. Then, finally, the study found the overall removal efficiency of the CETP was 47% (**Figure 4.5**).

**Table 4.4 Removal efficiency (%) for Cationic parameters**

| <b>Parameters<br/>(mg/L)</b>                                                                         | <b>Influent<br/>(Avg)</b> | <b>Effluent<br/>(Avg)</b> | <b>% Removal</b> | <b>DoE-BD, 2023</b> | <b>ISI-<br/>2000</b> |
|------------------------------------------------------------------------------------------------------|---------------------------|---------------------------|------------------|---------------------|----------------------|
| Ca                                                                                                   | 225                       | 98.3                      | 53.6%            | -                   | -                    |
| Cr                                                                                                   | 79.2                      | 6.1                       | 92%              | 0.5                 | 0.1                  |
| Na                                                                                                   | 1884                      | 1814                      | 3.7%             | -                   | -                    |
| Cu                                                                                                   | 1.8                       | 0.94                      | 48%              | 0.5                 | 2                    |
| Zn                                                                                                   | 1.7                       | 0.93                      | 46%              | 5                   | 5                    |
| Fe                                                                                                   | 2.7                       | 2.05                      | 24%              | 2                   | -                    |
| Pb                                                                                                   | 0.36                      | 0.26                      | 29%              | 0.01                | 0.2                  |
| Mn                                                                                                   | 0.6                       | 0.2                       | 66.6%            | 5                   | -                    |
| K                                                                                                    | 1.6                       | 1.3                       | 17.6%            | -                   | -                    |
| Overall efficiency (Cationic parameters):<br>$[(53.6+92+3.7+48+46+24+29+66.6+17.6) / 9]100\% = 42\%$ |                           |                           |                  |                     |                      |



**Figure 4.5 Removal Efficiency of the CETP**

#### 4.1.6 Characterization of the sediments

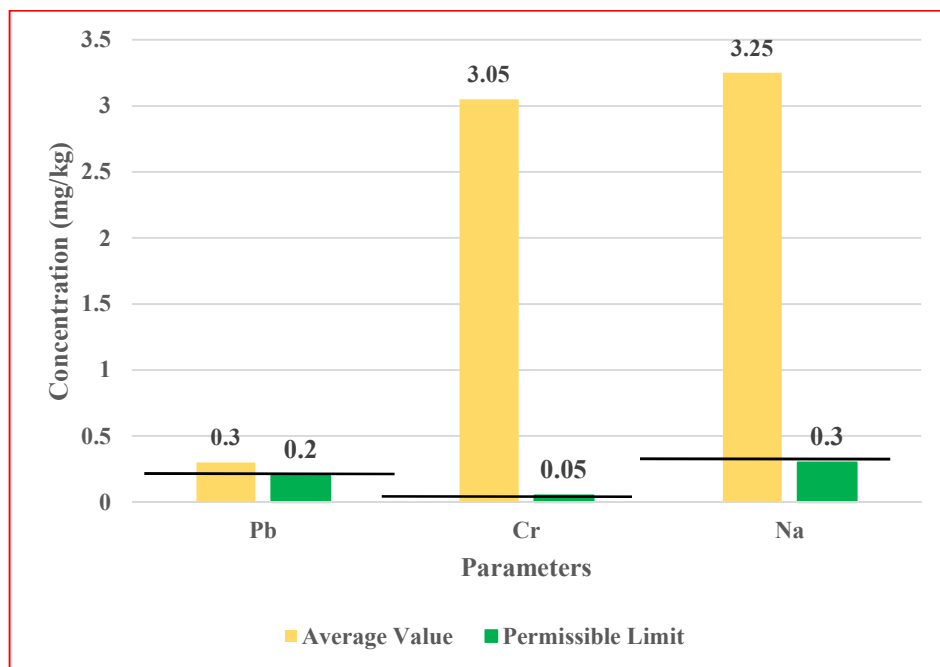
The characterization of the sediments collected from the CETP dumping area at Savar is listed in **Table 4.5**. The sediments was collected three times (pre-monsoon, monsoon, and post-monsoon) in a year, from the monsoon of 2021 to the pre-monsoon of 2023.

**Table 4.5 Characterization of the sediments collected from the CETP dumping area at Savar.**

| <b>Parameters<br/>(mg/kg)</b> | <b>Mean±SD</b> | <b>Permissible limit<br/>(US-EPA, 2012)</b> |
|-------------------------------|----------------|---------------------------------------------|
| Zn                            | 0.0134±0.01    | 0.751-1.125                                 |
| Mn                            | 0.1303±0.01    | -                                           |
| Fe                            | 0.4801±0.02    | -                                           |
| Cu                            | 0.0292±0.03    | 0.45-0.6                                    |
| K                             | 0.2627±0.03    | -                                           |
| Pb                            | 0.3±0.01       | 0.1-0.2                                     |
| Cr                            | 3.0589±0.02    | 0.05-0.1                                    |
| Ca                            | 0.0043±0.01    | 4.51-6.00                                   |
| Ni                            | 0.0028±0.01    | -                                           |
| Cd                            | 0±0.0          | 0.451-0.60                                  |
| Na                            | 3.2512±0.02    | 0.226-0.30                                  |

Three Heavy metal pollutants Cr, Pb, and Na were detected in the sediments sample (**Figure 4.6**). The percentage of these three heavy metals in tannery sediments was much higher than that of permissible standard (US-EPA, 2012). The average concentrations of Pb, Na, and Cr in tannery sediments were 0.3, 3.3, and 3.1, with a standard deviation (SD) of 0.01, 0.02, and 0.02, respectively (**Table 4.5**), which were much higher than the acceptable limits. Metal ions contained in the sediments were in the following order: Na > Cr > Fe > Pb > K > Mn > Cu > Zn > Ni > Ca. The soil of the study area was silty clay loam with a texture composition of 22.5 to 52.5% (Sultana et al., 2017). Metal concentration was found due to performing chrome tanning process, and geological

factors such as mineralization, as well as the weathering of carbonate/bicarbonate minerals by percolation and infiltration of chemical fertilizers, and raw materials used during the processing of raw hides and skins, that contributed to the metal ions concentrations of the sediments in the study area (Zakir et al., 2011; Mostafa et al., 2017; Islam and Mostafa, 2021). A similar observation was stated by various researchers (Shakil and Mostafa, 2021; De, 2011; Devi et al., 2011).



**Figure 4.6 The concentration of pollutants in the sediments**

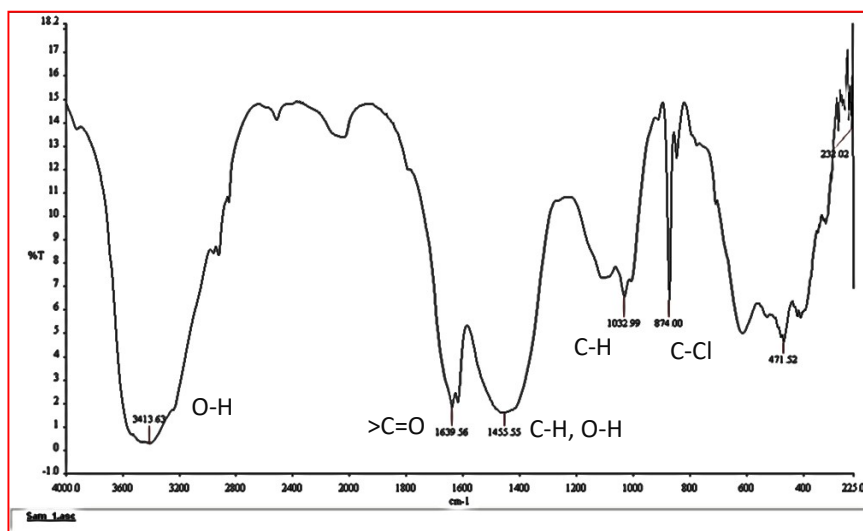
#### **4.1.7 Organic pollutants in the tannery influent and effluent**

Organic contaminants have serious environmental consequences. Many organic contaminants that stay in the environment for a prolonged period of time accumulate in the food chain and harm human health, animals, and plants. One of the biggest sources of organic contaminants is industrial effluent. Chlorinated phenols, monomeric phenols, acetaldehyde, lignin, resins, fatty acids, formic acid, acetic acid, quinone derivatives, methanol, methylglyoxal, and other chemicals are commonly found in tannery wastewater. These are the chemicals that degrade raw materials, and additives. In the tannery industry, almost 250 types of chemicals are used (Lacorte et al., 2003; Singh et

al., 2019). As a result, there is a serious risk of organic pollutants in the study area. Therefore, FTIR analysis (**Table 4.6**) of the influent and effluent collected from the CETP was conducted to identify the organic functional groups.

#### 4.1.7.1 FTIR analysis of the tannery influent and effluent

Fourier Transform Infrared Spectroscopy, also known as FTIR Analysis, is an established analytical technique used to identify organic functional groups. Functional groups are identified by particular peaks of the FTIR spectrum (**Table 4.6**).

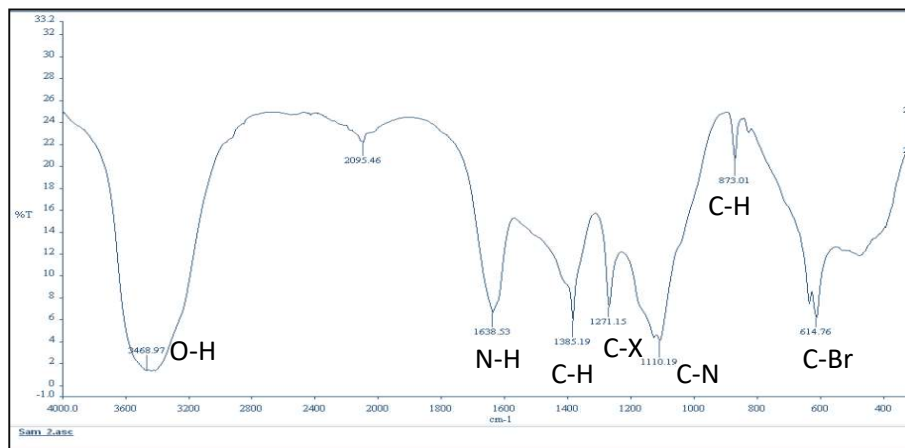


**Figure 4.7 FTIR analysis of tannery influent**

For influent, FTIR peaks 3413, 1639, 1455, 1032, and 874,  $\text{cm}^{-1}$  were detected (**Figure 4.7**).

The peak at 3413  $\text{cm}^{-1}$  was ascribed to -OH stretching vibration for H-bonded  $\text{H}_2\text{O}$  uptake, indicating the presence of alcoholic, and phenolic functional groups in the influent (Coradi et al., 2018; Repon et al., 2017; Bilba et al., 2007). The presence of a broadband peak at 1639  $\text{cm}^{-1}$  assigned C=C and C=O stretching, specified the existence of amide, ketone, and quinone conjugated carbonyl of lignin functional groups in the influent (El-Zaher et al., 2019). A sharp peak at about 1455  $\text{cm}^{-1}$  was consigned to C-H and O-H bending, directing the presence of alkane in the influent (Wang et al., 2016). The broadband peak at 1032  $\text{cm}^{-1}$  corresponds to asymmetric and symmetric ether linkage C-N stretching, indicating the presence of aliphatic amines in the influent (Repon

et al., 2017). The peak at  $874\text{ cm}^{-1}$  was characterized as a C-H bending, representative of the existence of 1, 2, 4 – trisubstituted, functional groups in the influent (Deveoglu et al., 2019; Arai et al., 2004).



**Figure 4.8 FTIR analysis of tannery effluent**

So, the study concluded that for influent, FTIR peaks 3413, 1639, 1455, 1032, and  $874\text{ cm}^{-1}$  were detected (**Figure 4.7**), which indicated the presence of alcohols, phenols, amide, ketone, quinone conjugated carbonyl of lignin, alkanes, 1, 2, 4 – trisubstituted, aromatic and aliphatic amines, functional groups in the influent (**Table 4.6**)

For effluent, FTIR peaks 3468, 1638, 1385, 1271, 1110, 873, and  $614\text{ cm}^{-1}$  were detected (**Figure 4.8**). The peak at  $3468\text{ cm}^{-1}$  was ascribed to -OH stretching vibration for H-bonded  $\text{H}_2\text{O}$  uptake and indicating the presence of alcoholic, and phenolic functional groups in the effluent (Repon et al., 2017; Bilba et al., 2007). The presence of a broadband peak at  $1638\text{ cm}^{-1}$  assigned C=C and C=O stretching, specified the existence of amide, ketone, and quinone conjugated carbonyl of lignin functional groups in the effluent (El-Zaher et al., 2019). A sharp peak at about  $1385\text{ cm}^{-1}$  was consigned to C-H and O-H bending, directing the presence of alkane in the effluent (Wang et al., 2016). The sharp peaks at 1271 and  $1110\text{ cm}^{-1}$  correspond to asymmetric and symmetric ether linkage C-N stretching and indicate the presence of aliphatic and aromatic amines in the effluent (Repon et al., 2017). The peak at  $873\text{ cm}^{-1}$  was characterized as a C-H bending and representative of the existence of 1, 2, 4 – trisubstituted functional groups in the

effluent (Deveoglu et al., 2019; Arai et al., 2004). The peaks at  $614\text{ cm}^{-1}$  corresponded to C-Br stretching vibration and indicated the presence of alkyl halide functional groups in the effluent (Abd El Aty et al., 2018).

So, we can conclude that for effluent, FTIR peaks 3468, 1638, 1385, 1271, 1110, 873, and  $614\text{ cm}^{-1}$  were detected (**Figure 4.8**), which indicated the presence of alcohols, phenols, amide, ketone, quinone conjugated carbonyl of lignin, alkanes, 1, 2, 4 – trisubstituted, alkyl halides, aromatic and aliphatic amines functional groups in the effluent (**Table 4.6**).

Among the identified functional groups, phenolic compounds, ketone, amide, quinone, lignins, aromatic and aliphatic amines are mostly toxic to human health and the environment (Gama et al., 2012; EHS, 2021; ScienceDirect. 2021). They are responsible for bioaccumulation, cytotoxic, mutagenic, hepatotoxic, carcinogenic, genotoxic, and mutagenic effects (Shakil and Mostafa, 2021; Islam and Mostafa, 2022).

**Table 4.6 Functional groups of the tannery influent and effluent by FTIR analysis**

| Range of band (cm <sup>-1</sup> ) | Influent (cm <sup>-1</sup> ) | Effluent (cm <sup>-1</sup> ) | Bond                             | Functional group                                         | References                                  |
|-----------------------------------|------------------------------|------------------------------|----------------------------------|----------------------------------------------------------|---------------------------------------------|
| 3500-3200                         | 3413                         | 3468                         | O-H stretching<br>H-bond         | Alcohols, phenols                                        | Coradi et al., 2018<br>Bilba et al., 2007   |
| 1650-1640                         | 1639                         | 1638                         | C=C stretching<br>C=O stretching | Amide, ketone, and quinone conjugated carbonyl of lignin | El-Zaher et al., 2019                       |
| 1460-1380                         | 1455                         | 1385                         | C-H bending<br>O-H bending       | Alkanes, O-H of phenol                                   | Wang et al., 2016                           |
| 1342-1266                         | -                            | 1271                         | C-N stretching                   | Aromatic amine                                           | Repon et al., 2017                          |
| 1250-1020                         | 1032                         | 1110                         | C-N stretching                   | Amines                                                   | Repon et al., 2017                          |
| 880-860                           | 874                          | 873                          | C-H bending                      | 1,2,4-trisubstituted                                     | Deveoglu et al., 2019;<br>Arai et al., 2004 |
| 850-550                           | -                            | 614                          | C-Br stretching                  | Alkyl halides or Organobromines                          | Abd El Aty et al., 2018                     |

## **4.2 Characterization of surface water**

The surface water five samples were collected three times (pre-monsoon, monsoon, and post-monsoon) in a year, from the monsoon of 2021 to the pre-monsoon of 2023 to analyze various physicochemical parameters (detailed results in Appendix II).

### **4.2.1 Physicochemical characterization of surface water**

The surface water samples were analyzed for some physic-chemical parameters, such as temperature, EC, DO, pH, TSS, TDS, TH, BOD, and COD and these are stated below:

#### **4.2.1.1 Temperature**

Temperature is an important parameter for assessing the quality of water. All aquatic life has a preferred temperature range (UNIDO, 2000). During the study, the highest surface water temperature (27°C) was recorded at the sample site SW1 with a standard deviation (SD) of 4.5, although most of the sample temperatures were 25°C. The temperature slightly dropped with increasing distance from the CETP discharge site in the study area. The temperature was found within the Bangladesh surface water standard in all sampling sites (**Table 4.7**). According to another study report, the minimum and maximum temperatures of the surface water were 25°C and 30°C, respectively (Hussein, 2013). When temperatures rise or fall much above or below this optimum range, the species is unable to survive in the body of water. Because warm water has less dissolved oxygen (DO) than cool water, aquatic organisms can't survive at low DO levels (Shakil and Mostafa, 2021). Furthermore, water temperature affects water chemistry (Islam and Mostafa, 2020). According to the study, the observed temperature of the surface water was near the room temperature. A similar observation was stated by Chowdhury et al. (2015), which supported the present study.

#### **4.2.1.2 pH**

The pH range of 6.5-8.5 is preferred by the majority of aquatic species (UNIDO, 2000). The pH level beyond this range has an adverse effect on the aquatic ecology (Yusuff and Sonicare, 2004; Rouse, 1979). The maximum pH of the surface water was 7.8 with a standard deviation (SD) of 0.5 at the SW1 sample site, but the pH of all sampling sites

was found to be 7.6. All of the pH values were within the acceptable range (**Table 4.7**). Ghosh and Hossain (2019) illustrated that the concentration of pH varied from 7.4 to 7.9, which supported the present findings.

#### **4.2.1.3 Dissolved Oxygen (DO)**

The concentration of Dissolved Oxygen (DO) in a body of water is a key indicator of water quality. A low DO level indicates contaminated water. The DO concentration in the surface water ranged from 1.6 to 5.5 mg/L. The concentration of DO increased with distance from the CETP discharge point. Surface water DO levels were below the permitted level at all the sampling sites (**Table 4.7**). Releasing organic pollutants from tannery industrial effluent induces DO depletion in the surface water. Aquatic organisms cannot breathe in a water body with a low DO level (Akan et al., 2007). Mishra et al. (2013) illustrated a similar observation, where the DO ranged from 1.2 to 6 mg/L.

#### **4.2.1.4 Electrical Conductivity (EC)**

The Electrical Conductivity (EC) of water represents the concentration of electrically charged ions dissolved in water (Venkatesh et al., 2008). The EC of the surface water body in the research area ranged from 407.5 to 2465  $\mu\text{S}/\text{cm}$  (**Table 4.7**). The highest recorded EC level of the surface water was 2465  $\mu\text{S}/\text{cm}$  with a standard deviation (SD) of 1101 at the SW1 sampling station. The values declined with distance from the CETP discharge point. At sampling location SW1, the EC level exceeded the allowable limit. The presence of a substantial volume of electrically charged ions in the tannery effluent raised the EC level of the surface water body. Devi et al. (2011) reported that the concentration of EC varied from 290 to 2720  $\mu\text{S}/\text{cm}$ , which supported the current study.

#### **4.2.1.5 Turbidity**

Turbidity is one of the most common and significant physical indicators of surface water. The surface water turbidity ranged from 28 to 30.5 NTU. The values declined with distance from the CETP discharge point. In Bangladesh, there is no surface water turbidity standard (**Table 4.7**). It is caused by the presence of particles and colored compounds in water. A parallel reflection was reported by Devi et al. (2011), which supported the present study.

**Table 4.7 Physical parameters of surface water around the CETP discharge area**

| Parameters         | Mean $\pm$ SD            |                |                |                       |                       | DoE-<br>BD,<br>2023 |
|--------------------|--------------------------|----------------|----------------|-----------------------|-----------------------|---------------------|
|                    | Sample Location          |                |                |                       |                       |                     |
|                    | SW1<br>(Mixing<br>point) | SW2<br>(100m)  | SW3<br>(500m)  | SW4<br>(1km)          | SW5<br>(2km)          |                     |
| Temp<br>(°C)       | 27 $\pm$ 4.5             | 25.6 $\pm$ 3.8 | 25 $\pm$ 3.5   | 25 $\pm$ 3.4          | 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<br>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         | $\geq 5$            |
| EC<br>$\mu$ S/cm   | 2465 $\pm$ 1<br>101      | 417 $\pm$ 257  | 410 $\pm$ 248  | 407.5 $\pm$ 243.<br>5 | 407.5 $\pm$ 234.<br>1 | 1200                |
| Turbidity<br>(NTU) | 30.5 $\pm$ 2.<br>5       | 28.5 $\pm$ 2.5 | 28.4 $\pm$ 2.4 | 28.4 $\pm$ 2.4        | 28.3 $\pm$ 2.4        | -                   |

#### 4.2.1.6 Total Suspended Solids (TSS)

Total Suspended Solids (TSS) is comprised of clay, algae, bacteria, degraded organic particles, and waste materials (Casey, 1997). These substances could be responsible for water contamination. The TSS level in the surface water body in the study area ranged from 46.5 to 265 mg/L. The maximum concentration of TSS in the surface water bodies was 265 with a standard deviation (SD) of 4.1 in SW1 sampling areas. It declined with distance from the CETP discharge point. However, the TSS concentrations at most of the sampling spots exceeded the permissible level (**Table 4.8**). Raw materials from the leather manufacturing process may enter the effluent and raise the TSS level of the surface water body. Various researchers conveyed the parallel observation (Mishra et al., 2013; Rouse, 1979).

#### **4.2.1.7 Total Dissolved Solids (TDS)**

The Total Dissolved Solids (TDS) are mainly a combination of cationic and anionic substances. The surface water TDS values in the CETP discharge areas ranged from 797.5 to 1440 mg/L. It declined with distance from the CETP release point. However, the TDS values were within the allowable range of surface water except for the SW1 sampling point (**Table 4.8**). The higher EC value indicates there were more cations and anions in the discharged tannery effluent. The increased conductivity altered the chelating physiognomies of water bodies (Akan et al., 2007). Various auxiliaries from the leather manufacturing process may enter the effluent and raise the TDS level of the surface water body. Venkatesh et al. (2008) reported that the concentration of TDS varied from 450 to 2300 mg/L, which supported the present findings.

#### **4.2.1.8 Biochemical Oxygen Demand (BOD)**

Biochemical Oxygen Demand (BOD) is the amount of oxygen consumed by bacteria or other microorganisms while decomposing organic materials under aerobic circumstances at a particular temperature. BOD is a key parameter for evaluating water quality because it represents the amount of organic contaminants. The BOD concentration of the surface water in the study area varied from 52.5 to 72.8 mg/L. The height BOD concentration of the surface water was 72.8 mg/L, with a standard deviation (SD) of 4.6 at the SW1 sampling areas. It declined with distance from the CETP release area. However, the BOD values at all the sampling sites exceeded the standard level (**Table 4.8**). Organic pollutants released from tannery effluent resulted in a high volume of BOD in the surface water. BOD was found to be the main pollutant during the research period. Various studies delivered the same observations (Shakil and Mostafa, 2021; Giri et al., 2014; Devi et al., 2011).

#### **4.2.1.9 Chemical Oxygen Demand (COD)**

Chemical Oxygen Demand (COD) denotes the volume of oxygen required to oxidize the organic and inorganic substances existing in water. COD is a key indicator for evaluating water quality as it specifies the amount of organic and inorganic contaminants. The highest concentration (282 mg/L) of COD in the surface water was found at the SW1 sampling site, whereas the minimum concentration (52.5 mg/L) was obtained at the SW5

sampling site. The COD declined with distance from the CETP release area. At all the sampling sites, COD values exceeded the permissible limit of surface water (**Table 4.8**). Organic and inorganic pollutants released from leather effluent resulted in a high volume of COD in surface water. COD was found to be the main pollutant during the research period like BOD. Several researchers conveyed similar opinions (Chowdhury et al., 2015; Giri et al., 2014; De, 2011).

#### 4.2.1.10 Total Hardness (TH)

Total Hardness (TH) is very substantial and significant for industrial, drinking, and irrigation purposes (Islam and Mostafa, 2022). TH is not caused by a single constituent by a diverse type of dissolved metal ions, including Ca and Mg, and anions, including carbonate, and bicarbonate (WHO, 2011). The TH of the surface water in the study area ranged from 123 to 262 mg/L (**Table 4.8**). The highest concentration (262.5mg/L) of TH was observed at the SW1 sampling areas. It declined with distance from the CETP release area. Raw materials used in the leather manufacturing process may come into effluent and increase the TH level of the surface water. Mishra et al. (2013), reported that the values of TH varied from 53 to 400 mg/L, which supported the present findings. Based on the concentration of the physicochemical parameter, the study observed that at the SW1 sampling point, aquatic life may be stressed. But the pollution level decreases with increasing distance.

**Table 4.8 Physiochemical parameters of surface water around the CETP discharge area**

| Parameters<br>(mg/L) | Mean ± SD (mg/L)         |               |               |              |              | DoE-<br>BD,<br>2023 |
|----------------------|--------------------------|---------------|---------------|--------------|--------------|---------------------|
|                      | Sample Location          |               |               |              |              |                     |
|                      | SW1<br>(Mixing<br>point) | SW2<br>(100m) | SW3<br>(500m) | SW4<br>(1km) | SW5<br>(2km) |                     |
| TSS                  | 265±4.1                  | 231±2.5       | 85.8±34.7     | 71.5±28      | 46.5±5.2     | 150                 |
| TDS                  | 1440±291.7               | 832.5±49.2    | 823.8±49.4    | 806±50.9     | 797.5±32     | 1000                |
| BOD                  | 72.8±4.6                 | 64.5±1.9      | 53.8±3        | 51.8±2.2     | 52.5±1.9     | 30                  |
| COD                  | 282±13.0                 | 237±12.6      | 228±14.4      | 215±10       | 205±19       | 100                 |
| Hardness             | 262.5±126.5              | 138±28.43     | 126.8±25.9    | 124.5±32.2   | 123±37.4     | -                   |

## 4.2.2 Anionic parameters in surface water

Anions are the counter of cations that form salts, and in the study, five anions like chloride ion ( $\text{Cl}^-$ ), sulfate ion ( $\text{SO}_4^{2-}$ ), nitrate nitrogen ( $\text{NO}_3^- \text{N}$ ), phosphate ion ( $\text{PO}_4^{3-}$ ), and bicarbonate ion ( $\text{HCO}_3^-$ ) of surface water samples were analyzed. The analyzed results of surface water samples are illustrated in **Table 4.9**.

### 4.2.2.1 Chloride ion ( $\text{Cl}^-$ )

The chloride ion ( $\text{Cl}^-$ ) exists naturally in water. However, the concentration in the effluent may vary. The  $\text{Cl}^-$  ion concentrations of the surface water bodies in the research region ranged from 21.6 to 1032 mg/L. At the SW1 sampling point, the highest concentration (1032 mg/L) of  $\text{Cl}^-$  ion was found with a standard deviation (SD) of 55.5. It declined with distance from the CETP release area. At most of the sampling locations,  $\text{Cl}^-$  levels were within the permissible range of surface water, except for the sampling point SW1 (**Table 4.9**). Excess use of chloride salt and chrome tanning powder during the preservation and processing (chrome tanning) of leather may increase the concentration in the surface water bodies. De (2011) illustrated that the concentration of  $\text{Cl}^-$  varied from 15.4 to 1700 mg/L, which supported the present findings.

### 4.2.2.2 Sulfate ion ( $\text{SO}_4^{2-}$ )

The sulfate ion ( $\text{SO}_4^{2-}$ ) is an essential anion contributing to water hardness. Sulfate ion concentrations of the surface water in the study area ranged from 60.1 to 113.9 mg/L. The highest concentration (113.9 mg/L) of  $\text{SO}_4^{2-}$  ion was found at the SW1 sampling point with a standard deviation (SD) of 24.5. It declined with distance from the CETP discharge point in the CETP discharge area. Sulfate ion concentrations were within the surface water standard at all sampling sites (**Table 4.9**). Many auxiliary chemicals like  $\text{H}_2\text{SO}_4$  and  $\text{Na}_2\text{S}$  used in the tanning industry during the processing of hides/ skins, may be responsible for the sulfate concentration in the surface water bodies. Giri et al. (2014), observed that the value of  $\text{SO}_4^{2-}$  varied from 50.8 to 189 mg/L, which sustained the current investigations.

#### 4.2.2.3 Nitrate nitrogen ( $\text{NO}_3^-$ -N)

The nitrate-nitrogen ( $\text{NO}_3^-$ -N) exists naturally in water in trace amounts. However, higher levels of nitrate–nitrogen in surface water obtained may be due to pollution sources (industrial effluent). The nitrate-nitrogen concentration of the surface water in the CETP discharge areas varied from 4.4 to 13.8 mg/L (**Table 4.9**). It declined with distance from the effluent release area. At most of the sampling sites, the nitrate-nitrogen concentration exceeded the allowable range of the surface water. Additionally, numerous additives such as water conditioners, deformers, scale inhibitors, silicides, biocides, dyes and pigments, and wet and dry strength nitrogen compound additions may contribute to the concentration. According to Slade et al. (2004), nitrate-nitrogen from bleaching processes might enter tannery wastewater. A parallel explosion was delivered by Chandra et al. (2018), which supported the present study.

#### 4.2.2.4 Phosphate ( $\text{PO}_4^{3-}$ )

The phosphate ( $\text{PO}_4^{3-}$ ) ion concentrations in surface water bodies should have remained low since they may cause eutrophication at high concentrations (Zhang et al., 2011). The levels of phosphate ions in the research area ranged from 2.32 to 7.1 mg/L. At the SW1 sampling point, the highest phosphate ion concentration (7.1 mg/L) was found with a standard deviation (SD) of 0.51. It declined with distance from the CETP release area (**Table 4.9**). In Bangladesh, there is no allowable limit of phosphate ions for surface water. Slade et al. (2004) reported that bleaching processes may release phosphate ions into the leather effluent. However, various additives, including water conditioners, defoamers, scale inhibitors, slimicides, biocides, dyes and pigments, and wet and dry-strength additives containing phosphorus compounds may increase the concentration. Giri et al. (2014) illustrated that the concentration of  $\text{PO}_4^{3-}$  varied from 1.9 to 12.3mg/L, which supported the present findings.

#### 4.2.2.5 Bicarbonate ion ( $\text{HCO}_3^-$ )

The concentrations of bicarbonate ions ( $\text{HCO}_3^-$ ) in the study area ranged from 117.8 to 240 mg/L. It declined with distance from the CETP discharge point. In Bangladesh, there is no standard level of bicarbonate ion in surface water (**Table 4.9**). Bicarbonate ions ( $\text{HCO}_3^-$ ) are naturally occurring ions and exist as Mg, Na, and Ca carbonate. Various

studies delivered the same observations (Shakil and Mostafa, 2021; De, 2011; Devi et al., 2011).

**Table 4.9 Anionic parameters of surface water around the CETP discharge area**

| Parameters<br>(mg/L)            | Mean ± SD (mg/L)         |            |            |                |                | DoE-<br>BD,<br>2023 |
|---------------------------------|--------------------------|------------|------------|----------------|----------------|---------------------|
|                                 | Sample Location          |            |            |                |                |                     |
|                                 | SW1<br>(Mixing<br>point) | SW2(100m)  | SW3(500m)  | SW4(1km)       | SW5(2km)       |                     |
| Cl <sup>-</sup>                 | 1032<br>±55.5            | 25.6 ±4.4  | 23.5 ±2.9  | 22.8 ±1.8      | 21.6 ±2.9      | 600                 |
| SO <sub>4</sub> <sup>2-</sup>   | 113.85<br>±24.5          | 95.25 ±2.2 | 66.8 ±21.9 | 62.1 ±7.7      | 60.05 ±3.7     | 400                 |
| NO <sub>3</sub> <sup>-</sup> -N | 13.8<br>±0.8             | 13.5 ±0.5  | 12.1 ±4.4  | 8.5 ±0.5       | 4.4 ±0.2       | 10                  |
| PO <sub>4</sub> <sup>3-</sup>   | 7.08<br>±0.51            | 6.63 ±1.0  | 3.81 ±0.32 | 3.305<br>±0.35 | 2.32 ±0.69     | 0.1                 |
| HCO <sub>3</sub> <sup>-</sup>   | 240<br>±101.5            | 166 ±181.4 | 139 ±29.51 | 131 ±22.8      | 117.8<br>±14.3 | -                   |

Based on the concentration of the anionic parameters, the study observed that at the SW1 sampling point, aquatic life may be stressed. But the pollution level decreases with increasing distance.

## 4.2.3 Cationic parameters in surface water

The surface water five samples were collected three times (pre-monsoon, monsoon, and post-monsoon) in a year, from the monsoon of 2021 to the pre-monsoon of 2023, and analyzed some major cations such as sodium ions (Na<sup>+</sup>), potassium ions (K<sup>+</sup>), calcium ions (Ca<sup>2+</sup>), and magnesium ions (Mg<sup>2+</sup>). The analyzed results are described below:

### 4.2.3.1 Sodium ion (Na<sup>+</sup>)

The sodium ions (Na<sup>+</sup>) concentrations of the surface water body in the CETP discharge areas varied from 8.9 to 350 mg/L. It decreased with distance from the CETP discharge

area. At the entire sampling site, sodium ion concentrations were within the permissible limit of surface water except for the SW1 sampling point (**Table 4.10**). Excess use of sodium chloride salt during the primary preservation and processing of leather may be responsible for the concentration in the surface water bodies. So, based on sodium concentration aquatic life may be stressed at the SW1 sampling point. Venkatesh et al. (2008) illustrated that the concentration of sodium ions varied from 6.4 to 630 mg/L, which supported the present findings.

#### **4.2.3.2 Potassium ion ( $K^+$ )**

The maximum concentration of potassium ions ( $K^+$ ) in the surface water bodies of the CETP discharge areas was 1 mg/L with a standard deviation (SD) of 0.45. It decreased with distance from the CETP discharge point. At all the sampling sites, potassium ion concentrations were within the permissible limit of surface water (**Table 4.10**). Potassium soap is used as a surfactant in the leather recycling process. It may cause excessive potassium ion concentrations in the wastewater (Okchemblog, 2016). Kumar et al. (2003) reported a similar observation, which supported the present study.

#### **4.2.3.3 Calcium ion ( $Ca^{2+}$ )**

The maximum concentration of calcium ions ( $Ca^{2+}$ ) in the surface water bodies of the CETP discharge areas was 45 mg/L at the SW1 sampling point. It decreased with distance from the CETP discharge point. At all the sampling sites, calcium ion concentrations were within the permissible limit of surface water (**Table 4.10**). Raw materials used during the processing of leather may be responsible for the concentration in the surface water bodies. Ghosh and Hossain (2019), displayed that the values of calcium ions varied from 1.1 to 59 mg/L, which sustained the current findings.

#### **4.2.3.4 Magnesium ion ( $Mg^{2+}$ )**

The magnesium ions ( $Mg^{2+}$ ) concentrations of the surface water body in the CETP discharge areas ranged from 15.3 to 43.8 mg/L. It decreased with distance from the CETP discharge point. There is no standard level of magnesium ion for surface water in Bangladesh (**Table 4.10**). Various auxiliary chemicals used during the processing of leather may be responsible for the concentration in the surface water bodies. A similar observation was stated by Chowdhury et al. (2013), which supported the present study.

**Table 4.10 Cationic parameters of surface water around the CETP discharge area**

| Parameters<br>(mg/L) | Mean ± SD (mg/L)         |               |               |              |              | DoE-BD,<br>2023 |
|----------------------|--------------------------|---------------|---------------|--------------|--------------|-----------------|
|                      | Sample Location          |               |               |              |              |                 |
|                      | SW1<br>(Mixing<br>point) | SW2<br>(100m) | SW3<br>(500m) | SW4<br>(1km) | SW5<br>(2km) |                 |
| Na <sup>+</sup>      | 350±6.9                  | 10.9±0.5      | 9.9±0.23      | 9.2±1.2      | 8.9±0.2      | 200             |
| K <sup>+</sup>       | 1.0±0.45                 | 0.45±0.1      | 0.3±0.2       | 0.3±0.2      | 0.3±0.2      | 12              |
| Ca <sup>2+</sup>     | 45±0.8                   | 29.8±1.5      | 25±4.2        | 1.7±0.05     | 1.3±0.5      | 75              |
| Mg <sup>2+</sup>     | 43.8±5                   | 28±8.7        | 23.9±10.1     | 18.4±11.8    | 15.3±7.8     | -               |

#### 4.2.4 Surface water (Heavy metals)

Metals that have relatively high densities are termed heavy metals. Several heavy metals are usually present in natural water at a trace level, but many of them are toxic even at very low concentrations. Heavy metals in the surface water body may come from pollution sources (industrial effluent), and above the permissible limit, they cause serious harm to the aquatic environment. The most common toxic heavy metals in wastewater are chromium (Cr), zinc (Zn), lead (Pb), copper (Cu), iron (Fe), manganese (Mn), and nickel (Ni). In the surface water body of the CETP discharge areas, the maximum concentrations of chromium (Cr), zinc (Zn), lead (Pb), copper (Cu), iron (Fe), manganese (Mn), and nickel (Ni) were 5.3, 9.8, 1.7, 0.72, 0.1, and 0.1 mg/L, respectively. The heavy metal concentration sequence in the water bodies was Zn > Cr > Pb > Cu > Ni > Fe > Mn. Except for Zn, Cr, Pb, and Cu, other heavy metal concentrations were within the permissible limit of surface water (**Table 4.11**). So the continuous discharge of this type of effluent without proper treatment is a great threat to the environment.

**Table 4.11 Heavy metals of surface water in the tannery CETP discharge area**

| Parameters<br>(mg/L) | Mean ± SD (mg/L)         |               |               |              |              | DoE-BD,<br>2023 |
|----------------------|--------------------------|---------------|---------------|--------------|--------------|-----------------|
|                      | Sample Location          |               |               |              |              |                 |
|                      | SW1<br>(Mixing<br>point) | SW2<br>(100m) | SW3<br>(500m) | SW4<br>(1km) | SW5<br>(2km) |                 |
| Fe                   | 0.1±0.135                | 0.1±0.08      | 0.1±0.08      | 0.1±0.1      | 0.04±0.1     | 3               |
| Cu                   | 0.72±0.5                 | 0.65±0.44     | 0.64±0.5      | 0.58±0.4     | 0.53±0.4     | 3               |
| Zn                   | 9.8±6.5                  | 5.4±3.6       | 1.6±2.4       | 0.5±0.3      | 0.4±0.3      | 5               |
| Mn                   | 0.1±0.04                 | 0.1±0.05      | 0.1±0.05      | 0.1±0.05     | 0.1±0.1      | 2               |
| Pb                   | 1.7±0.005                | 0.1±0.04      | 0.1±0.04      | 0.1±0.05     | 0.1±0.05     | 0.1             |
| Cr                   | 5.3±3.5                  | 0.6±0.7       | 0.43±0.3      | 0.23±0.14    | 0.20±0.2     | 0.5             |
| Ni                   | 0.23±0.15                | 0.22±0.15     | 0.20±0.15     | 0.1±0.05     | 0.05±0.04    | 1               |

### 4.3 Characterization of groundwater

The groundwater five samples were collected three times (pre-monsoon, monsoon, and post-monsoon) in a year, from the monsoon of 2021 to the pre-monsoon of 2023 to analyze various physicochemical parameters (detailed results in Appendix II).

#### 4.3.1 Physicochemical characterization of groundwater

The groundwater samples were analyzed for some physic-chemical parameters, such as temperature, EC, DO, pH, TSS, TDS, TH, BOD, and COD and these are stated below:

##### 4.3.1.1 Temperature

Water temperature affects the water chemistry. It has a particular impact on the dissolved gas content and the equilibrium reactions in water (Shakil and Mostafa, 2021; Sethy et al., 2016). The degree of chemical reactions normally increases at higher temperatures (Saha et al., 2008). However, at extreme temperatures, more substances can dissolve in groundwater. At the GW1, GW2, GW3, GW4, and GW5 sampling points the groundwater temperatures were 25.9, 25.8, 25.5, 25.4, and 25.2 °C, respectively. The standard deviation (SD) varied from 3.6 to 6.5. Temperatures were found within the Bangladesh drinking water standard (BDS) permitted limit at all sample sites (**Table 4.12**). Groundwater temperature normally varies between 25 and 30 °C. A similar observation was stated by Saha and Azam (2021), which supported the present study.

##### 4.3.1.2 pH

Although pH has no traditional consequences for the consumer, it is one of the most significant and necessary water quality criteria (WHO, 2011). The pH levels of groundwater in the GW1, GW2, GW3, GW4, and GW5 sampling points were 7.20, 7.10, 7.10, 7.10, and 7.0, respectively. The standard deviation (SD) ranged between 0.15 and 0.30. It was found within the allowable limit of the drinking water standard at all sampling sites (**Table 4.12**). The soil of the study area was silty clay loam with a texture composition of 22.5 to 52.5% (Sultana et al., 2017). The neutral nature of the samples was due to the cause of mineralization as well as the weathering of carbonate and or bicarbonate minerals by percolation and infiltration during ground aquifer recharging

(Islam et al., 2017a; Mostafa et al., 2017). In a study, Amano et al. (2020) illustrated that the pH concentration varied from 7.1 to 7.4, which supported the present findings.

**Table 4.12 Physicochemical parameters of groundwater around the CETP discharge area**

| Parameters | Mean ± SD (mg/L) |           |          |          |          | DoE-BD,<br>2023 |
|------------|------------------|-----------|----------|----------|----------|-----------------|
|            | Sample Location  |           |          |          |          |                 |
|            | GW1              | GW2       | GW3      | GW4      | GW5      |                 |
| Temp       | 25.9±6.4         | 25.8±6.5  | 25.5±6.3 | 25.4±3.6 | 25.2±3.6 | 20-30           |
| pH         | 7.17±0.15        | 7.1±0.21  | 7.1±0.22 | 7.1±0.3  | 7.0±0.3  | 6.5-8.5         |
| DO         | 4.2±0.06         | 4.2±0.1   | 4.1±0.05 | 4.3±0.5  | 4.3±0.5  | >6              |
| EC         | 658±40           | 653±16    | 635±10.7 | 632±10.7 | 630±10.5 | 1500            |
| Turbidity  | 4.8±0.07         | 4.6±0.21  | 4.5±0.15 | 4.5±0.16 | 4.5±0.13 | 5               |
| TSS        | 8.4±0.08         | 8.23±0.18 | 7.3±0.9  | 7.3±0.9  | 7.1±0.8  | 10              |
| TDS        | 466±28           | 449±15.1  | 449±15   | 445±15   | 442±14.9 | 1000            |
| BOD        | 9±15             | 8±17      | 8±13     | 7.9±14   | 7.8±17   | 0.2             |
| COD        | 17±12            | 16±13     | 16±12    | 15±12    | 15±13    | 4               |

\*(All parameters expressed in mg/L, except turbidity in NTU, pH, EC in  $\mu$ S/cm, and temperature in  $^{\circ}$ C).

#### 4.3.1.3 Dissolved Oxygen (DO)

The Dissolved Oxygen (DO) concentrations of groundwater in the GW1, GW2, GW3, GW4, and GW5 sampling points were 4.20, 4.20, 4.10, 4.30, and 4.30 mg/L, respectively. The standard deviation (SD) varied from 0.05 to 0.50. The DO level was within the required limit for drinking water at all sampling sites (**Table 4.12**). For groundwater, DO normally remains between the ranges of 4 and 6 mg/L (Chegbeleh et al., 2020). A parallel statement was reported by Onwuka et al. (2004), which supported the present study.

#### 4.3.1.4 Electrical Conductivity (EC)

The Electrical Conductivity (EC) of groundwater illustrates the concentration of electrically charged ions dissolved in water. The EC of groundwater in the GW1, GW2, GW3, GW4, and GW5 sampling points were 658, 653, 635, 632, and 630  $\mu\text{S}/\text{cm}$ , respectively. The standard deviation (SD) varied from 10.5 to 40. EC was found within the DoE-BD, 2023 guidelines at all sampling sites (**Table 4.12**). Several investigations have shown that groundwater in shallow aquifers has a high electrical conductivity value (Bhuiyan et al., 2010; Mirza et al., 2012; Islam et al., 2016; Ahmed et al., 2018). The high concentrations are often caused by anthropogenic and geochemical processes such as industrial effluent infiltration, rainwater percolation and infiltration, evaporation, ion exchange, and soil/sediment dissolution (Yidana et al., 2012; Saha et al., 2008; Chegbeleh et al., 2020). Water with a high EC value may have an unpleasant taste, discolor, and create scale on the walls of water containers and supply pipes (Saha et al., 2008). In their research, Rashid et al. (2018) reported that the concentration of EC varied from 623 to 689  $\mu\text{S}/\text{cm}$ , which supported the current findings.

#### 4.3.1.5 Turbidity

Turbidity measures the degradation of transparency caused by suspended solids such as clay, silt, and other organic or inorganic components in water. Turbidity is an essential measure for determining the amount of suspended contaminants (Saha et al., 2008). The turbidities of groundwater in the GW1, GW2, GW3, GW4, and GW5 sampling points were 4.80, 4.60, 4.50, 4.50, and 4.50 NTU, respectively. The standard deviation (SD) varied from 0.07 to 0.21. It was found within the permitted limit of drinking water standards at all sampling sites (**Table 4.12**). A similar opinion was stated by Karimi et al. (2020), which sustained the present investigation.

#### 4.3.1.6 Total Suspended Solids (TSS)

Total Suspended Solids (TSS) in groundwater is made up of clay, silt, and other organic or inorganic particles. The TSS of groundwater in the GW1, GW2, GW3, GW4, and GW5 sampling points were 8.40, 7.23, 7.30, 7.30, and 7.10 mg/L, respectively. The standard deviation (SD) ranged from 0.08 to 0.90. At all the sampling locations, it was discovered within the acceptable range of drinking water standards (**Table 4.12**). A

parallel statement was listed by Organization et al. (2019), which supported the present study.

#### **4.3.1.7 Total Dissolved Solids (TDS)**

Total Dissolved Solids (TDS) usually specify the dissolved organic and inorganic constituents. TDS are the dissolved inorganic salts, minerals, and minor quantities of organic matter in water (Yidana et al., 2012). A higher TDS indicates that the water is highly mineralized (Meride and Ayenew, 2016). The TDS of groundwater in the GW1, GW2, GW3, GW4, and GW5 sampling points were 466, 449, 449, 445, and 442 mg/L, respectively. The standard deviation (SD) varied from 14.9 to 28. At all the sampling locations, it was observed within the allowable range of drinking water standards (**Table 4.12**). A higher value of total dissolved solids (TDS) in drinking water may affect human health, i.e., people suffering from constipation, heart disease, and kidney functioning (Sasikaran et al., 2012). During a study, Venkatesh et al. (2008) reported that the concentration of TDS varied from 450 to 500 mg/L, which supported the present findings.

#### **4.3.1.8 Biochemical Oxygen Demand (BOD)**

Biochemical Oxygen Demand (BOD) is a significant factor for evaluating water quality as it denotes the amount of organic contaminants. The BOD of groundwater in the GW1, GW2, GW3, GW4, and GW5 sampling points were 9, 8, 8, 7.9, and 7.8 mg/L, respectively. The standard deviation (SD) ranged between 13 and 17. BOD levels exceeded the permitted limit of the drinking water standard at all sample sites (**Table 4.12**). Infiltration of organic contaminants may raise the BOD levels of groundwater in the studied area. Various studies delivered the same observations (Saha and Azam, 2021; Shakil and Mostafa, 2021; Giri et al., 2014; Devi et al., 2011).

#### **4.3.1.9 Chemical Oxygen Demand (COD)**

Chemical Oxygen Demand (COD) is an important indicator for measuring water quality since it shows the amount of organic and inorganic contaminants. The COD of groundwater in the GW1, GW2, GW3, GW4, and GW5 sampling points were 17, 16, 16, 15, and 15 mg/L, respectively. The standard deviation (SD) varied from 12 to 13. COD levels surpassed the permitted limit of the drinking water standard at all sample sites

(Table 4.12). Infiltration of organic or inorganic contaminants may raise the COD level of groundwater in the studied region. Several researchers conveyed similar opinions (Amano et al., 2020; Chowdhury et al., 2015; Giri et al., 2014; De, 2011).

### 4.3.2 Anionic parameters in groundwater

Anions are the counter of cations that form salts, and in the study, five anion like chloride ion ( $\text{Cl}^-$ ), sulfate ion ( $\text{SO}_4^{2-}$ ), nitrate nitrogen ( $\text{NO}_3^- \text{N}$ ), phosphate ion ( $\text{PO}_4^{3-}$ ), and bicarbonate ion ( $\text{HCO}_3^-$ ) of groundwater samples were analyzed. The analyzed results of groundwater samples are illustrated in Table 4.13.

#### 4.3.2.1 Chloride ion ( $\text{Cl}^-$ )

The concentrations of chloride ions ( $\text{Cl}^-$ ) in groundwater at the GW1, GW2, GW3, GW4, and GW5 sampling points were 255, 250, 249, 248, and 248 mg/L, respectively. The standard deviation (SD) ranged from 2.1 to 3.6. At all the sampling locations, it was observed within the allowable range of drinking water standards except for GW1 and GW2 sampling points (Table 4.13). Every mineral and rock contains trace amounts of  $\text{Cl}^-$  in the form of NaCl, KCl, and  $\text{CaCl}_2$ , and it is extremely mobile in ground aquifers (WHO, 1996; Kelly et al., 2012). Except in cases of heart issues, chloride has no toxicity in humans; however, an excess of  $\text{Cl}^-$  as NaCl can cause hypertension and corrode water supply metal pipes (Fadeeva, 1971; WHO, 2011). Onwuka et al. (2004) illustrated that the concentration of  $\text{Cl}^-$  varied from 50 to 270 mg/L, which supported the present findings.

#### 4.3.2.2 Sulfate ion ( $\text{SO}_4^{2-}$ )

The concentrations of sulfate ions ( $\text{SO}_4^{2-}$ ) in groundwater at the GW1, GW2, GW3, GW4, and GW5 sampling points were 27.90, 27.80, 26.90, 26.90, and 26.80 mg/L, respectively. The standard deviation (SD) varied from 0.81 to 3.6. At all the sampling spots, it was observed within the permitted range of drinking water standards (Table 4.13). Sulfate is a general anion of groundwater that results from the industrial effluent infiltration, dissolution/weathering of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  sulfate minerals, as well as some types of surfactants (e.g., sodium dodecyl sulfate) (de Araújo et al., 2018). In an investigation, Rashid et al. (2018) observed that the value of  $\text{SO}_4^{2-}$  varied from 50.8 to 189 mg/L, which sustained the current investigations.

#### 4.3.2.3 Nitrate nitrogen ( $\text{NO}_3^-$ -N)

The concentrations of nitrate nitrogen  $\text{NO}_3^-$ -N in groundwater at the GW1, GW2, GW3, GW4, and GW5 sampling points were 3.20, 3.02, 2.47, 2.45, and 2.45 mg/L, respectively. The standard deviation (SD) ranged between 0.17 and 0.64. At all the sampling positions, it was shown within the tolerated range of drinking water standards (**Table 4.13**). Inorganic nitrogen fertilizers, wastewater treatment, and septic tanks are major sources of  $\text{NO}_3^-$  in water (Winton et al., 1971). A similar reflection was reported by Karimi et al. (2020), which supported the present study.

#### 4.3.2.4 Phosphate ion ( $\text{PO}_4^{3-}$ )

The concentrations of phosphate ions ( $\text{PO}_4^{3-}$ ) in groundwater at the GW1, GW2, GW3, GW4, and GW5 sampling points were 4.10, 4.0, 4.0, 4.0, and 3.9 mg/L, respectively. The standard deviation (SD) varied from 0.05 to 0.09. At all the sampling spots, it was discovered within the acceptable range of drinking water standards (**Table 4.13**). Phosphate arises in the groundwater body from the infiltration of phosphorus-containing fertilizers and various auxiliaries (phosphorus-containing) used in the industrial manufacturing process (Zhang et al., 2011). In their study, Organization et al. (2019) illustrated that the concentration of  $\text{PO}_4^{3-}$  varied from 2.9 to 5.3 mg/L, which supported the present findings.

#### 4.3.2.5 Bicarbonate ion ( $\text{HCO}_3^-$ )

The concentrations of bicarbonate ions ( $\text{HCO}_3^-$ ) in groundwater at the GW1, GW2, GW3, GW4, and GW5 sampling points were 341, 339, 339, 339, and 338 mg/L, respectively. The standard deviation (SD) ranged from 11 to 28. However, there is no drinking water standard for bicarbonate ions in Bangladesh (**Table 4.13**). The bicarbonate ion persists as Na, Mg, and Ca bicarbonate, which are the most prevalent and plentiful minerals in the aquifer system. It is extremely important in a variety of biological functions (Casey, 2006). Various studies delivered the same observations (Saha and Azam, 2021; Shakil and Mostafa, 2021; De, 2011; Devi et al., 2011).

### 4.3.3 Cationic parameters in groundwater

The groundwater five samples were collected three times (pre-monsoon, monsoon, and post-monsoon) in a year, from the monsoon of 2021 to the pre-monsoon of 2023, and analyzed some major cations such as sodium ions ( $\text{Na}^+$ ), potassium ions ( $\text{K}^+$ ), calcium ions ( $\text{Ca}^{2+}$ ), and magnesium ions ( $\text{Mg}^{2+}$ ). The analyzed results are described below:

#### 4.3.3.1 Sodium ion ( $\text{Na}^+$ )

The concentrations of sodium ions ( $\text{Na}^+$ ) in groundwater at the GW1, GW2, GW3, GW4, and GW5 sampling points were 220, 214, 214, 214, and 213 mg/L, respectively. At all the sampling locations, it surpasses the accepted range of drinking water standards (**Table 4.14**). Due to the excess use of sodium salt during the processing of raw hides and skins, which may infiltrate into groundwater, a higher concentration of sodium was obtained during the study period. A similar observation was illustrated by Amano et al. (2020), which supported the present study.

#### 4.3.3.2 Potassium ion ( $\text{K}^+$ )

The concentrations of potassium ions ( $\text{K}^+$ ) in groundwater at the GW1, GW2, GW3, GW4, and GW5 sampling points were 0.35, 0.30, 0.29, 0.29, and 0.29 mg/L, respectively. At all the sampling spots, it was observed within the tolerable range of drinking water standards (**Table 4.14**). Potassium (K) is commonly present in groundwater as chloride, bicarbonate, nitrate, and sulfate, and its concentration is lower than that of other major cations in water (Whelton et al., 2007). In their research, Onwuka et al. (2004) illustrated that the concentration of sodium ions varied from 0.4 to 0.6 mg/L, which supported the present findings.

#### 4.3.3.3 Calcium ion ( $\text{Ca}^{2+}$ )

The concentrations of calcium ions ( $\text{Ca}^{2+}$ ) in groundwater at the GW1, GW2, GW3, GW4, and GW5 sampling points were 1.3, 1.3, 1.2, 1.2, and 1.27 mg/L, respectively. At all the sampling positions, it was recorded within the allowable range of drinking water standards (**Table 4.14**). Calcium ( $\text{Ca}^{2+}$ ) is a common mineral found in the earth's crust (Tandogan and Ulusu, 2005; Pravina et al., 2012). In an investigation, Rashid et al.

(2018), displayed that the values of calcium ions varied from 1.1 to 1.7 mg/L, which sustained the current findings.

**Table 4.13 Anionic parameters of groundwater around the CETP discharge area**

| Parameters<br><br>(mg/L)        | Mean ± SD (mg/L) |           |           |           |           | DoE-BD,<br><br>2023 |
|---------------------------------|------------------|-----------|-----------|-----------|-----------|---------------------|
|                                 | Sample Location  |           |           |           |           |                     |
|                                 | GW1              | GW2       | GW3       | GW4       | GW5       |                     |
| Cl <sup>-</sup>                 | 255±3.6          | 250±3.5   | 249±2.1   | 248±2.1   | 248±2.3   | 250                 |
| SO <sub>4</sub> <sup>2-</sup>   | 27.9±0.88        | 27.8±2.3  | 26.9±0.82 | 26.9±0.81 | 26.8±0.81 | 250                 |
| NO <sub>3</sub> <sup>-</sup> -N | 3.2±0.64         | 3.02±0.32 | 2.47±0.17 | 2.45±0.18 | 2.45±0.17 | 10                  |
| PO <sub>4</sub> <sup>3-</sup>   | 4.1±0.09         | 4.0±0.07  | 4.0±0.05  | 4.0±0.05  | 3.9±0.07  | 6                   |
| HCO <sub>3</sub> <sup>-</sup>   | 341±28           | 339±13    | 339±11    | 339±13    | 338±12    | -                   |

#### 4.3.3.4 Magnesium ion (Mg<sup>2+</sup>)

The concentrations of magnesium ions (Mg<sup>2+</sup>) in groundwater at the GW1, GW2, GW3, GW4, and GW5 sampling points were 48, 39, 38, 38, and 35 mg/L, respectively. At all the sampling spots, it surpasses the tolerable range of drinking water standards (**Table 4.14**). Due to the excess use of salt during the processing of raw hides and skins, which may infiltrate into groundwater, a higher concentration of magnesium salt was obtained during the study period. A similar statement was stated by Karimi et al. (2020), which supported the present study.

#### 4.3.4 Heavy metals

Numerous trace heavy metals typically exist in groundwater at trace levels. Infiltration of these metals from industrial wastewater may result in heavy metal contamination of groundwater. Heavy metal contamination may pose major consequences for groundwater users. In the groundwater body of the tannery effluent discharge areas, the maximum concentrations of Zn, Fe, Cr, and Pb were 5.3, 1.5, 0.25, and 0.13 mg/L, respectively. The heavy metal concentration sequence in the groundwater was Zn > Fe > Cu > Cr > Pb (**Table 4.14**). Besides these heavy metals other heavy metal concentrations were within

the permissible range. It was due to performing chrome tanning process, and geological factors such as mineralization, as well as the weathering of carbonate/bicarbonate minerals by percolation and infiltration of chemical fertilizers, and raw materials used during the processing of raw hides and skins, that contributed to the Zn, Cr, Fe, and Pb ions concentration of the groundwater in the study area (Zakir et al., 2011; Mostafa et al., 2017; Islam and Mostafa, 2021). A similar observation was stated by various researchers (Shakil and Mostafa, 2021; De, 2011; Devi et al., 2011).

**Table 4.14 Cationic parameters and trace heavy metal of groundwater around the CETP discharge area**

| Parameters<br><br>(mg/L) | Mean ± SD (mg/L) |           |           |           |           | DoE-BD,<br><br>2023 |
|--------------------------|------------------|-----------|-----------|-----------|-----------|---------------------|
|                          | Sample Location  |           |           |           |           |                     |
|                          | GW1              | GW2       | GW3       | GW4       | GW5       |                     |
| Na                       | 220±2.8          | 214±2.2   | 214.0±1.7 | 214±1.8   | 213±1.5   | 200                 |
| K                        | 0.35±0.6         | 0.30±0.5  | 0.29±0.5  | 0.29±0.5  | 0.29±0.4  | 12                  |
| Ca                       | 1.3±3.9          | 1.3±2.6   | 1.2±2.4   | 1.2±2.4   | 1.2±2.8   | 75                  |
| Mg                       | 48±0.64          | 39±0.27   | 38±0.23   | 38±0.25   | 35±0.21   | 30-35               |
| Fe                       | 1.5±0.09         | 1.5±0.07  | 1.49±0.03 | 1.49±0.03 | 1.43±0.04 | 0.3-1.0             |
| Cu                       | 1.03±0.0         | 1.01±0.0  | 1.02±0.0  | 1.01±0.01 | 1.01±0.02 | 1.5                 |
| Zn                       | 5.3±0.02         | 5.1±0.00  | 5.1±0.00  | 5.0±0.01  | 4.9±0.01  | 5                   |
| Mn                       | 0.3±0.0          | 0.2±0.0   | 0.2±0.0   | 0.3±0.02  | 0.2±0.01  | 0.4                 |
| Pb                       | 0.13±0.01        | 0.11±0.0  | 0.11±0.00 | 0.10±0.01 | 0.10±0.02 | 0.01                |
| Cr                       | 0.25±0.01        | 0.23±0.00 | 0.22±0.00 | 0.22±.001 | 0.21±0.02 | 0.05                |

#### 4.4 Seasonal variation (surface water)

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 4.15**). 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 et al., 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 Dissolved Oxygen (DO) and standard deviation (SD) of all collected surface water samples varied from 4.02 to 4.5mg/L and 1.2 to 1.45, respectively (**Table 4.15**). 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 et al. (2001) found the highest (5.0) DO concentration in the monsoon period, which showed similarity with the present study.

The biyearly mean of EC, TDS, TSS, turbidity, BOD, and COD (**Table 4.15**) for all collected surface water samples varied from 677 to 1045.3 µS/cm, 820.4 to 1054 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 4.15**) 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 found in the following order pre-monsoon > post-monsoon > monsoon. Various studies delivered the same observations (Peavy et al., 1985; Davis and Cornwell, 1998; Kabir et al., 2002; Phiri et al., 2005; Sultan et al., 2009; Momtaz et al., 2012). The higher value of these parameters is an indication of polluted water. So,

pollution levels were found higher in the pre-monsoon season as compared to other seasons.

**Table 4.15 Biyearly average values and standard deviations of the physicochemical parameters in the surface water around the CETP discharge area**

| Parameters      | Mean±SD                |                             |                            |
|-----------------|------------------------|-----------------------------|----------------------------|
|                 | Monsoon<br>(2021-2022) | Post-monsoon<br>(2021-2022) | Pre-monsoon<br>(2022-2023) |
| Tem ( °C)       | 26.2±2.5               | 22.6±2.7                    | 27.8±2.8                   |
| pH              | 7.3±0.81               | 6.9±0.44                    | 6.5±0.18                   |
| DO (mg/L)       | 4.5±1.45               | 4.2±1.2                     | 4.02±1.3                   |
| EC (µS/cm)      | 677.0±442              | 741.7±185                   | 1045.3±105                 |
| Turbidity (NTU) | 26.0±2.5               | 27.3±2.8                    | 32.5±2.5                   |
| TSS(mg/L)       | 135.0±5.2              | 140.0±5.1                   | 145.0±5.9                  |
| TDS(mg/L)       | 820.4±50.1             | 944.6±48.2                  | 1054.2±40.1                |
| BOD(mg/L)       | 53.3±15.9              | 60.4±10.3                   | 63.5±10.3                  |
| COD(mg/L)       | 183.4±29.30            | 233.4±15.30                 | 283.4±15.45                |
| TH(mg/L)        | 102.5±28.4             | 193.0±25.9                  | 169.5±32.2                 |

The biyearly average and standard deviation (SD) of Total Hardness (TH) for all collected surface water samples varied from 102.5 to 193 mg/L and 25.9 to 28.4, respectively (**Table 4.15**). In the case of TH during the pre and post-monsoon the water samples were hard to very hard type and were in the following order post-monsoon> pre-monsoon> monsoon. Jesmin et al. (2009) found that the value of TH varied from 112 to 195 mg/L, which is similar to the present study.

**Table 4.16 Biyearly average values and standard deviations of the anionic parameters in the surface water around the CETP discharge area**

| Parameters<br>(mg/L)            | Mean±SD                |                             |                            |
|---------------------------------|------------------------|-----------------------------|----------------------------|
|                                 | Monsoon<br>(2021-2022) | Post-monsoon<br>(2021-2022) | Pre-monsoon<br>(2022-2023) |
| Cl <sup>-</sup>                 | 215.32±13.10           | 223.72±2.8                  | 236.26±2.5                 |
| SO <sub>4</sub> <sup>2-</sup>   | 81.74±14.50            | 124.72±5.30                 | 714±5.45                   |
| NO <sub>3</sub> <sup>-</sup> -N | 6.5±5.3                | 8.7±5.0                     | 15.3±5.1                   |
| PO <sub>4</sub> <sup>3-</sup>   | 3.22±0.51              | 4.42±0.32                   | 6.22±0.60                  |
| HCO <sub>3</sub> <sup>-</sup>   | 111±101                | 121±180                     | 243.8±29.5                 |

Biyearly average values of the anionic parameters like Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>-N, HCO<sub>3</sub><sup>-</sup>, and PO<sub>4</sub><sup>3-</sup> (**Table 4.16**) 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<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>-N, HCO<sub>3</sub><sup>-</sup>, and PO<sub>4</sub><sup>3-</sup> 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. **Table 4.16** illustrates that the biyearly anionic parameters concentration was 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. Except for Cl<sup>-</sup>, other anionic parameters show remarkable seasonal variation because Cl<sup>-</sup> is naturally present in surface water and remains in contact with Cl<sup>-</sup> containing geological formation (Wetzel, 1975; Bartram and Balance, 1996; Al-Manharawi and Hafiz, 1997). Several studies conveyed the same explanations (Kabir et al., 2002; Phiri et al., 2005; Khalid et al., 2014). The biyearly average anionic parameters concentration of the surface water samples in the study area was in the following order pre-monsoon > post-monsoon > monsoon.

**Table 4.17 Biyearly average values and standard deviations of the cationic parameters in the surface water around the CETP discharge area**

| Parameters<br>(mg/L) | Mean±SD                |                             |                            |
|----------------------|------------------------|-----------------------------|----------------------------|
|                      | Monsoon<br>(2021-2022) | Post-monsoon<br>(2021-2022) | Pre-monsoon<br>(2022-2023) |
| Na <sup>+</sup>      | 74.42±5.7              | 76.06±0.5                   | 82.86±0.25                 |
| K <sup>+</sup>       | 0.296±0.40             | 0.714±0.49                  | 0.402±5.1                  |
| Ca <sup>2+</sup>     | 19.76±4.3              | 21.32±4.12                  | 20.6±4.15                  |
| Mg <sup>2+</sup>     | 19.48±2.5              | 27.08±3.2                   | 31.08±2.1                  |

Biyearly mean values of the cationic parameters like Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> (**Table 4.17**) in the surface water around the CETP discharge area varied from 74.42 to 82.86mg/L, 0.3 to 0.7mg/L, 19.76 to 21.32mg/L, and 19.48 to 31.08 mg/L, respectively. The standard deviation (SD) of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> for all collected surface water samples varied from 0.25 to 5.7, 0.40 to 5.1, 4.12 to 4.3, and 2.1 to 3.2, respectively. Except for Na<sup>+</sup> and Ca<sup>2+</sup> other cationic parameters show remarkable seasonal variation because Na<sup>+</sup> and Ca<sup>2+</sup> are naturally occurring in surface water due to weathering of various rocks (Wetzel, 1975; Bartram and Balance, 1996; Al-Manharawi and Hafiz, 1997). Industrial and domestic waste is rich in sodium and calcium ions which increases the concentration of sodium and calcium ions after their discharge into the water bodies (Bartram and Balance, 1996). Biyearly mean values of the cationic parameters were found lower in monsoon compared to other seasons due to the dilution effect of rainwater. A parallel reflection was stated by various studies (Davis and Cornwell, 1998; Rahman et al., 2013). The biyearly average cationic concentrations of the surface water samples in the study area were in the following order pre-monsoon > post-monsoon > monsoon.

**Table 4.18 Biyearly average values and standard deviations of the heavy metal in the surface water around the CETP discharge area**

| <b>Parameters<br/>(mg/L)</b> | <b>Mean±SD</b>                 |                                     |                                    |
|------------------------------|--------------------------------|-------------------------------------|------------------------------------|
|                              | <b>Monsoon<br/>(2021-2022)</b> | <b>Post-monsoon<br/>(2021-2022)</b> | <b>Pre-monsoon<br/>(2022-2023)</b> |
| Fe                           | 0.05±0.003                     | 0.06±0.021                          | 0.08±0.011                         |
| Pb                           | 0.30±0.009                     | 0.41±0.005                          | 0.45±0.008                         |
| Cu                           | 0.54±0.01                      | 0.60±0.01                           | 0.72±0.02                          |
| Ni                           | 0.14±0.02                      | 0.15±0.01                           | 0.18±0.02                          |
| Cr                           | 1.14±0.03                      | 1.38±0.03                           | 1.56±0.02                          |
| Zn                           | 2.65±0.01                      | 3.45±0.01                           | 4.55±0.03                          |
| Mn                           | 0.04±0.02                      | 0.05±0.02                           | 0.08±0.03                          |

Biyearly average values of the trace heavy metals like Fe, Pb, Cu, Ni, Cr, Zn, and Mn in the surface water around the CETP discharge area varied from 0.05 to 0.08mg/L, 0.30 to 0.45mg/L, 0.54 to 0.72mg/L, 0.14 to 0.18mg/L, 1.14 to 1.56mg/L, 2.65 to 4.55mg/L, and 0.04 to 0.08 mg/L, respectively (**Table 4.18**). Biyearly average trace heavy metals parameters concentration was found to be higher in the pre-monsoon season due to a decrease in the water level and anthropogenic sources including industrial effluent, leaching action, fertilizers, and human and animal waste. The biyearly average trace heavy metals concentrations of the surface water samples in the study area were in the following order pre-monsoon> post-monsoon> monsoon. Various studies delivered the same observations(Sultan et al., 2009; Momtaz et al., 2012).

From the above discussion, we can conclude that during the study period pollution levels for surface water were found in the following order pre-monsoon> post-monsoon> monsoon.

#### 4.5 Seasonal variation (Groundwater)

The biyearly average temperature of all collected groundwater samples varied from 24.9 to 25.6 °C. The maximum and minimum mean temperatures were observed in the pre-monsoon (25.6°C) and monsoon (24.9 °C) seasons with a standard deviation (SD) of 2.8 and 2.5, respectively (**Table 4.19**). Pre-monsoon is a summer season in which temperatures naturally remain high. Sultan et al. (2009) observed 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 groundwater samples varied from 6.8 to 7.42. The slightly acidic nature (6.8) of groundwater during the pre-monsoon period was mostly due to natural biogeochemical activities, plant-root respiration, and the leaching of organic acid from the decomposition of peripheral organic materials (Sethy et al., 2016). The neutral (7.1) and slightly basic (7.4) nature of samples during the monsoon and post-monsoon periods was due to the cause of mineralization, as well as the weathering of carbonate/bicarbonate minerals by percolation and infiltration during ground aquifer recharging (Islam et al., 2017a; Mostafa et al., 2017). The study area's soil was silty clay loam type with a texture composition of 22.5 to 52.5% (Sultana et al., 2017). In the post-monsoon seasons, higher (7.4) pH levels with enhanced  $\text{HCO}_3^-$  concentrations (406.6 mg/L) designated the free  $\text{H}^+$  bond to the buffering agent  $\text{HCO}_3^-$ . Through equilibrium states, bicarbonate ( $\text{HCO}_3^-$ ) controlled the acidic and alkaline nature of the water solution (Islam and Mostafa, 2021). Helal et al. (2011) made a parallel observation.

**Table 4.19 Biyearly average values and standard deviations of the physicochemical parameters in the groundwater around the CETP discharge area**

| Parameters      | Mean±SD                |                             |                            |
|-----------------|------------------------|-----------------------------|----------------------------|
|                 | Monsoon<br>(2021-2022) | Post-monsoon<br>(2021-2022) | Pre-monsoon<br>(2022-2023) |
| Tem ( °C)       | 24.86±2.5              | 24.96±2.7                   | 25.56±2.8                  |
| pH              | 7.1±0.81               | 7.42±0.44                   | 6.8±0.18                   |
| DO (mg/L)       | 4.32±1.45              | 4.12±1.2                    | 4.24±1.3                   |
| EC (µS/cm)      | 653.6±442              | 667.8±185                   | 603.8±105                  |
| Turbidity (NTU) | 4.56±2.8               | 4.9±2.5                     | 4.28±2.5                   |
| TSS (mg/L)      | 7.6±5.2                | 8.0±5.1                     | 7.36±5.9                   |
| TDS (mg/L)      | 431.8±50.1             | 495.4±48.2                  | 423±40.1                   |
| BOD (mg/L)      | 8.46±15.9              | 9.86±10.3                   | 6.14±10.3                  |
| COD (mg/L)      | 15.2±29.30             | 18.3±15.30                  | 13.9±15.45                 |

The biyearly average Dissolved Oxygen (DO) and standard deviation (SD) of all collected groundwater samples varied from 4.12 to 4.32mg/L and 1.2 to 1.45, respectively (**Table 4.19**). For groundwater DO normally remain between the ranges of 4 to 6 mg/L (Chegbeleh et al., 2020). The biyearly mean DO was found in the following order monsoon (4.32mg/L) > pre-monsoon (4.24mg/L) > post-monsoon (4.12mg/L). A parallel reflection was stated by Sunil et al. (2001).

The biyearly mean EC, TDS, TSS, turbidity, BOD, and COD (**Table 4.19**) of all collected groundwater samples varied from 603.8 to 667.8 µS/cm, 423 to 495.4 mg/L, 7.36 to 8.0 mg/L, 4.3 to 4.9 NTU, 6.14 to 9.86 mg/L, and 13.9 to 18.3 mg/L, respectively. The biyearly standard deviation (SD) of EC, TDS, TSS, turbidity, BOD, and COD (**Table 4.19**) for all collected groundwater 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. A higher average EC, TDS, Turbidity, TSS, BOD, and COD values were found in the monsoon and post-monsoon season compared to the pre-monsoon could be because of the significant mineralization of water during surface run-off and percolation during the rainy season (Saha et al., 2008; Helal et al., 2011). Large values of these parameters are often identified by anthropogenic

and geochemical activities such as industrial run-off, rainwater percolation and infiltration, evaporation, ion exchange, and soil/sediment dissolution, which vary widely over space (Saha et al., 2008). The research area's soil was silty clay loam type with a texture composition of 22.5 to 52.5% (Sultana et al., 2017). During the monsoon season, surface run-off of precipitation enters the silty clay loam-type soil by percolation and infiltration and eventually reaches the aquifer with higher mineral concentrations (Yidana et al., 2012; Chegbeleh et al., 2020). As a result of the decomposition or weathering of rocks/minerals with water, more ions or electrolytes become accessible in groundwater, resulting in a higher value for these parameters. The findings of the investigation revealed that greater values of the physicochemical parameters were discovered in the post-monsoon (immediately after the rainy season) sampling period compared to the pre-monsoon due to aquifer mineralization (Ledesma-Ruiz et al., 2015). Various studies found similar observations (Chen et al., 2005; Leeuwen et al., 2000). The higher value of these parameters is an indication of polluted water. So, pollution levels for groundwater were found higher in the post-monsoon season as compared to other seasons.

**Table 4.20 Biyearly average values and standard deviations of the anionic parameters in the groundwater around the CETP discharge area**

| Parameters<br>(mg/L)            | Mean±SD                |                             |                            |
|---------------------------------|------------------------|-----------------------------|----------------------------|
|                                 | Monsoon<br>(2021-2022) | Post-monsoon<br>(2021-2022) | Pre-monsoon<br>(2022-2023) |
| Cl <sup>-</sup>                 | 249.8±13.10            | 255.2±2.8                   | 245±2.5                    |
| SO <sub>4</sub> <sup>2-</sup>   | 25.96±14.50            | 57.14±5.45                  | 24.06±5.30                 |
| NO <sub>3</sub> <sup>-</sup> -N | 2.64±5.3               | 3.31±5.0                    | 2.21±5.1                   |
| PO <sub>4</sub> <sup>3-</sup>   | 3.54±0.51              | 4.44±0.32                   | 4.02±0.60                  |
| HCO <sub>3</sub> <sup>-</sup>   | 337.0±101              | 406.6±180                   | 273.2±29.5                 |

Biyearly average values of the anionic parameters like Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>-N, HCO<sub>3</sub><sup>-</sup>, and PO<sub>4</sub><sup>3-</sup> (**Table 4.20**) in the groundwater around the CETP discharge area varied from 245 to 255.2 mg/L, 24.06 to 57.14 mg/L, 2.21 to 3.31 mg/L, 273.2 to 406.6 mg/L, and 3.54 to 4.44 mg/L, respectively. The standard deviation (SD) of Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>-N, HCO<sub>3</sub><sup>-</sup>, and PO<sub>4</sub><sup>3-</sup> for all collected groundwater samples varied from 2.5 to 13.10, 5.30 to 14.50, 5.1 to

5.3, 29.5 to 180, and 0.32 to 0.60, respectively. The results (**Table 4.20**) exposed that the biyearly average anionic concentrations were found in the order of the post-monsoon > monsoon > pre-monsoon sampling periods. This could be due to industrial run-off, over-exploitation of groundwater, cation exchange, decreased river flow, excessive dissolving of carbonate minerals, soil (silty clay loam) erosion, and carbonic acid dissolution (Islam and Mostafa, 2022a; Mostafa et al., 2017). Several studies delivered the same observation (Wetzel, 1975; Bartram and Balance, 1996; Al-Manharawi and Hafiz, 1997).

**Table 4.21 Biyearly average values and standard deviations of the cationic parameters in the groundwater around the CETP discharge area**

| <b>Parameters<br/>(mg/L)</b> | <b>Mean±SD</b>                 |                                     |                                    |
|------------------------------|--------------------------------|-------------------------------------|------------------------------------|
|                              | <b>Monsoon<br/>(2021-2022)</b> | <b>Post-monsoon<br/>(2021-2022)</b> | <b>Pre-monsoon<br/>(2022-2023)</b> |
| Na <sup>+</sup>              | 224.2±5.7                      | 236±0.5                             | 148.8±0.25                         |
| K <sup>+</sup>               | 0.25±0.40                      | 0.46±0.49                           | 0.20±5.1                           |
| Ca <sup>2+</sup>             | 1.22±1.3                       | 1.36±1.12                           | 1.14±1.15                          |
| Mg <sup>2+</sup>             | 35.6±2.5                       | 51.6±3.2                            | 31.08±2.1                          |

Biyearly mean values of the cationic parameters like Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and, Mg<sup>2+</sup> (**Table 4.21**) in the groundwater around the CETP discharge area varied from 148.8 to 236 mg/L, 0.20 to 0.46 mg/L, 1.14 to 1.36 mg/L, and 31.08 to 51.6 mg/L, respectively. The standard deviation (SD) of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and, Mg<sup>2+</sup> for all collected surface water samples varied from 0.25 to 5.7, 0.40 to 5.1, 1.12 to 1.15, and 2.1 to 3.2, respectively. The results (**Table 4.21**) show that the biyearly average cationic concentrations were found in the order of the post-monsoon > monsoon > pre-monsoon sampling periods because earth metal ions are typically derived from industrial run-off, carbonate minerals (calcite, aragonite, and/or dolomite) when CO<sub>2</sub> is stimulated by oxic and anoxic organic matter

decomposition (Halim et al., 2009). When calcite ( $\text{CaCO}_3$ ) and dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) react with  $\text{CO}_2$ , the quantities of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{HCO}_3^-$  in groundwater increase. During the monsoon season,  $\text{CO}_2$  in rainwater can aid in the breakdown of carbonate minerals. A parallel reflection was conveyed by Islam and Mostafa (2022a).

Hence, in the study, the concentration of the biyearly average anionic and cationic concentrations of groundwater in the post-monsoon sampling period were comparatively greater than in the pre-monsoon.

**Table 4.22 Biyearly average values and standard deviations of the heavy metal in the groundwater around the CETP discharge area**

| Parameters<br>(mg/L) | Mean±SD                |                             |                            |
|----------------------|------------------------|-----------------------------|----------------------------|
|                      | Monsoon<br>(2021-2022) | Post-monsoon<br>(2021-2022) | Pre-monsoon<br>(2022-2023) |
| Fe                   | 1.50±0.03              | 1.86±0.02                   | 1.08±0.02                  |
| Pb                   | 0.11±0.01              | 0.13±0.04                   | 0.09±0.02                  |
| Cu                   | 1.08±0.03              | 1.14±0.03                   | 0.84±0.02                  |
| Cr                   | 0.23±0.03              | 0.27±0.02                   | 0.17±0.02                  |
| Zn                   | 4.93±0.01              | 5.48±0.01                   | 4.83±0.02                  |
| Mn                   | 0.26±0.02              | 0.36±0.02                   | 0.16±0.01                  |

Biyearly average values of the trace heavy metals like Fe, Pb, Cu, Cr, Zn, and Mn in the groundwater around the CETP discharge area varied from 1.08 to 1.86mg/L, 0.09 to 0.13mg/L, 0.84 to 1.14 mg/L, 0.17 to 0.27 mg/L, 4.83 to 5.484 mg/L, and 0.16 to 0.36 mg/L, respectively (**Table 4.22**). The result (**Table 4.22**) revealed that the biyearly average trace metal concentrations were found in the order of the post-monsoon> monsoon > pre-monsoon sampling periods. The principal anthropogenic sources of trace metals in groundwater consist of industrial run-off, natural compounds leached into the soil (silty clay loam) system or rocks, pesticide residue, precise release from sewage treatment plants, and uncontrolled releases or escape from landfill sites (Islam and Mostafa, 2022a; Halim et al., 2009). Various studies found similar observations (Bartram and Balance, 1996; Chen et al., 2005; Leeuwen et al., 2000).

From the above discussion, we can conclude that during the study period pollution levels for groundwater were found in the following order post-monsoon>monsoon>pre-monsoon.

## 4.6 Water Quality Index (*WQI*)

A useful method for communicating water quality data is the water quality index (*WQI*) (Islam and Mostafa, 2021b). One of the best methods for determining the level of water pollution is the water quality index (*WQI*), which is universally recognized and used (Islam and Mostafa, 2021c; Alobaidy et al., 2010; Shakil and Mostafa, 2021b; Lumb et al., 2011). *WQI*, a unit less 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 and Mostafa, 2021c; Rai et al., 2012). *WQI* essentially presents complex data on water quality in a way that is mathematically clear and practical for both ordinary people and decision- policy-makers. To estimate water quality, a number of water quality indicators have been created. In this study, various indexing models, like the Canadian Council of Ministers of the Environment (*CCME*), Meireles Water Quality Index (*MWQI*), Weight Average Water Quality Index (*WWQI*), Irrigation Water Quality Index (*IWQI*), Nemerow's Pollution Index (*NPI*), Single-Factor Pollution Index (*I<sub>f</sub>*), Compound Pollution Index (*CPI*), Metal Index (*MI*), Heavy Metal Pollution Index (*HMPI*), Heavy Metal Evaluation Index (*HMEI*), Degree of Contamination (*C<sub>d</sub>*), Nemerow Index (*NeI*), Ecological Risk Measurement (*ERI*), and carcinogenic and non-carcinogenic Hazard Index (*HI<sub>total</sub>*), were used to determine the pollution level of the surface and groundwater in the study area. Several computer software were used for analyzing the experimental data.

### 4.6.1 Water quality index of surface and groundwater

To evaluate the quality of the water near the locations where the treated leather effluent from the CETP was discharged, the Canadian Council of Ministers of the Environment (*CCME*) water quality index (*WQI*) was used.

**Table 4.23 The *CCME WQI* calculated terms for the surface water body in the CETP discharge area**

| Sample location | Scope F <sub>1</sub> | Frequency F <sub>2</sub> | $\Sigma$ Excursion | NSE  | Amplitude F <sub>3</sub> | <i>WQI</i> score | Ranking  |
|-----------------|----------------------|--------------------------|--------------------|------|--------------------------|------------------|----------|
| SW1             | 60.9                 | 55.1                     | 86.9               | 1.26 | 55.73                    | 42.71            | Poor     |
| SW2             | 30.4                 | 27.5                     | 205.1              | 2.97 | 74.82                    | 50.8             | Marginal |
| SW3             | 34.78                | 28.98                    | 151.1              | 2.2  | 68.65                    | 52.5             | Marginal |
| SW4             | 39.13                | 34.78                    | 112.98             | 1.64 | 62.1                     | 53.103           | Marginal |
| SW5             | 39.13                | 28.98                    | 85.26              | 1.24 | 55.27                    | 57.5             | Marginal |

The *WQI* score was computed using the standard values of the parameters. The surface and groundwater *CCME WQI* calculated terms are provided in **Tables 4.23 and 4.24**. The surface and groundwater *WQI* scores ranged from 42.71 to 57.5 and 40.21 to 55.3, respectively. Except for the SW1 and GW1 sampling points all of the sampling locations had marginal water quality ratings, which showed that those places' surface and groundwater quality were in danger and frequently departed from natural or desirable conditions. But at the SW1 and GW1 sampling points surface and groundwater quality were “poor” indicating the water's quality was often protected but rarely threatened and occasionally deviated from acceptable or natural levels and no aquatic life can survive at the SW1 and GW1 sampling points according to *CCME WQI* score. The high values of EC, TSS, total hardness (TH), BOD, COD, turbidity, HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>-N, SO<sub>4</sub><sup>2-</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cu, Zn, Pb, Cr, and Na<sup>+</sup> were responsible for influencing the lowering of the *CWQI* values. In a study, Hasan et al. (2020) illustrate a similar observation.

**Table 4.24 CCME Score and Category of Groundwater**

| Sampling location | Scope F <sub>1</sub> | Frequency F <sub>2</sub> | $\Sigma$ Excursion | NSE | Amplitude | WQI Score | Ranking  |
|-------------------|----------------------|--------------------------|--------------------|-----|-----------|-----------|----------|
| GW1               | 54.54                | 48.48                    | 182.6              | 2.8 | 73.44     | 40.21     | Poor     |
| GW2               | 45.45                | 40.9                     | 149.4              | 2.3 | 69.36     | 46.61     | Marginal |
| GW3               | 36.36                | 36.36                    | 149.4              | 2.3 | 69.35     | 50.15     | Marginal |
| GW4               | 34.30                | 34.50                    | 149.1              | 2.1 | 67.20     | 52.2      | Marginal |
| GW5               | 34.10                | 34.25                    | 149.1              | 2.1 | 67.10     | 55.3      | Marginal |

The performance of the *CWQI* model was realistic when at least ten or more parameters were included over at least two 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 F<sub>1</sub> did not respond when a few variables were measured. So, we also consider other remaining indexing models.

The premeditated terms of the Weight Average Water Quality Index (*WWQI*) and Meireles Water Quality Index (*MWQI*) for the surface and groundwater are displayed in **Tables 4.25 and 4.26**. The surface and groundwater *WWQI* scores ranged from 13.99 to 161.83 and 15.10 to 17.80, respectively. Except for the SW1 sampling point, the water quality (*WWQI*) scores were "excellent" indicating that the surface and groundwater quality in those areas were satisfactory for irrigation. But at the SW1 sampling point surface water quality was "poor" indicating the quality of the water was not suitable for irrigation and aquatic biota. The high EC value of the present samples provided the higher *WWQI* value, at the SW1 sampling point. High values of EC, TDS, turbidity, and TH (Ca<sup>2+</sup>, Mg<sup>2+</sup>, and HCO<sub>3</sub><sup>-</sup>) also contributed to high index values at the (CETP discharge point) SW1 sampling point. High concentrations of EC, TDS, TSS, Cl<sup>-</sup>, and

$\text{NO}_3^-$ -N were responsible for that result. 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. But this model is easy to calculate and various important water quality parameters were used to assess the irrigation water quality for this the study performed this model. In their research, Shakil and Mostafa (2021) delivered a similar observation.

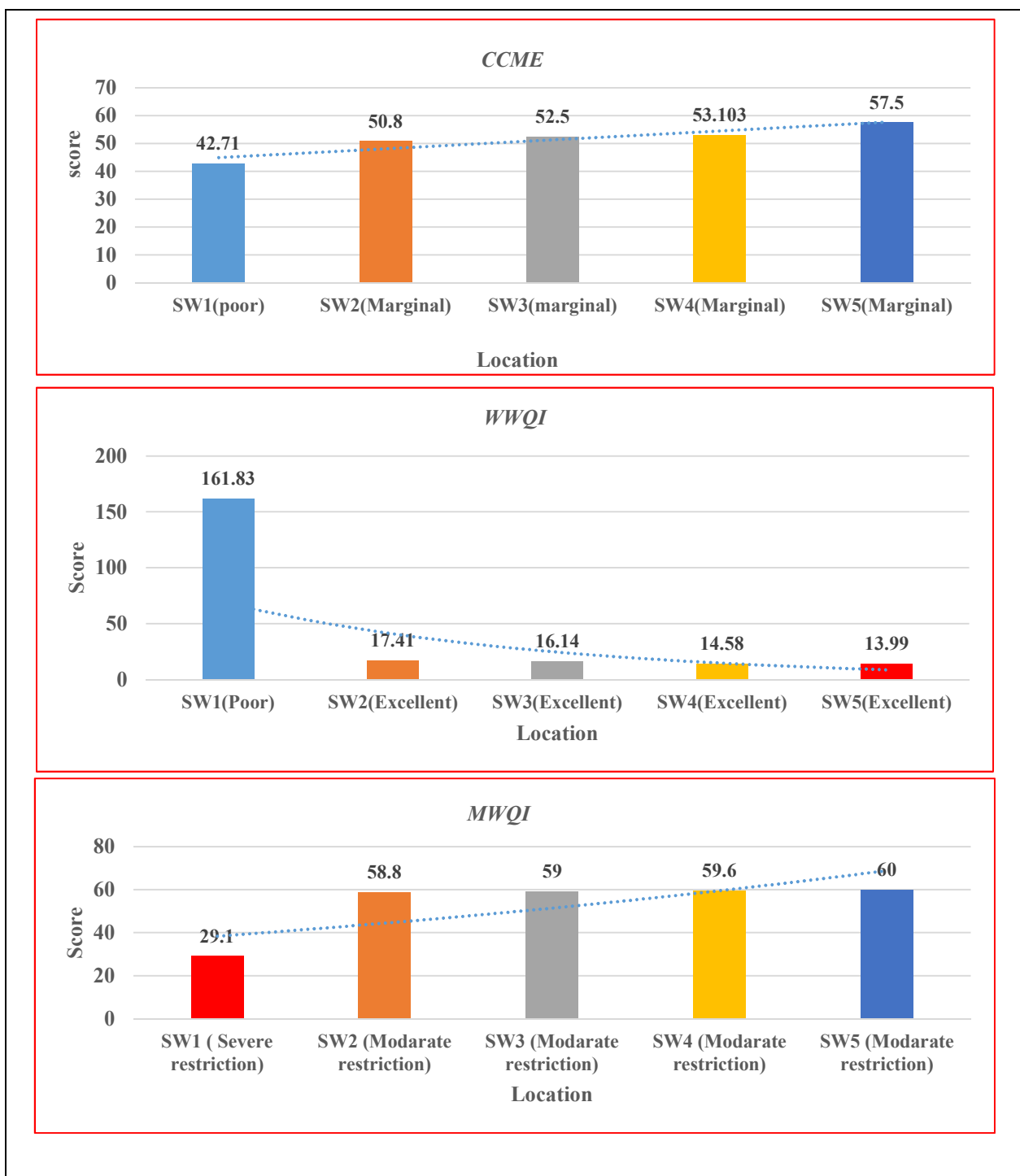
Considering the demerits of *CWQI* and *WWQI* models the study uses the *MWQI* to evaluate the water quality for irrigation purposes. According to Islam and Mostafa (2021), *MWQI* is the best method for assessing the water quality for irrigation purposes. The surface and groundwater *MWQI* scores ranged from 29.1 to 60 and 64.6 to 66, respectively. Except for the SW1 sampling point, the water quality rankings were "moderate" indicating that the surface and groundwater quality in those areas were appropriate for irrigation. However, at the SW1 sampling point, the surface water quality fell under the "severe" category, which indicated the water quality was not fit 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 (Bhuiya *et al.* 2015). Here only five parameters which are briefly discussed in the methodology sections were taken into consideration. The high values of EC,  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{Na}^+$  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. Various researchers delivered the same observation (Bhuiya *et al.*, 2015, 2016; Islam *et al.*, 2017; Ahmed *et al.*, 2018).

**Table 4.25 The *WWQI* and *MWQI* calculated terms for the surface water body in the CETP discharge area**

| <b>Location</b> | <b><i>WWQI</i> score</b> | <b>Water Type</b> | <b><i>MWQI</i> Score</b> | <b>Category</b>      |
|-----------------|--------------------------|-------------------|--------------------------|----------------------|
| <b>SW1</b>      | 161.83                   | Poor              | 29.1                     | Severe restriction   |
| <b>SW2</b>      | 17.41                    | Excellent         | 58.8                     | Moderate restriction |
| <b>SW3</b>      | 16.14                    | Excellent         | 59                       | Moderate restriction |
| <b>SW4</b>      | 14.58                    | Excellent         | 59.6                     | Moderate restriction |
| <b>SW5</b>      | 13.99                    | Excellent         | 60                       | Moderate restriction |

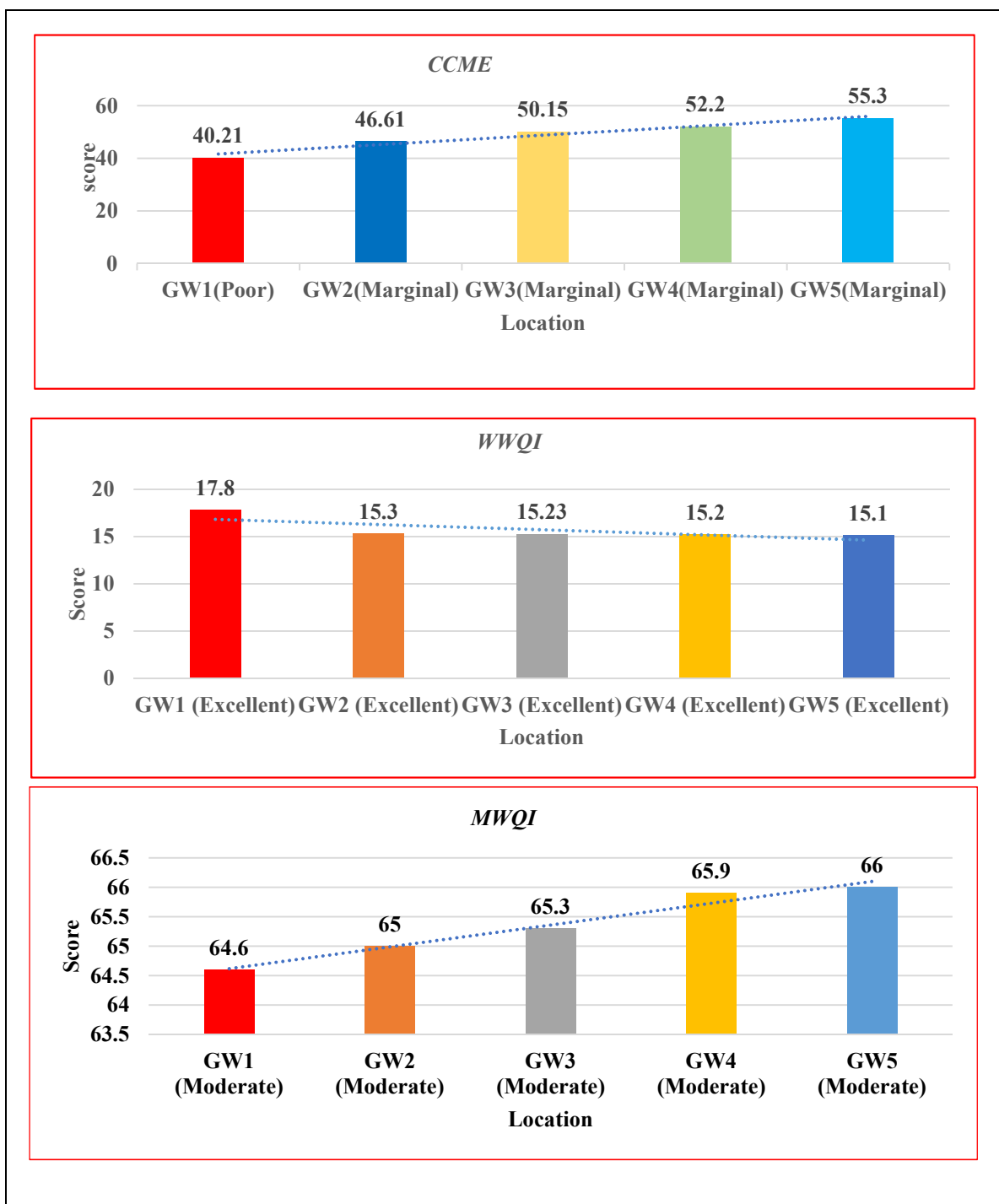
**Table 4.26 *WWQI* and *MWQI* Score and Category of Groundwater**

| <b>Location</b> | <b><i>WWQI</i> Score</b> | <b>Category</b> | <b><i>MWQI</i> Score</b> | <b>Category</b> |
|-----------------|--------------------------|-----------------|--------------------------|-----------------|
| GW1             | 17.80                    | Excellent       | 64.6                     | Moderate        |
| GW2             | 15.30                    | Excellent       | 65                       | Moderate        |
| GW3             | 15.23                    | Excellent       | 65.3                     | Moderate        |
| GW4             | 15.20                    | Excellent       | 65.9                     | Moderate        |
| GW5             | 15.10                    | Excellent       | 66                       | Moderate        |



**Figure 4.9 CCME, WWQI, and MWQI scores of the surface water body around the leather CETP discharge area**

The surface and groundwater *CCME*, *WWQI*, and *MWQI* scores around the CETP discharge region are displayed in **Figures 4.9 and 4.10**. From the site, SW1 to SW5 and GW1 to GW5, the *CCME* and *MWQI* ratings of the surface and groundwater near the CETP discharge area were increasing. The high values of EC,  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{Na}^+$  were responsible for that result, and due to the dilution effect that pattern may occur. This pattern suggests that the surface and groundwater quality at the SW1 and GW1 sampling points were negatively impacted by the leather effluent and that the water quality has since gradually improved to distance. A parallel observation was reflected by Islam and Mostafa (2021).



**Figure 4.10 *CCME*, *WWQI*, and *MWQI* scores of the groundwater body around the CETP discharge area**

From sites SW1 to SW5 and GW1 to GW2 (**Figures 4.9 and 4.10**), the *WQI* ratings for the *WWQI* of the surface and groundwater near the CETP discharge area were decreasing. High concentrations of EC, TDS, TSS,  $\text{Cl}^-$ , and  $\text{NO}_3^-$ -N were responsible for that result, and due to the dilution effect that pattern may occur. This pattern recommends that the surface and groundwater quality at the SW1 and GW1 sampling sites were adversely impacted by the leather effluent and that the water quality has since steadily developed to distance. Shakil and Mostafa (2021) delivered a similar observation.

### **Irrigation Water Quality Index (*IWQI*)**

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 Magnesium Adsorption Ratio (*MAR*), Sodium Adsorption Ratio (*SAR*), Soluble Sodium Percentage (*SSP*), Percentage Sodium ( $\% \text{Na}$ ), and Kelly's Ratio (*KR*) (Bhuiya et al., 2015, 2016; Islam et al., 2017; Ahmed et al., 2018).

The calculated terms of the *MAR* for the surface and groundwater are shown in **Tables 4.27 and 4.28**. The surface and groundwater *MAR* scores ranged from 59.4 to 93.8 and 87.7 to 98.6, respectively. The water quality rating was greater than 50 (**Table 3.3**) in practically all of the sampling locations, which indicated they were harmful to soil and aquatic life (Ayers and Westcot, 1985). When the magnesium adsorption ratio (*MAR*) exceeds 50, it has a negative impact on the soil (Gupta and Gupta 1987). Additionally, soil containing high concentrations of exchangeable  $\text{Mg}^{2+}$  causes infiltration complications (Ayers and 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 and Mostafa 2021c). The High Concentration of magnesium plays the dominant part in this investigation. A parallel observation was delivered by Ahmed et al. (2017).

**Tables 4.27 and 4.28** Displays the premeditated terms of the *SAR* for the surface and groundwater. The surface and groundwater *SAR* scores ranged from 0.3 to 8.8 and 0.25 to 2.8, respectively. The water quality rankings was  $<10$ , (**Table 3.3**) in all the sampling sites, indicating they were suitable for irrigation (Islam and Mostafa, 2021c; Ayers and Westcot, 1985; Islam and Mostafa, 2021c; Simsek and Gunduz, 2007). Here sodium

plays a vital role. In a study, Islam & Mostafa (2021c) illustrate a similar observation. The presence of  $\text{Na}^+$  in irrigation water reacts with soil to restrict permeability, and frequent use makes the soil impermeable, whereas high  $\text{Na}^+$  causes alkali soil formation. High  $\text{Na}^+$  saturation also causes  $\text{Ca}^{2+}$  insufficiency. Frequent irrigation with high  $\text{Na}^+$  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  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  salts in irrigation water mitigates the negative effects of sodium by improving soil permeability (Punmia and Lal 1981; Asaduzzaman 1985).

The deliberate terms of the *SSP* for the surface and groundwater are illustrated in **Tables 4.27 and 4.28**. The surface and groundwater *SSP* scores ranged from 11.4 to 72 and 3.0 to 4.1, respectively. Practically, all of the sampling sites had water quality values  $< 20$  or  $20 - 40$  except (**Table 3.3**) for the SW1 sampling point, which displayed that besides the SW1 sampling point, all other surface and groundwater were 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 the dominant part in this analysis. An analogous statement was delivered by Ahmed et al. (2017).

**Tables 4.27 and 4.28** indicate the considered terms for the % *Na* in the surface and groundwater. The surface and groundwater % *Na* score ranged from 1.81 to 21.13 and 2.8 to 3.7, respectively. The water quality value was  $< 40$  (**Table 3.3**) in practically all of the sampling positions, which represents they were recommended for irrigation purposes (US SL, 1954). ). Here sodium plays a vital role. In their research, Islam & Mostafa (2021c) illustrate a similar observation. Excess  $\text{Na}^+$  also causes concerns with agricultural water uptake, seedling emergence, aeration, plant and root infections, and so on (Ayers and Westcot 1985).

Kelley's ratio (*KR*) in water suggests a balance of  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  ions. A (*KR*) greater than one indicates an overabundance of  $\text{Na}^+$  in the water. Kelley (1963) recommended that the ratio of irrigation water should not exceed 1. The premeditated terms of the *KR* for surface and groundwater are displayed in **Tables 4.27 and 4.28**. The surface and groundwater *KR* scores ranged from 12.5 to 257 and 3.2 to 3.8, respectively. The water quality rating was greater than one (**Table 3.3**) in practically all of the

sampling places, which indicates they were unsuitable for irrigation purposes due to excess levels of  $\text{Na}^+$  (Islam and Mostafa, 2021c; Shammi et al., 2016; Shakil and Mostafa, 2021; Kelly, 1940; Kelly, 1951). Here sodium also plays a vigorous part. Various researchers delivered the same observation (Bhuiya et al., 2015, 2016; Islam et al., 2017; Ahmed et al., 2018).

However, we get confusing results from *IWQI* because *MAR* and *KR* suggest all the sampling sites samples were not suitable for irrigation purposes where *SAR* and *% Na* provided opposite information and *SSP* illustrates that except for the SW1 sampling point surface water was suitable for irrigation purposes. So, we may avoid the result of this indexing or roughly deliver that the surface water at all the sampling points was suitable for irrigation purposes, except for the SW1 sampling point.

**Table 4.27 The *IWQI* calculated terms for the surface water body in the CETP discharge area**

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

**Table 4.28 The *IWQI* calculated terms for the groundwater body in the CETP discharge area**

| Indexing<br>name | Sampling Point |      |      |      |      |
|------------------|----------------|------|------|------|------|
|                  | GW1            | GW2  | GW3  | GW4  | GW5  |
| <i>MAR</i>       | 98.1           | 87.7 | 98.6 | 98.6 | 97.9 |
| <i>SAR</i>       | 2.8            | 0.25 | 0.26 | 0.26 | 0.26 |
| <i>SSP</i>       | 4.1            | 3.3  | 3.6  | 3.0  | 3.5  |
| <i>% Na</i>      | 3.7            | 3.1  | 3.4  | 2.8  | 3.3  |
| <i>KR</i>        | 3.8            | 3.2  | 3.5  | 3.5  | 3.4  |

**Table 4.29 The *NPI* calculated terms for the surface water body in the CETP discharge area**

| Parameters                      | <i>NPI</i> for<br>SW1 | <i>NPI</i> for<br>SW2 | <i>NPI</i> for<br>SW3 | <i>NPI</i> for<br>SW4 | <i>NPI</i> for<br>SW5 |
|---------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| DO                              | 3.12                  | 1.47                  | 0.94                  | 0.93                  | 0.90                  |
| EC                              | 2.05                  | 0.35                  | 0.34                  | 0.34                  | 0.34                  |
| TSS                             | 1.8                   | 1.54                  | 0.57                  | 0.48                  | 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 <sup>-</sup>                 | 1.72                  | 0.04                  | 0.039                 | 0.038                 | 0.036                 |
| NO <sub>3</sub> <sup>-</sup> -N | 1.38                  | 1.35                  | 1.21                  | 0.85                  | 0.44                  |
| Na <sup>+</sup>                 | 1.75                  | 0.0545                | 0.0495                | 0.046                 | 0.0445                |
| Zn                              | 1.96                  | 1.08                  | 0.32                  | 0.1                   | 0.08                  |
| Pb                              | 17                    | 1                     | 1                     | 1                     | 1                     |
| Cr                              | 10.6                  | 1.2                   | 0.86                  | 0.46                  | 0.4                   |

### Nemerow's pollution index (*NPI*)

Nemerow's pollution index (*NPI*) methods indicate which parameters were responsible for polluting the sampling sites. An *NPI* value greater than one means they were responsible for polluting the sites. The study showed that COD, EC, BOD, TSS,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , Zn, Pb, Cr, and  $\text{Na}^+$  were responsible for polluting most of the sampling sites (**Table 4.29 and 4.30**). Several researchers conveyed a similar statement (Shammi et al., 2016; Shakil and Mostafa, 2021; Kelly, 1940; Kelly, 1951).

**Table 4.30 The *NPI* calculated terms for the groundwater body in the CETP discharge area**

| Parameters    | <i>NPI</i> for GW1 | <i>NPI</i> for GW2 | <i>NPI</i> for GW3 | <i>NPI</i> for GW4 | <i>NPI</i> for GW5 |
|---------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| BOD           | 45                 | 40                 | 40                 | 39.5               | 39                 |
| COD           | 4.3                | 4                  | 4                  | 3.8                | 3.8                |
| $\text{Cl}^-$ | 1.02               | 1.00               | 0.97               | 0.99               | 0.99               |
| $\text{Na}^+$ | 1.1                | 1.07               | 1.07               | 1.07               | 1.07               |
| Zn            | 1.06               | 1.02               | 1.02               | 1                  | 0.98               |
| Pb            | 13                 | 11                 | 11                 | 10                 | 10                 |
| Cr            | 5.0                | 4.6                | 4.4                | 4.4                | 4.2                |
| Fe            | 1.5                | 1.5                | 1.49               | 1.49               | 1.43               |

### Heavy Metal Pollution Indices:

Some Heavy Metal water quality indices, such as the Metal Index (*MI*), the Heavy Metal Evaluation Index (*HMEI*), the Heavy Metal Pollution Index (*HMPI*), the Nemerow Index (*NeI*), the Ecological Risk Measurement (*ERI*), the Hazard Index (*HI*), the Degree of Contamination (*C<sub>d</sub>*), the Single-Factor Pollution Index (*I<sub>i</sub>*) and the Compound Pollution Index (*CPI*) were calculated from five (5) surface and groundwater samples. The values of these indices are shown in **Tables 4.31 and 4.32**. The average value of the metal concentration was taken into account in the investigation.

**Table 4.31 Calculated terms of all metal indices for surface water**

| <b>Location</b> | <b><i>MI</i></b> | <b><i>HMEI</i></b> | <b><i>HMPI</i></b> | <b><i>C<sub>d</sub></i></b> | <b><i>I<sub>t</sub></i></b> | <b><i>CPI</i></b> | <b><i>ERI</i></b> | <b><i>NeI</i></b> | <b><i>HI<sub>nc</sub></i></b> | <b><i>HI<sub>ca</sub></i></b> |
|-----------------|------------------|--------------------|--------------------|-----------------------------|-----------------------------|-------------------|-------------------|-------------------|-------------------------------|-------------------------------|
| SW1             | 289.3            | 282.4              | 3744.03            | 282.3                       | 303.22                      | 27.6              | 75                | 20.1              | 237.7                         | 86.05                         |
| SW2             | 34.46            | 26.8               | 350.75             | 24.9                        | 47.1                        | 4.3               | 67.1              | 9.3               | 32.9                          | 11.9                          |
| SW3             | 29.8             | 21.9               | 327.65             | 20.21                       | 42.2                        | 3.8               | 65.32             | 5.3               | 26.8                          | 9.7                           |
| SW4             | 20.7             | 16.5               | 263.03             | 11.1                        | 31.9                        | 2.9               | 59.1              | 3.9               | 22.4                          | 8.1                           |
| SW5             | 17.35            | 15.3               | 236.1              | 7.75                        | 27.6                        | 2.5               | 54.1              | 3.6               | 20.61                         | 7.5                           |

The Metal Index (*MI*) was employed to assess the water quality in the region of the sites where the treated effluent from the CETP was released. The standard values of the parameters were used to calculate the *MI* score. The computed *MI* values for the surface and groundwater are shown in **Tables 4.31 and 4.32**. The *MI* scores of the surface and groundwater ranged from 17.35 to 289.3 and 19.8 to 25.04, respectively. That suggests that all of the sampling locations were highly contaminated with heavy metals (**Table 3.5**) and they were unfit for drinking or use in the home. High concentrations of Cu, Zn, Pb, and Cr were responsible for that result. A similar observation was stated by Islam and Mostafa (2021).

The Heavy Metal Evaluation Index (*HMEI*) was used to evaluate the water quality in the district of the locations where the treated effluent from the CETP was released. The standard values of the parameters were used to analyze the *HMEI* score. The calculated *HMEI* values for the surface and groundwater are revealed in **Tables 4.31 and 4.32**. The *HMEI* score of the surface and groundwater ranged from 15.3 to 282.4 and 19.70 to 22.8, respectively. This shows that there was medium to high contamination at all of the sampling sites (**Table 3.5**) and they were inappropriate for drinking. That result was caused by high concentrations of Cu, Zn, Pb, and Cr. In a study, Shammi et al. (2016) illustrate a parallel reflection.

The Heavy Metal Pollution Index (*HMPI*) was retained to measure the water quality in the area of the spots where the treated effluent from the CETP was released. The standard values of the parameters were used to calculate the *HMPI* score. The computed *HMPI* values for the surface and groundwater are presented in **Tables 4.31 and 4.32**. The *HMPI* scores of the surface and groundwater ranged from 236.1 to 3744.03 and 261.1 to 308.3, respectively. That displays a high level of contamination at each of the sampling points

(Table 3.5) and they would not be used for drinking. That was caused by high concentrations of Cu, Zn, Pb, and Cr. Various researchers delivered the same observation (Shammi et al., 2016; Shakil and Mostafa, 2021; Kelly, 1940; Kelly, 1951).

The degree of Contamination index ( $C_d$ ) was employed to assess the water quality in the region of the sites where the treated effluent from the CETP was released. The standard values of the parameters were used to calculate the  $C_d$  score. The computed  $C_d$  values for the surface and groundwater are shown in Tables 4.31 and 4.32. The  $C_d$  score of the surface and groundwater ranged from 7.75 to 282.3, and 12.35 to 15.7, respectively. This shows that there was low to high contamination at all of the sampling sites (Table 3.5) and they were inappropriate for drinking. High concentrations of Cu, Zn, Pb, and Cr were responsible for that result. A parallel reflection was stated by Ahmed et al. (2017).

The Single-Factor Pollution Index ( $I_t$ ) and Compound Pollution Index ( $CPI$ ) were used to weigh the water quality in the area of the sites where the treated effluent from the CETP was released. The standard values of the parameters were used to determine the  $I_t$  and  $CPI$  scores. The calculated  $I_t$  and  $CPI$  values for the surface and groundwater are displayed in Tables 4.31 and 4.32. The  $I_t$  scores ranged from 27.6 to 303.22, and 19.3 to 22.8, and the  $CPI$  scores ranged from 2.5 to 27.6 and 1.7 to 2.1, for the surface and groundwater, respectively. It recommends heavy metal contamination at each sampling site (Table 3.5) and they were not appropriate for drinking or carrying out domestic tasks. That result was caused by high concentrations of Cu, Zn, Pb, and Cr. A similar observation was stated by Islam and Mostafa (2021).

The Nemerow Pollution Index ( $NeI$ ), and non-carcinogenic and carcinogenic Health Index ( $HI_{nc}$  and  $HI_{ca}$ ) were employed to assess the water quality in the region of the sites where the CETP was released. The standard values of the parameters were used to calculate the  $NeI$ ,  $HI_{nc}$ , and  $HI_{ca}$  scores. The computed  $NeI$ ,  $HI_{nc}$ , and  $HI_{ca}$  values for the surface and groundwater are shown in Tables 4.31 and 4.32. The  $NeI$  scores ranged from 3.6 to 20.1, and 9.8 to 10.6, the  $HI_{nc}$  scores ranged from 20.61 to 237.7, and 34.35 to 38.4, and the  $HI_{ca}$  scores ranged from 7.5 to 86.05, and 12.30 to 13.9, for the surface and groundwater, respectively. This demonstrates that there was heavy metal contamination at all of the test sites, raising concerns about both the possibility of non-carcinogenic and carcinogenic effects (Table 3.5). That was caused by high concentrations of Cu, Zn, Pb,

and Cr. They were not appropriate for drinking or usage in the home. Several researchers conveyed a similar statement (Shammi et al., 2016; Shakil and Mostafa, 2021; Kelly, 1940; Kelly, 1951).

The Ecological Risk Index (*ERI*) was used to evaluate the water quality in the section of the spots where the treated effluent from the CETP was released. The standard values of the parameters were used to analyze the *ERI* score. The subtracted *ERI* values for the surface and groundwater are exposed in **Tables 4.31 and 4.32**. The *ERI* scores of the surface and groundwater ranged from 54.1 to 75 and 21.8 to 23.9, respectively. High concentrations of Cu, Zn, Pb, and Cr were responsible for that result. It indicates there was little ecological danger at all of the sampling sites (**Table 3.5**). In their research, Islam & Mostafa (2021c) illustrate a similar observation.

**Table 4.32 Calculated terms of all metal indices for groundwater**

| <b>Location</b> | <b><i>MI</i></b> | <b><i>HMEI</i></b> | <b><i>HMPI</i></b> | <b><i>Cd</i></b> | <b><i>I<sub>t</sub></i></b> | <b><i>CPI</i></b> | <b><i>ERI</i></b> | <b><i>NeI</i></b> | <b><i>HI<sub>nc</sub></i></b> | <b><i>HI<sub>ca</sub></i></b> |
|-----------------|------------------|--------------------|--------------------|------------------|-----------------------------|-------------------|-------------------|-------------------|-------------------------------|-------------------------------|
| GW1             | 25.04            | 22.8               | 308.3              | 15.7             | 22.8                        | 2.1               | 23.9              | 10.6              | 38.4                          | 13.9                          |
| GW2             | 22.3             | 19.97              | 262.79             | 12.93            | 20                          | 1.83              | 22.3              | 10.3              | 34.65                         | 12.59                         |
| GW3             | 22.01            | 19.77              | 261.9              | 12.68            | 19.8                        | 1.80              | 22.3              | 10.2              | 34.60                         | 12.50                         |
| GW4             | 22.0             | 19.75              | 261.5              | 12.50            | 19.5                        | 1.73              | 22.0              | 10                | 34.50                         | 12.45                         |
| GW5             | 19.8             | 19.70              | 261.1              | 12.35            | 19.3                        | 1.70              | 21.8              | 9.8               | 34.35                         | 12.30                         |

The above heavy metal pollution indices were used for the justification of the investigation, that the study area samples were not suitable for drinking purposes.

The *MI*, *HMEI*, *HMPI*, *C<sub>d</sub>*, *I<sub>t</sub>*, *CPI*, *ERI*, *NeI*, *HI<sub>nc</sub>*, and *HI<sub>ca</sub>* scores of the surface and groundwater body near the CETP discharge regions are shown in (**Figures 4.11 (a, b) and 4.12 (a, b)**). The *MI*, *HMEI*, *HMPI*, *C<sub>d</sub>*, *I<sub>t</sub>*, *CPI*, *ERI*, *NeI*, *HI<sub>nc</sub>*, and *HI<sub>ca</sub>* ratings of the surface and groundwater close to the leather industries show a declining trend from site SW1 to SW5 and site GW1 to GW5, respectively. Due to the dilution effect that may occur. This pattern implies that as distance increased, the surface and groundwater quality gradually improved. A parallel reflection was stated by Ahmed et al. (2017).

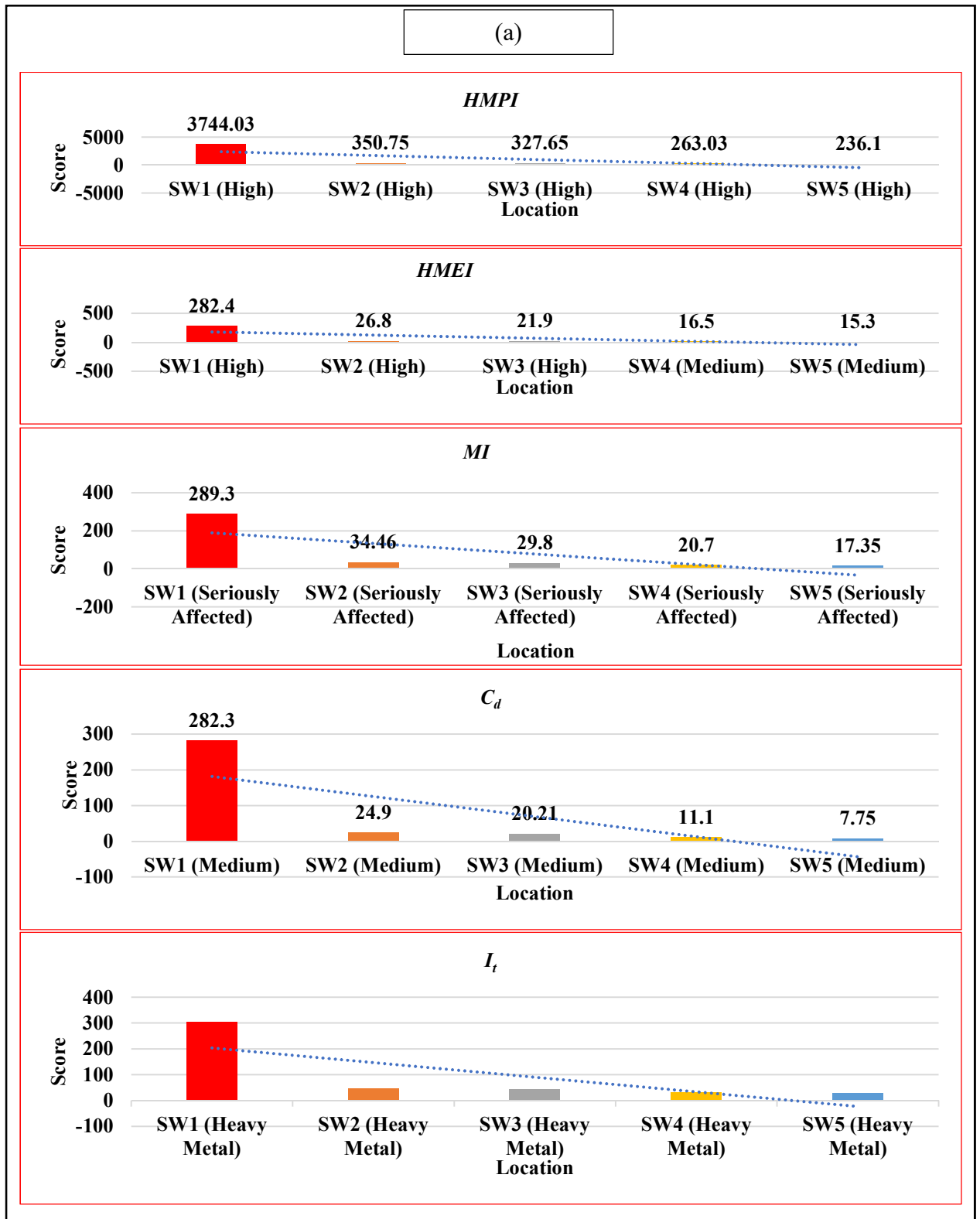
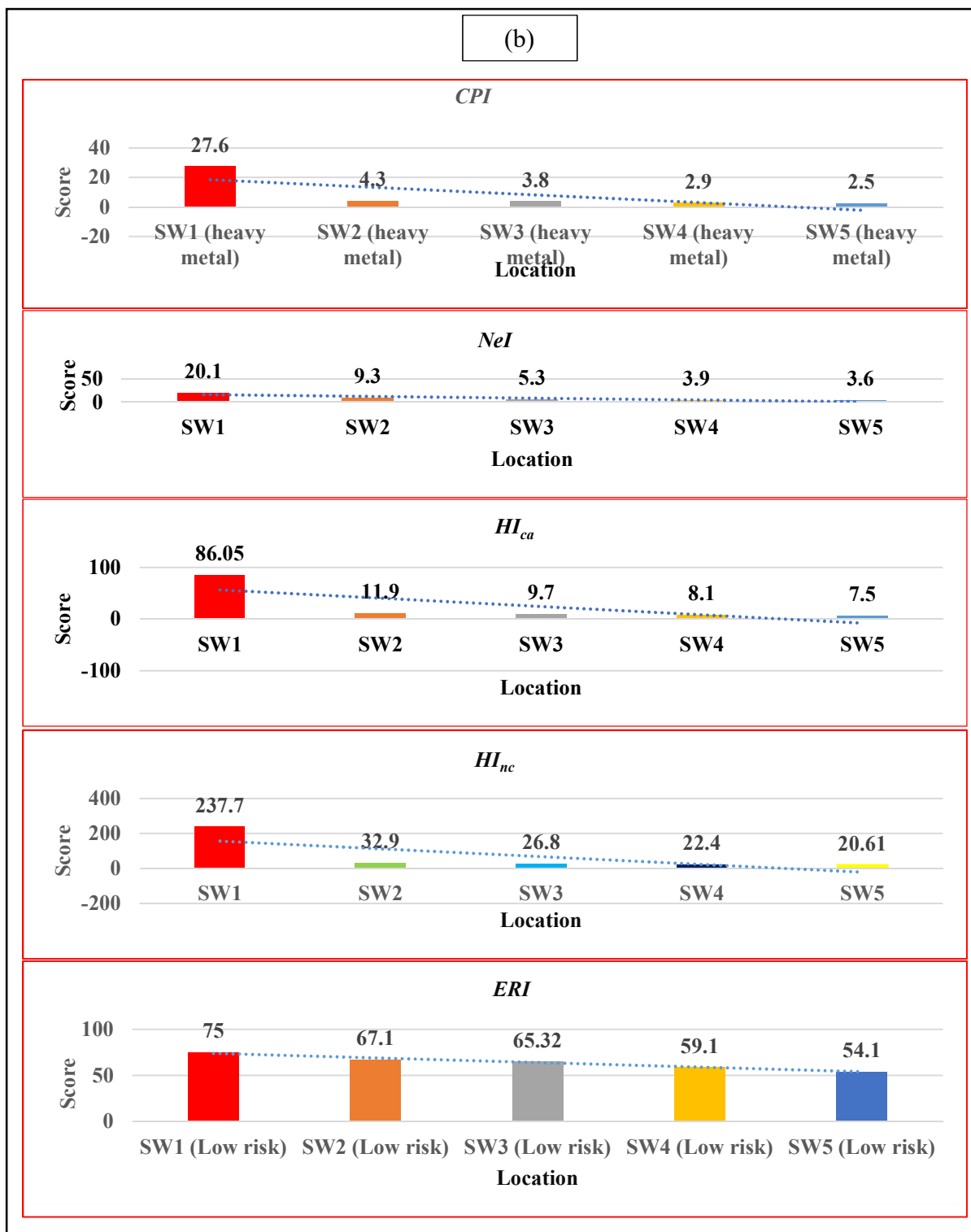


Figure 4.11 (a) *HMEI*, *HMPI*, *MI*, *C<sub>d</sub>*, and *I<sub>t</sub>* scores of the surface water body around the CETP discharge area



**Figure 4.11(b) *CPI*, *NeI*, *HI<sub>ca</sub>*, *HI<sub>nc</sub>*, and *ERI* scores of the surface water body around the CETP discharge area**

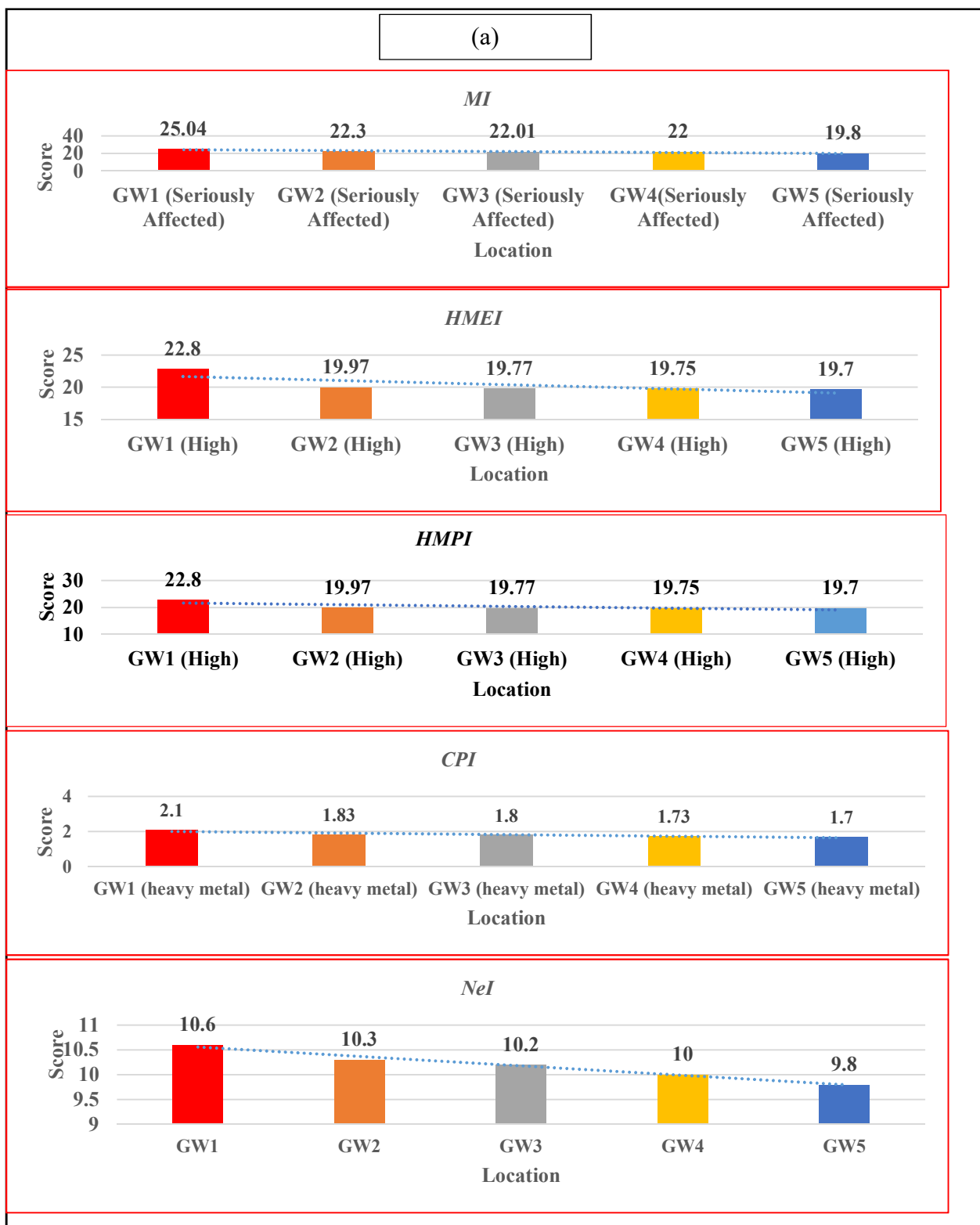


Figure 4.12 (a) *MI*, *HMEI*, *HMPI*, *CPI*, and *NeI* scores of the groundwater body around the CETP discharge area

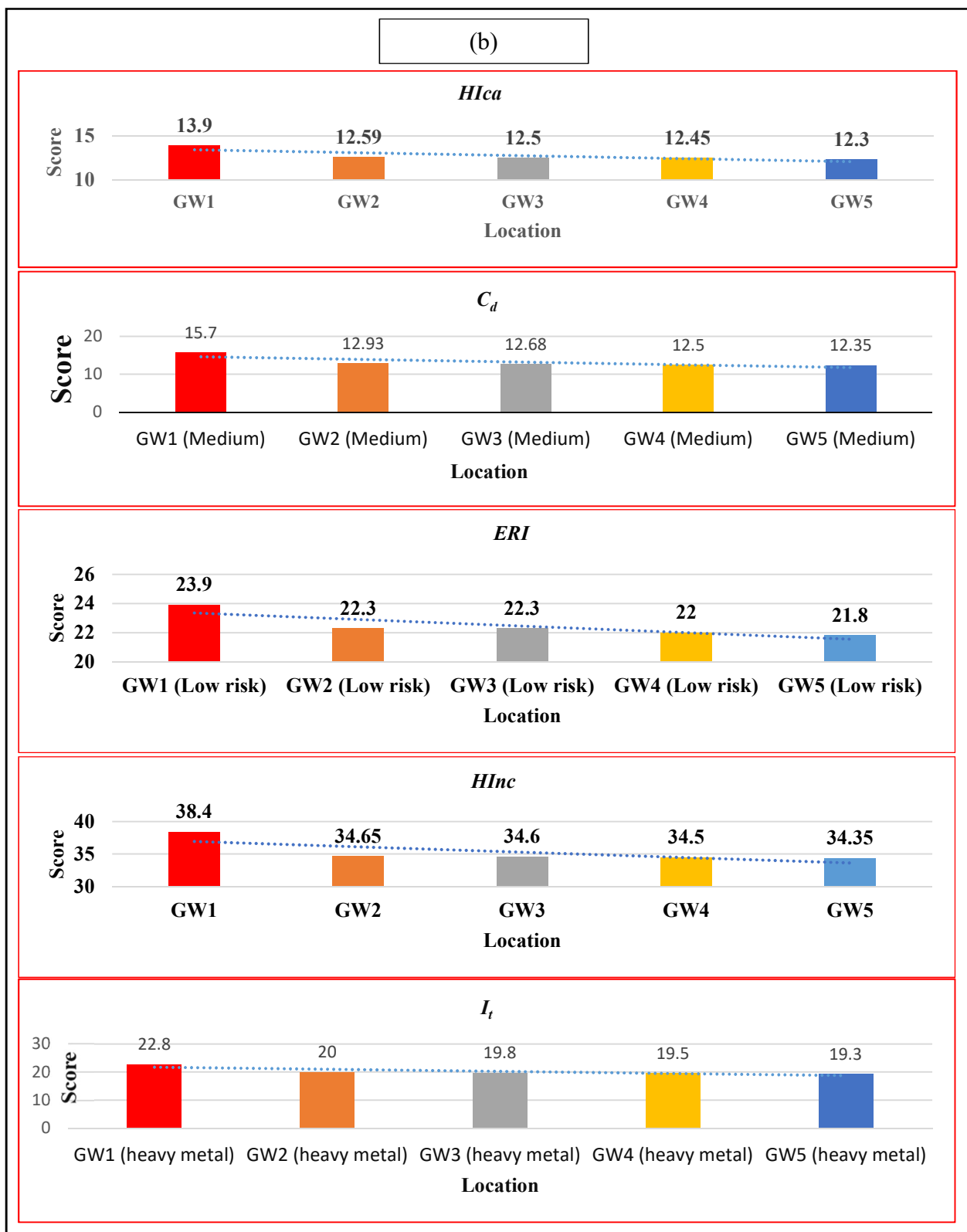


Figure 4.12 (b)  $HI_{ca}$ ,  $HI_{inc}$ ,  $ERI$ ,  $C_d$ , and  $I_t$  scores of the groundwater body around the CETP discharge area

## 4.7 Principal Component Analysis (PCA)

Principal Components Analysis (PCA) is a powerful and adaptable technique that has the potential to be applied to a wide range of statistical analyses. It is a data reduction approach that examines a multivariate dataset to support the clarification of a vast series of data and to illustrate the connections between the variables (Morell et al., 1996; Gazley et al., 2015; Markopoulos et al., 2017). The principal components were extracted based on eigenvalues equal to or greater than 1, with the PCs being arranged in decreasing order of variance, such that 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 et al., 1960; Jimenez-Espinosa et al., 1993). Generally, the factors influencing the chemistry of the surface and groundwater in the area would have some degree of correlation. A varimax rotation was used to ensure that the factors did not correlate with each other and that variables did not correlate significantly with more than one factor. Varimax rotation generates orthogonal factor rotation, resulting in uncorrelated and understandable factors (Yidana et al., 2012; Dempster et al., 2013). The final factor model produced two components based on the above-mentioned categorization. Typically, parameters with high commonalities are the parameters that contribute suggestively to the factors (Chen et al., 2015). Due to huge concentration variation between the physicochemical parameters and trace heavy metals, we divided the analysis into two steps 1<sup>st</sup>ly PCA analysis for physicochemical parameters and 2<sup>nd</sup>ly for trace heavy metals for surface and groundwater.

### 4.7.1 Physicochemical parameter

The PCA analysis considered the extracted PCs from the variables with eigenvalues greater than 1.00 for the surface and groundwater samples. Two PCs were extracted for the surface and groundwater principal component analysis (**Tables 4.33 and 4.34**). The variance explanations for PC1, and PC2 in the surface water were 88.902 and 8.912%, and in the groundwater were 86.7 and 6.7%, respectively. PC1 for surface water was found to be strongly correlated (over 0.75) with temperature, COD, pH, BOD, EC, TDS, Turbidity, TH,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Mg}^{2+}$ . Still, the role of the second component (PC2) in this variable was very insignificant because their eigenvalues were less than 1.00 (Jimenez-Espinosa et al., 1993; Markopoulos et al., 2017). PC1 was also negatively correlated with DO, PC2 with TSS, BOD,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,

$\text{PO}_4^{3-}$ , and  $\text{Ca}^{2+}$ , therefore, they were not contributing to the variables (Irabar et al., 2008).

PC1 for groundwater was observed to be strongly correlated (over 0.75) with temperature, COD, pH, BOD, EC, TDS, Turbidity, TSS,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{NO}_3^-$ -N,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  but the role of the PC2 in this variable was negligible because their eigenvalues were less than 1.00 (Dempster et al., 2013; Markopoulos et al., 2017). PC1 was also negatively correlated with DO, PC2 with COD, pH, Turbidity,  $\text{Cl}^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{Ca}^{2+}$ , therefore, they were not contributing to the variables (Gazley et al., 2015; Irabar et al., 2008).

The source of PC1 loading could be released from the anthropogenic sources specifically derived from the industrial effluent in the study area. A parallel observation was delivered by many studies (Kumar, 2014; Kraiem et al., 2014). The total sample variance for the surface and groundwater of the two PCs extracted showed about 97.815 and 93.3 %, respectively. About 85 % of the total variance was displayed in the first loadings (**Tables 4.33 and 4.34**). The axis with the greatest variance becomes the first principal component (PCI) (Jimenez-Espinosa et al., 1993). The parameters that subsidize most of the components typically have a high degree of commonality (Islam and Mostafa, 2022).

**Table 4.33 Principal components (two-component extracted) of the analyzed (physicochemical) parameters for surface water**

| Parameters                    | Component |        |
|-------------------------------|-----------|--------|
|                               | 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 <sup>-</sup>               | 0.939     | 0.341  |
| SO <sub>4</sub> <sup>2-</sup> | 0.956     | -0.244 |
| NO <sub>3</sub> <sup>-</sup>  | 0.707     | -0.619 |
| PO <sub>4</sub> <sup>3-</sup> | 0.872     | -0.471 |
| HCO <sub>3</sub> <sup>-</sup> | 0.999     | -      |
| Na <sup>+</sup>               | 0.939     | 0.339  |
| K <sup>+</sup>                | 0.985     | 0.164  |
| Ca <sup>2+</sup>              | 0.890     | -0.352 |
| Mg <sup>2+</sup>              | 0.988     | -      |
| Eigenvalue                    | 16.891    | 1.693  |
| % Variance                    | 88.902    | 8.912  |
| Cumulative %                  | 88.902    | 97.815 |

**Table 4.34 Principal components (two-component extracted) of the analyzed (physicochemical) parameters for groundwater**

| Parameters                    | Component |        |
|-------------------------------|-----------|--------|
|                               | PC1       | PC2    |
| Temperature                   | 0.982     | –      |
| pH                            | 0.905     | -0.214 |
| DO                            | -0.485    | 0.825  |
| EC                            | 0.959     | 0.143  |
| Turbidity                     | 0.992     | -0.116 |
| TSS                           | 0.946     | 0.155  |
| TDS                           | 0.920     | 0.146  |
| BOD                           | 0.964     | 0.275  |
| COD                           | 0.950     | -0.268 |
| TH                            | 0.944     | 0.230  |
| Cl <sup>-</sup>               | 0.943     | -0.140 |
| SO <sub>4</sub> <sup>2-</sup> | 0.940     | 0.136  |
| NO <sub>3</sub> <sup>-</sup>  | 0.932     | 0.259  |
| PO <sub>4</sub> <sup>3-</sup> | 0.992     | -0.116 |
| HCO <sub>3</sub> <sup>-</sup> | 0.997     | -      |
| Na <sup>+</sup>               | 0.984     | 0.277  |
| K <sup>+</sup>                | 0.951     | 0.176  |
| Ca <sup>2+</sup>              | 0.966     | -0.101 |
| Mg <sup>2+</sup>              | 0.980     | -      |
| Eigenvalue                    | 15.6      | 1.2    |
| % Variance                    | 86.7      | 6.7    |
| Cumulative %                  | 86.7      | 93.3   |

### 4.7.2 Heavy Metals

The PCA analysis reflected the extracted PCs from the variables with eigenvalues greater than 1.00 for the surface and groundwater samples. Two PCs were extracted for the surface and groundwater principal component analysis (**Tables 4.35 and 4.36**). The variance explanations for PCs in surface water were 75.477 and 19.65%, respectively, while in groundwater they were 76.6 and 17.1%, respectively for PC1 and PC2.

PC1 for the surface water was observed to be strongly correlated (over 0.75) with Cu, Zn, Pb, and Cr, but the character of the second component (PC2) in this variable was very irrelevant because their eigenvalues were less than 1.00 (Markopoulos et al., 2017). PC2 was also negatively correlated with Zn, Pb, and Cr, therefore, they were not subordinate to the parameters (Irabar et al., 2008; Kraiem et al., 2014).

PC1 for the groundwater was found to be strongly correlated (over 0.75) with Cr, Cu, Zn, and Fe but the role of the second component (PC2) in this variable was very insignificant because their eigenvalues were less than 1.00 (Dempster et al., 2013). PC2 was also negatively correlated with Pb, therefore, they were not contributing to the parameters (Gazley et al., 2015).

The source of PC1 loading could be released from the anthropogenic sources, specifically consequent from the industrial effluent in the study area. A similar observation was delivered by Kraiem et al., 2014. In the PCA analysis for the surface and groundwater, all extracted PCs from the variables that had eigenvalues larger than 1.00 were kept and considered. The total sample variance for the surface and groundwater of the two PCs extracted showed about 95.1 and 93.7 %, respectively. About 75 % of the total variance was exhibited in the first loadings (**Tables 4.35 and 4.36**). The parameters that contribute most to the components typically have a high degree of commonality (Kraiem et al., 2014; Islam and Mostafa, 2022).

**Table 4.35 Principal components (two-component extracted) of the analyzed parameters (heavy metals) for surface water**

| <b>Component Matrix</b> |                  |        |
|-------------------------|------------------|--------|
| <b>Parameters</b>       | <b>Component</b> |        |
|                         | PC1              | PC2    |
| Fe                      | 0.739            | 0.328  |
| Cu                      | 0.979            | 0.178  |
| Zn                      | 0.990            | -0.185 |
| Pb                      | 0.984            | -0.493 |
| Cr                      | 0.987            | -0.445 |
| Ni                      | 0.863            | 0.429  |
| Eigenvalue              | 4.529            | 1.179  |
| % Variance              | 75.477           | 19.651 |
| % Cumulative            | 75.477           | 95.127 |

**Table 4.36 Principal components (two-component extracted) of the analyzed parameters (heavy metals) for groundwater**

| <b>Component Matrix</b> |                  |        |
|-------------------------|------------------|--------|
| <b>Parameters</b>       | <b>Component</b> |        |
|                         | PC1              | PC2    |
| Fe                      | 0.980            | -      |
| Cu                      | 0.904            | -      |
| Zn                      | 0.992            | -      |
| Mn                      | 0.461            | 0.866  |
| Pb                      | 0.813            | -0.519 |
| Cr                      | 0.981            | -      |
| Eigenvalue              | 4.6              | 1.03   |
| % Variance              | 76.6             | 17.1   |
| % Cumulative            | 76.6             | 93.7   |

## 4.8 Correlation matrix

Using the SPSS (version 24) software, the Pearson correlation matrix was assembled. The results of the PCA are often constant with correlations between the physicochemical characteristics, which is convenient in verifying definite novel relationships between the parameters that were not clearly directed in the former studies (Al-Onran et al., 2016; Saman et al., 2021).

### 4.8.1 Correlation matrix of physicochemical parameter

According to the values of the correlation coefficients in the surface water (**Table 4.37**), a strong 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 significant level 0.01. However, DO show a negative correlation with all parameters at a significant level of 0.01 and justifies the PCA analysis (Freeze and Cherry, 1979).

Allowing the values of the correlation coefficients in the groundwater (**Table 4.38**), a strong correlation (\*\*) subsists between Temperature with Turbidity, EC, TSS,  $Cl^-$ ,  $SO_4^{2-}$ ,  $Na^+$ , and  $K^+$ , EC with TSS,  $SO_4^{2-}$ ,  $NO_3^-$ -N, and  $Ca^{2+}$ , TSS with  $SO_4^{2-}$ ,  $NO_3^-$ -N, and  $Na^+$ , TDS with  $Cl^-$ ,  $SO_4^{2-}$ ,  $Na^+$ ,  $K^+$ , and  $Ca^{2+}$ ,  $Cl^-$  with  $NO_3^-$ -N, and  $Ca^{2+}$ , and  $PO_4^{3-}$  with  $Na^+$ ,  $K^+$ , and  $Ca^{2+}$  at a significant level 0.01. However DO display a negative correlation with all parameters at a significant level of 0.01 and validates the PCA analysis (Saman et al., 2021).

**Table 4.37 Correlation matrix of physicochemical parameters in surface water**

|                               | Temp                | pH                  | DO                  | EC                  | Turbidity           | TSS                | TDS                | BOD                | COD                | TH                 | Cl <sup>-</sup>     | SO <sub>4</sub> <sup>2-</sup> | NO <sub>3</sub> <sup>-</sup> | PO <sub>4</sub> <sup>3-</sup> | HCO <sub>3</sub> <sup>-</sup> | Na <sup>+</sup>    | K <sup>+</sup>    | Ca <sup>2+</sup>  | Mg <sup>2+</sup> |
|-------------------------------|---------------------|---------------------|---------------------|---------------------|---------------------|--------------------|--------------------|--------------------|--------------------|--------------------|---------------------|-------------------------------|------------------------------|-------------------------------|-------------------------------|--------------------|-------------------|-------------------|------------------|
| Temp                          | 1                   |                     |                     |                     |                     |                    |                    |                    |                    |                    |                     |                               |                              |                               |                               |                    |                   |                   |                  |
| pH                            | .954 <sup>+</sup>   | 1                   |                     |                     |                     |                    |                    |                    |                    |                    |                     |                               |                              |                               |                               |                    |                   |                   |                  |
| DO                            | -.974 <sup>**</sup> | -.862               | 1                   |                     |                     |                    |                    |                    |                    |                    |                     |                               |                              |                               |                               |                    |                   |                   |                  |
| EC                            | .955 <sup>*</sup>   | 1.000 <sup>**</sup> | -.864               | 1                   |                     |                    |                    |                    |                    |                    |                     |                               |                              |                               |                               |                    |                   |                   |                  |
| Turbidity                     | .995 <sup>**</sup>  | .980 <sup>**</sup>  | -.945 <sup>+</sup>  | .981 <sup>**</sup>  | 1                   |                    |                    |                    |                    |                    |                     |                               |                              |                               |                               |                    |                   |                   |                  |
| TSS                           | .875                | .697                | -.962 <sup>**</sup> | .700                | .823                | 1                  |                    |                    |                    |                    |                     |                               |                              |                               |                               |                    |                   |                   |                  |
| TDS                           | .964 <sup>**</sup>  | .999 <sup>**</sup>  | -.880 <sup>+</sup>  | .999 <sup>**</sup>  | .986 <sup>**</sup>  | .725               | 1                  |                    |                    |                    |                     |                               |                              |                               |                               |                    |                   |                   |                  |
| BOD                           | .957 <sup>*</sup>   | .830                | -.997 <sup>**</sup> | .832                | .923 <sup>+</sup>   | .973 <sup>**</sup> | .850               | 1                  |                    |                    |                     |                               |                              |                               |                               |                    |                   |                   |                  |
| COD                           | .962 <sup>**</sup>  | .912 <sup>+</sup>   | -.952 <sup>+</sup>  | .914 <sup>+</sup>   | .955 <sup>+</sup>   | .887 <sup>+</sup>  | .931 <sup>+</sup>  | .940 <sup>+</sup>  | 1                  |                    |                     |                               |                              |                               |                               |                    |                   |                   |                  |
| TH                            | .978 <sup>**</sup>  | .995 <sup>**</sup>  | -.907 <sup>+</sup>  | .996 <sup>**</sup>  | .994 <sup>**</sup>  | .763               | .998 <sup>**</sup> | .879 <sup>+</sup>  | .943 <sup>+</sup>  | 1                  |                     |                               |                              |                               |                               |                    |                   |                   |                  |
| Cl <sup>-</sup>               | .955 <sup>+</sup>   | 1.000 <sup>**</sup> | -.863               | 1.000 <sup>**</sup> | .980 <sup>**</sup>  | .699               | .999 <sup>**</sup> | .831               | .913 <sup>+</sup>  | .996 <sup>**</sup> | 1                   |                               |                              |                               |                               |                    |                   |                   |                  |
| SO <sub>4</sub> <sup>2-</sup> | .942 <sup>+</sup>   | .804                | -.993 <sup>**</sup> | .806                | .904 <sup>+</sup>   | .986 <sup>**</sup> | .827               | .997 <sup>**</sup> | .940 <sup>+</sup>  | .858               | .805                | 1                             |                              |                               |                               |                    |                   |                   |                  |
| NO <sub>3</sub> <sup>-</sup>  | .615                | .468                | -.715               | .471                | .571                | .816               | .510               | .731               | .784               | .534               | .471                | .772                          | 1                            |                               |                               |                    |                   |                   |                  |
| PO <sub>4</sub> <sup>3-</sup> | .835                | .650                | -.933 <sup>+</sup>  | .653                | .780                | .992 <sup>**</sup> | .683               | .945 <sup>+</sup>  | .879 <sup>+</sup>  | .720               | .653                | .966 <sup>**</sup>            | .878                         | 1                             |                               |                    |                   |                   |                  |
| HCO <sub>3</sub> <sup>-</sup> | .987 <sup>**</sup>  | .932 <sup>+</sup>   | -.975 <sup>**</sup> | .934 <sup>+</sup>   | .979 <sup>**</sup>  | .901 <sup>+</sup>  | .948 <sup>+</sup>  | .960 <sup>**</sup> | .992 <sup>**</sup> | .962 <sup>**</sup> | .933 <sup>+</sup>   | .955 <sup>+</sup>             | .725                         | .879 <sup>+</sup>             | 1                             |                    |                   |                   |                  |
| Na <sup>+</sup>               | .955 <sup>+</sup>   | 1.000 <sup>**</sup> | -.864               | 1.000 <sup>**</sup> | .981 <sup>**</sup>  | .700               | .999 <sup>**</sup> | .832               | .914 <sup>+</sup>  | .996 <sup>**</sup> | 1.000 <sup>**</sup> | .806                          | .472                         | .654                          | .934 <sup>+</sup>             | 1                  |                   |                   |                  |
| K <sup>+</sup>                | .996 <sup>**</sup>  | .977 <sup>**</sup>  | -.950 <sup>+</sup>  | .978 <sup>**</sup>  | 1.000 <sup>**</sup> | .831               | .983 <sup>**</sup> | .929 <sup>+</sup>  | .956 <sup>+</sup>  | .992 <sup>**</sup> | .977 <sup>**</sup>  | .910 <sup>+</sup>             | .577                         | .788                          | .981 <sup>**</sup>            | .978 <sup>**</sup> | 1                 |                   |                  |
| Ca <sup>2+</sup>              | .830                | .723                | -.878               | .725                | .802                | .889 <sup>+</sup>  | .755               | .896 <sup>+</sup>  | .928 <sup>+</sup>  | .774               | .725                | .906 <sup>+</sup>             | .897 <sup>+</sup>            | .905 <sup>+</sup>             | .890 <sup>+</sup>             | .726               | .806              | 1                 |                  |
| Mg <sup>2+</sup>              | .959 <sup>**</sup>  | .898 <sup>+</sup>   | -.958 <sup>+</sup>  | .900 <sup>+</sup>   | .948 <sup>+</sup>   | .903 <sup>+</sup>  | .919 <sup>+</sup>  | .950 <sup>+</sup>  | .999 <sup>**</sup> | .933 <sup>+</sup>  | .900 <sup>+</sup>   | .950 <sup>+</sup>             | .797                         | .895 <sup>+</sup>             | .990 <sup>**</sup>            | .900 <sup>+</sup>  | .951 <sup>+</sup> | .941 <sup>+</sup> | 1                |

**Table 4.38 Correlation matrix of physicochemical parameters in groundwater**

|                               | Temp  | pH   | DO   | EC    | Turbidity | TSS   | TDS   | BOD  | COD | Cl <sup>-</sup> | SO <sub>4</sub> <sup>2-</sup> | NO <sub>3</sub> <sup>-</sup> | PO <sub>4</sub> <sup>3-</sup> | HCO <sub>3</sub> <sup>-</sup> | Na <sup>+</sup> | K <sup>+</sup> | Ca <sup>2+</sup> | Mg <sup>2+</sup> |
|-------------------------------|-------|------|------|-------|-----------|-------|-------|------|-----|-----------------|-------------------------------|------------------------------|-------------------------------|-------------------------------|-----------------|----------------|------------------|------------------|
| Temp                          | 1     |      |      |       |           |       |       |      |     |                 |                               |                              |                               |                               |                 |                |                  |                  |
| pH                            | .91*  | 1    |      |       |           |       |       |      |     |                 |                               |                              |                               |                               |                 |                |                  |                  |
| DO                            | -.48  | -.5  | 1    |       |           |       |       |      |     |                 |                               |                              |                               |                               |                 |                |                  |                  |
| EC                            | .97** | .79  | -    | 1     |           |       |       |      |     |                 |                               |                              |                               |                               |                 |                |                  |                  |
| Turbidity                     | .99** | .93* | -.57 | .94*  | 1         |       |       |      |     |                 |                               |                              |                               |                               |                 |                |                  |                  |
| TSS                           | .93** | .78  | -.31 | .99** | .93*      | 1     |       |      |     |                 |                               |                              |                               |                               |                 |                |                  |                  |
| TDS                           | .83   | .80  | -.40 | .83   | .88*      | .80   | 1     |      |     |                 |                               |                              |                               |                               |                 |                |                  |                  |
| BOD                           | .76   | .72  | -.30 | .78   | .81       | .75   | .99   | 1    |     |                 |                               |                              |                               |                               |                 |                |                  |                  |
| COD                           | .93*  | .95* | -.68 | .83   | .97       | .81   | .88*  | .80* | 1   |                 |                               |                              |                               |                               |                 |                |                  |                  |
| Cl <sup>-</sup>               | .96** | .80  | -.59 | .95*  | .96*      | .95*  | .77** | .69  | .89 | 1               |                               |                              |                               |                               |                 |                |                  |                  |
| SO <sub>4</sub> <sup>2-</sup> | .96** | .78  | -.32 | .99** | .93*      | .99** | .78** | .73  | .81 | .95**           | 1                             |                              |                               |                               |                 |                |                  |                  |
| NO <sub>3</sub> <sup>-</sup>  | .93   | .73* | -.24 | .99** | .90**     | .99** | .82   | .80  | .78 | .92**           | .99**                         | 1                            |                               |                               |                 |                |                  |                  |
| PO <sub>4</sub> <sup>3-</sup> | .99*  | .93  | -.57 | .94   | 1*        | .93   | .88*  | .81  | .97 | .96             | .93*                          | .90                          | 1                             |                               |                 |                |                  |                  |
| HCO <sub>3</sub> <sup>-</sup> | .97   | .90  | -.50 | .94   | .99       | .92   | .95   | .90  | .96 | .92             | .91                           | .91                          | .99                           | 1                             |                 |                |                  |                  |
| Na <sup>+</sup>               | .85** | .80  | -.26 | .87   | .88**     | .85** | .99** | .98  | .84 | .77             | .83*                          | .88**                        | .88**                         | .94                           | 1               |                |                  |                  |
| K <sup>+</sup>                | .88** | .82* | -.37 | .89*  | .91       | .86*  | .99** | .98* | .88 | .82*            | .85                           | .88*                         | .91**                         | .97*                          | .99             | 1              |                  |                  |
| Ca <sup>2+</sup>              | .99** | .96  | -.48 | .93** | .98*      | .92   | .81** | .73  | .94 | .92**           | .93*                          | .88                          | .98**                         | .95                           | .83             | .85**          | 1                |                  |
| Mg <sup>2+</sup>              | .97   | .96  | -.54 | .91   | .99*      | .89   | .91   | .84  | .98 | .91             | .87*                          | .87                          | .99                           | .99                           | .91             | .93            | .97*             | 1                |

### 4.8.2 Correlation matrix of heavy Metals

Using the SPSS (version 24) program, the Pearson correlation matrix was constructed. The results of the PCA are often consistent with the correlations between the trace heavy metals, which is helpful in corroborating certain novel relationships between the trace heavy metals that were not clearly indicated in the earlier studies (Freeze and Cherry, 1979). According to the values of correlation coefficients in the surface water (**Table 4.39**), a strong (\*\*) correlation exists between Pb and Cr at a significant level of 0.01 and justifies the PCA analysis for the trace heavy metals (Al-Onran et al., 2016).

Rendering the values of the correlation coefficients in the groundwater (**Table 4.40**), a robust (\*\*) correlation subsists between Zn and Cr at a significant level of 0.01 and substantiates the PCA analysis for the trace heavy metals (Saman et al., 2021).

**Table 4.39 Correlation matrix of heavy metals in surface water**

|           | <b>Fe</b> | <b>Cu</b> | <b>Zn</b> | <b>Pb</b> | <b>Cr</b> | <b>Ni</b> |
|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| <b>Fe</b> | 1         |           |           |           |           |           |
| <b>Cu</b> | 0.727     | 1         |           |           |           |           |
| <b>Zn</b> | 0.434     | 0.895*    | 1         |           |           |           |
| <b>Pb</b> | 0.250     | 0.742     | 0.865     | 1         |           |           |
| <b>Cr</b> | 0.291     | 0.785     | 0.897*    | 0.997**   | 1         |           |
| <b>Ni</b> | 0.000     | 0.874     | 0.754     | 0.475     | 0.526     | 1         |

**Table 4.40 Correlation matrix of heavy metals in groundwater**

|           | <b>Fe</b> | <b>Cu</b> | <b>Zn</b> | <b>Mn</b> | <b>Pb</b> | <b>Cr</b> |
|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| <b>Fe</b> | 1         |           |           |           |           |           |
| <b>Cu</b> | 0.81      | 1         |           |           |           |           |
| <b>Zn</b> | 0.95*     | 0.92*     | 1         |           |           |           |
| <b>Mn</b> | 0.47      | 0.42      | 0.42      | 1         |           |           |
| <b>Pb</b> | 0.86      | 0.61      | 0.79      | -0.03     | 1         |           |
| <b>Cr</b> | 0.95*     | 0.87      | 0.99**    | 0.43      | 0.78      | 1         |

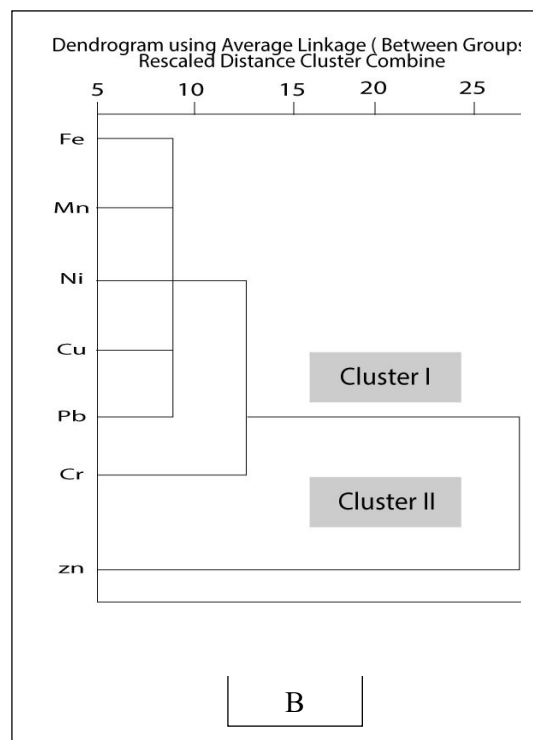
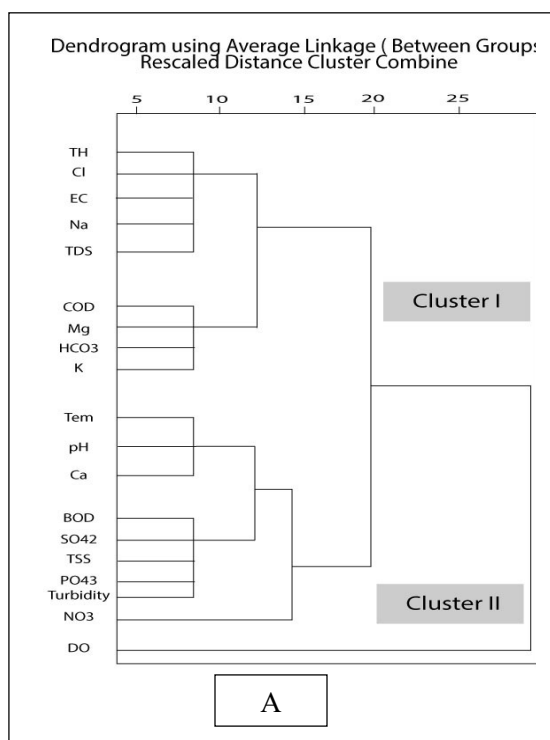
## 4.9 Cluster Analysis (CA)

The Cluster Analysis (CA) was performed to visualize the groupings in surface and groundwater-measured variables. The results of cluster Analysis (CA) are shown in **Figures 4.13 and 4.14**. The results of cluster analysis (CA) were accomplished by using the physicochemical and trace heavy metals of all surface and groundwater samples. 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 less relative, all of which are linked to make one large cluster (Chegbeleh et al., 2020). The Hierarchical cluster analysis produces two big clusters (cluster I and cluster II) based on surface and groundwater characteristics. Numerous mutual topographies were observed in that plot and were very similar to those examined in PCA.

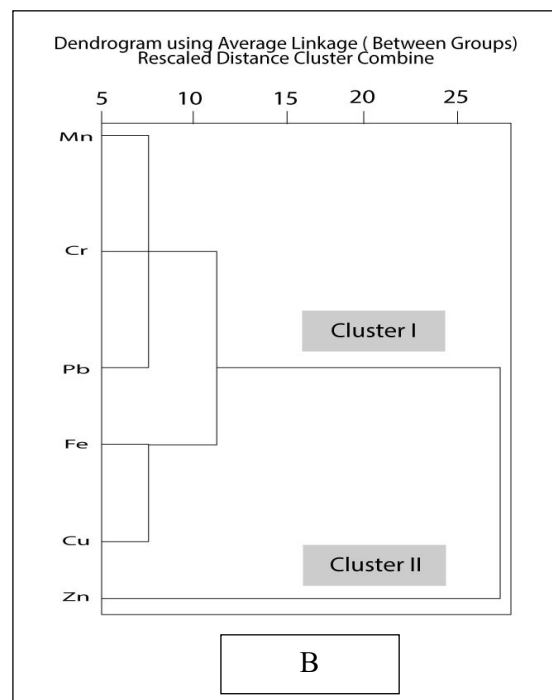
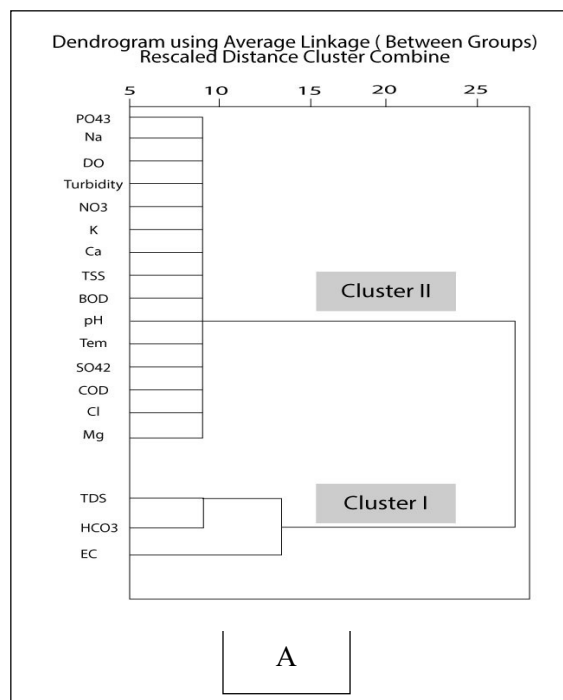
Here, for surface water two separate clusters, which diligently relate to the group of physicochemical parameters are marked: (1) Tem, pH,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , turbidity, BOD, COD, TDS,  $\text{HCO}_3^-$ , TSS, EC, TH,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ -N,  $\text{Cl}^-$ , and  $\text{PO}_4^{3-}$  (2) DO. Each cluster is separate from the others, and the remaining parameters create their cluster. In cluster I, TH,  $\text{Cl}^-$ , EC,  $\text{Na}^+$ , and TDS form one cluster, along with sub-clustering with COD,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$ , and  $\text{K}^+$ . However, BOD,  $\text{SO}_4^{2-}$ , TSS,  $\text{PO}_4^{3-}$ , and turbidity form another cluster, along with sub-clustering with tem, pH,  $\text{Ca}^{2+}$ , and  $\text{NO}_3^-$ -N (**Figure 4.13 A**). Above all clusters exist in cluster I. Finally, cluster I joins with cluster II (with DO) in surface water presented in (**Figure 4.13 A**). Industrial effluents and Chemical fertilizers, stimulus surface water  $\text{K}^+$ , BOD,  $\text{PO}_4^{3-}$ , COD, EC, TDS, TSS,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$  and  $\text{NO}_3^-$ -N content, since these effluents and fertilizers consist of mainly such chemicals (Amiri et al., 2014). Physicochemical, anionic, and cationic parameters represent a surface water system dominated by anthropogenic sources (industrial effluent) (Subyani and Ahmadi, 2010).

Here, for surface water two individual clusters, which closely relate to the group of trace elements, are marked: (1) Fe, Mn, Ni, Cu, Pb, and Cr, and (2) Zn. Each cluster is separate from the others, and the remaining parameters create their cluster. In cluster I, Fe, Mn, Ni, and Cu form one cluster, along with sub-clustering with Pb and Cr. The cluster (cluster I) made in Fe, Mn, Ni, Pb, Cr, and Cu joins with Zn (cluster II) in surface water

presented in **(Figure 4.13 B)**. The detected trace heavy metals Zn, Fe, Mn, Ni, Cr, Cu, and Pb in surface water are of anthropogenic origin (industrial effluent) (Ahmed et al., 2018).



**Figure 4.13 Surface water Hierarchical cluster analysis of physicochemical parameters (A) and trace metal (B)**



**Figure 4.14 Groundwater Hierarchical cluster analysis of physicochemical parameters (A) and trace metal (B)**

In groundwater, two distinct clusters, which closely relate to the group of physicochemical parameters are marked: (1) TDS,  $\text{HCO}_3^-$ , and EC (2) Tem, pH,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , turbidity, BOD, COD, DO, TSS,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ -N,  $\text{Cl}^-$ , and  $\text{PO}_4^{3-}$ . Cluster I is made up of TDS,  $\text{HCO}_3^-$ , and EC (**Figure 4.14 A**). TDS and  $\text{HCO}_3^-$  form a cluster which further sub-cluster with EC. A high concentration of EC is mainly caused by high  $\text{HCO}_3^-$  values. It suggests the dominance of groundwater by precipitation and interaction with atmospheric  $\text{CO}_2$  (Islam and Mostafa, 2022). Tem, pH,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , turbidity, BOD, COD, DO, TSS,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ -N,  $\text{Cl}^-$ , and  $\text{PO}_4^{3-}$  from one cluster namely cluster II (**Figure 4.14 A**). Cluster II indicated the probable impact of contamination in precipitation filtering, which was most likely caused by industrial effluent, agricultural fertilizers, and other anthropogenic activities (Miao et al., 2013; Amiri et al., 2014). Industrial effluents and Chemical fertilizers, stimulate groundwater  $\text{K}^+$ , BOD,  $\text{PO}_4^{3-}$ , COD, and  $\text{NO}_3^-$ -N content since these effluents and fertilizers consist of mainly such chemicals (Ahmadi, 2010). The soil of the study area was silty clay loam type with a texture composition of 22.5 to 52.5% (Sultana et al., 2017). Weathering of K-rich feldspar rock is associated with the release of  $\text{K}^+$  and other related ions in water (Amiri et al., 2014).  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Cl}^-$  illustrate a groundwater system dominated by water-rock interaction, which is most likely influenced by acidic groundwater conditions due to the lower pH (7 of the maximum samples in the research areas) (Subyani and Ahmadi, 2010). This interaction is characterized mostly by the dissolution of silicate and carbonate minerals (calcite and dolomite), which release such ions into the aquifer (Miao et al., 2013). Finally, cluster I joins with cluster II.

In groundwater; two different clusters, are closely related to the trace element group namely cluster I -Fe, Cr, Pb, Cu, and Mn, and cluster 2 -Zn. Pb and Mn form a cluster, further sub-cluster with Cr, Fe, and Cu (**Figure 4.14 B**). The cluster made in Cr, Pb, Fe, Cu, and Mn joins with Zn in groundwater presented in **Figure 4.14 B**. Low pH and soil type (silty clay loam) are responsible for higher concentrations of metals (mainly Fe, Mn, Pb, Cu, and Zn) (Islam and Mostafa, 2022). The detected heavy metals Cr, Fe, Mn, Zn, Cu, and Pb in groundwater are of geogenic and anthropogenic origin (industrial effluent) (Ahmed et al., 2018).

#### 4.10 Impacts of pollutants

The study found that the effluent containing high EC values varied from (407.5 to 2465)  $\mu\text{S}/\text{cm}$  (**Table 4.41**). Higher EC values indicate that the water contains more dissolved ions and salts (Shannon et al., 2020). To prevent acidic swelling during the pickling process, a massive amount of sodium salts was added. The higher electrical conductivity values of the effluent, therefore, indicated the presence of more salts in the effluent. A parallel reflection was stated by Ahmed et al. (2017).

The effluent containing a high level of TSS varied from 46.5 to 265 mg/L, (**Table 4.41**). Moreover, total suspended solids can cause turbidity, which reduces the quantity of light available for photosynthetic activity by impairing light penetration or perforation in the aquatic system. The soil fertility, soil porosity, texture, and water-holding capacity may all be affected by the high TSS value (Chowdhury et al., 2015).

A higher level of BOD and COD in the effluent decreased the DO level of water, indicating the existence of both inorganic and organic pollutants at high levels (Pandey et al., 2003). Low DO decreases fish populations and unbalances the aquatic ecology (Connolly et al., 2004). The concentrations of BOD and COD in all samples were very much higher than the standard limits. The results of the study showed that the high BOD values suggested that the tannery effluent had a significant organic content. Akan et al. 2007 illustrated that higher levels of BOD and COD in tannery effluent suppress organic and inorganic compounds that utilize dissolved oxygen, resulting in oxygen reduction, and may lead to hypoxic conditions, which would have a negative impact on aquatic life. Under such a condition, no aquatic biota can survive, except anaerobic microorganisms. Further, organic materials could inspire anaerobic activity, which could lead to the accumulation of dangerous compounds in the surface water bodies (Trivedy et al., 2009). Hepatotoxic, carcinogenic, cytotoxic, mutagenic, genotoxic, etc. effects are brought on by the presence of toxic organic pollutants. The waste contains Cr in the range of 0.2 – 5.3 mg/L (**Table 4.41**). Chromium in the effluent is in a trivalent form, which is less toxic than the hexavalent form. Rafiquallah et al. (2008) reported that poultry feed is made using solid wastes that contain a hexavalent form of chromium. Trivalent chromium appears to change into hexavalent chromium during the manufacturing of feed, posing a major problem for human health (Javed, 2005). Hexavalent chromium (Cr, VI) is easily

soluble in water and 100-fold more toxic than trivalent ones. Due to its capacity to produce mutations, irritation, and corrosion of the skin and respiratory tract in the majority of microorganisms as well as lung cancer in humans, it is one of the most dangerous environmental contaminants (Liu et al., 2005; Bhinde et al., 1996). A high level of Cr causes carcinogenicity, kidney disorders, ulcers, nervous disorders, etc. The waste contains Na in the range of 8.9–350 mg/L (**Table 4.41**). Sodium chloride (NaCl) used in the tannery industry could harm aquatic life in freshwater bodies when the salt concentration in a stream, lake, or canal becomes very high (Chowdhury et al., 2015).

The higher value of nitrate and phosphate is not good for water bodies because they cause eutrophication, algal bloom, etc (Bhinde et al., 1996). The effluent discharged from the tanneries poses high values of EC, BOD, COD, TSS, Cr, Na, etc. The values were much higher than the tolerance limits for industrial effluent discharged into land surfaces or into public water as prescribed by DoE-BD, 2023 standards. Hence, they were not suitable for irrigation or drinking purposes, unless they were properly treated. Hence, the samples were not suitable for any use by humans.

**Table 4.41 Impacts of pollutants**

| <b>Parameters</b>                        | <b>Range</b>       | <b>Permissible limit<br/>DoE-BD, 2023<br/>standard</b> | <b>Impacts</b>                                                                                                                                 |
|------------------------------------------|--------------------|--------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------|
| Low dissolved oxygen                     | 1.6-5.5            | 5-8                                                    | Acute stress, ecosystem disturbance, and fisheries decrease                                                                                    |
| High EC                                  | 407.5-2465         | 1200                                                   | The high volume of dissolved ions causes harm to the aquatic biota                                                                             |
| High TSS                                 | 46.5-265           | 150                                                    | Soil fertility decreasing, changing water-holding capacity, soil porosity, and texture                                                         |
| High BOD, COD                            | 52.5-72.8, 205-282 | 30, 100                                                | DO level decreasing, fisheries decrease, and death of aquatic organisms                                                                        |
| High turbidity                           | 28-30.5            | -                                                      | Reducing the rate of photosynthesis, the food supply of aquatic ecosystems, degrading spawning beds, and affecting the gill function of fishes |
| Toxic organic pollutants                 | -                  | -                                                      | Hepatotoxic, mutagenic, carcinogenic, cytotoxic, and genotoxic effects                                                                         |
| High NO <sub>3</sub> <sup>-</sup> -N     | 4.4-13.8           | 10                                                     | Blue baby syndrome, Algal bloom, eutrophication, and anoxia of surface water body                                                              |
| High PO <sub>4</sub> <sup>3-</sup> - ion | 2.32-7.08          | 0.1                                                    | Algal bloom and eutrophication                                                                                                                 |
| High Na <sup>+</sup>                     | 8.9-350            | 200                                                    | Salinity increase, heart diseases, and high blood pressure                                                                                     |
| High Cr                                  | 0.2-5.3            | 0.5                                                    | Carcinogenic leads to kidney disorders, ulcers, nervous disorder                                                                               |

**\*(All parameters are in mg/L, except EC in µS/cm and turbidity in NTU)**

## **CHAPTER 5**

### **Conclusion**

# CHAPTER 5

## Conclusion

An enormous amount of effluent that comprises a number of harmful substances is produced by the tannery industry. In Bangladesh, inadequately treated effluent discharge from the Central Effluent Treatment Plant (CETP) is a significant environmental and social issue. There is a Central Effluent Treatment Plant (CETP) at Savar Tannery Industrial Estate in Bangladesh to treat the composite tannery effluent, which consists of 132 tannery industries. The study aimed to assess the performance of the CETP and evaluate the surface water and groundwater quality in the effluent discharged area of the Savar tannery estate in Bangladesh. All the samples were collected three times (pre-monsoon, monsoon, and post-monsoon) in a year, from the monsoon of 2021 to the pre-monsoon of 2023. The composite effluent samples were collected before entering and discharging points of the CETP and analyzed for various physicochemical parameters to assess the performance of the CETP. There were five surface water samples collected from different locations, starting from the CETP discharge point and at different distances, i.e., 100, 500, 1000, and 2000 meters from the CETP discharge point, and the samples were named SW1, SW2, SW3, SW4, and SW5, respectively, as well as several groundwater samples collected around the CETP. The characterization of treated and untreated tannery effluent, surface water, and groundwater in the CETP discharged area considered major physicochemical, anionic, and cationic parameters. Seasonal variation was performed to assess the seasonal pollution level sequence of surface and groundwater. Additionally, FTIR analysis was carried out to identify the functional groups of organic contaminants. Then various indexing models were used to determine the pollution level of surface water and groundwater in the study area. Several computer software were used for analyzing the experimental data. Here, the findings and conclusions of the study are interpreted.

The values of the physicochemical and anionic parameters were above the standard permissible limits of effluent discharge prescribed by the ISW-BDS-ECR (2023), DoE-BD (2023), and NEQS (2000). The mean concentrations of TSS and TDS were 1671 and 6817 mg/L in the influent and 209 and 6486 mg/L in the effluent, respectively. The higher values of TDS and TSS in the tannery effluent were due to the presence of various organic and inorganic substances. The pH values were 8.6 and 7.5 in the influent and effluent, respectively, indicating a neutral to slightly alkaline range. The average values of DO, BOD, and COD were 0.7, 573, and 1646 mg/L in the influent and 0.9, 96.7, and 337 mg/L in the effluent, respectively, causing serious surface water pollution in the areas. Higher COD and BOD levels indicate reduced oxygen concentration, or lower DO values, in the influent and effluent. In the study, BOD and COD were indicated as the main pollutants. The average EC was 11430  $\mu\text{S}/\text{cm}$  in the influent and 10190  $\mu\text{S}/\text{cm}$  in the effluent, and the concentrations of anions, including  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{Cl}^-$ , were 60.18, 1900, 1200, 28.3, and 2417 mg/L in the influent and 4, 1850, 315, 7.2, and 1667 mg/L in the effluent, respectively. A higher concentration of these parameters was obtained due to the use of various auxiliary chemicals during the processing of rawhide and skins. Higher values of these parameters are an indication of polluted water. Based on the above parameters, the study reported that the samples were heavily polluted and potentially harmful to the environment. So, the tannery effluent should be properly treated before being released into surface water bodies.

The values of metal ions in the composite tannery influent and effluent were in the following order:  $\text{Na} > \text{Ca} > \text{Cr} > \text{Fe} > \text{Cu} > \text{Zn} > \text{Pb} > \text{Mn}$ . This may occur due to the excess use of sodium salt for primary preservation and performing the chrome tanning process, which uses excess chromium powder and water. The study summarized that the removal efficiency of the CETP was 50.4% for physicochemical parameters, 49.0% for anionic parameters, and 42.2% for cationic parameters, and the overall efficiency of the CETP was 47.0%. The study observed that the removal efficiency of the CETP for physicochemical and anionic parameters was better than cationic parameters. However, the overall removal efficiency of the CETP was not satisfactory enough, and thus the

insufficient treatment capacity of the CETP should not be allowed to discharge the effluent into the surface water body, which caused severe aquatic pollution.

Three heavy metals, i.e., Cr, Pb, and Na were found to be higher in the sludge samples than the standard permissible limits of the DoE-BD, 2023, which were collected from the discharge point of the CETP. The analysis results showed the metal ions contained in the sludge were in the following order:  $\text{Na} > \text{Cr} > \text{Fe} > \text{Pb} > \text{K} > \text{Mn} > \text{Cu} > \text{Zn} > \text{Ni} > \text{Ca}$ . Metal concentration was found due to performing chrome tanning process, and geological factors that contributed to the metal ions concentrations of the sludge in the study area. A similar organic functional group was found in influent and effluent by FTIR analysis like alcohols, phenols, amides, ketones, quinone-conjugated carbonyls of lignin, alkanes, 1, 2, 4,-trisubstituted, alkyl halides, as well as aromatic and aliphatic amine functional groups, which again proved that the CETP was not working effectively. Among the identified functional groups (FTIR analysis), phenolic compounds, ketone, amide, quinone, lignins, aromatic, and aliphatic amines are mostly toxic to human health and the environment because they are responsible for bioaccumulation, cytotoxic, mutagenic, hepatotoxic, carcinogenic, genotoxic, and mutagenic effects.

Physicochemical characterization of the surface water and groundwater around the treated tannery effluent from the CETP discharge areas showed that the concentrations of BOD and COD were found to be higher at all sampling points, suggesting improving the biological treatment capacity of the CETP. Moreover, EC, Na, and  $\text{Cl}^-$  at the (CETP discharge point) SW1 point and TSS,  $\text{NO}_3^-$ -N, at the SW1(CETP discharge area) and SW2 (500m downstream from the CETP discharge area) points exceeded the surface water standard, whereas the DO level ranged from 1.60 to 5.5, found below the Environmental Conservation Rules (ECR), 2023 standard. The study identified that the BOD and COD were the main pollutants for surface and groundwater and pollution levels were decreased with increasing distance. Due to a decrease in the water level and anthropogenic sources, seasonal pollution levels in surface water were found in the following order: pre-monsoon > post-monsoon > monsoon. For groundwater, it was in the following order: post-monsoon > monsoon > pre-monsoon. Due to aquifer mineralization, this type of sequence may occur in groundwater.

The study summarized that no aquatic life can survive at the SW1 and GW1 sampling points according to the *CCME WQI* score. The high values of EC, TSS, total hardness, BOD, COD, turbidity,  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ -N,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , Cu, Zn, Pb, Cr, and  $\text{Na}^+$  were responsible for influencing the lowering of the *CWQI* values. Except for the SW1 sampling point, the water quality (*WWQI*, *MWQI*, and *IWQI*) scores indicated that the surface and groundwater quality in those areas were satisfactory for irrigation. High concentrations of EC, TDS, TSS,  $\text{Cl}^-$ , and  $\text{NO}_3^-$ -N were responsible for that result in *WWQI* indexing. The high values of EC,  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{Na}^+$  were accountable for influencing the lowering of the *MWQI* values. The high concentrations of sodium and magnesium play a dominant role in the *IWQI* investigation. The *NPI* indicated that higher values of BOD, COD,  $\text{Cl}^-$ , Na, Zn, Pb, and Cr were responsible for polluting most of the sampling sites in surface and groundwater.

The analysis results of the heavy metals showed that four (4) metal ions, viz., Cu, Pb, Cr, and Zn in the surface water and five (5) metals like Mg, Fe, Zn, Pb, and Cr in the groundwater exceeded the concentration limit of the DoE-BD (2023) in most of the water sampling sites, indicating severe human health hazards. It may occur due to the infiltration of tannery effluent from the surface water into groundwater. The values of *I<sub>p</sub>* and *CPI* of these metals were very high, i.e., much greater than 1. The other metal concentrations were found within safe permissible ranges. The values of heavy metal pollution indices, viz., *MI*, *HMPI*, *HMEI*, and *C<sub>d</sub>*, showed a high degree of contamination at all the sampling sites. The *NeI* showed that most of the water samples were found to have medium to high levels of contamination in the study area. The values of the total carcinogenic and non-carcinogenic hazard index (*HI<sub>total</sub>*) in all sampling sites were found to be higher than 1, and thus, the water in the areas was not suitable for domestic purposes without treatment. High concentrations of Cu, Zn, Pb, and Cr were responsible for that result in heavy metal pollution indices. However, each sampling site poses a low ecological risk. The multivariate statistical analyses, such as principal component, cluster analysis, and correlation matrix showed significant anthropogenic intrusions of Cr and Pb in surface and groundwater in the study area. A strong positive correlation between these parameters indicated their common origin, especially from industrial effluent, which is responsible for the enrichment of these variables as they move together in surface and

groundwater. The analysis results revealed that SW1 and SW2 sampling points were at high risk due to the presence of heavy metals, and each index represented that the degree of pollution decreased with increasing distance.

The study suggested that surface and groundwater quality should be continually monitored, and tannery effluent must be appropriately treated before being released into the environment. The study observed that there are no details about the effluent quality and quantity of 132 tannery industries located in the Savar tannery industrial estate and the surrounding groundwater and surface water quality of the CETP. Further, there should be detailed research on the capacity of the CETP and an assessment of surrounding groundwater and surface water quality, as well as possible threats to humans and the environment. The findings of the study may be useful to researchers, policymakers, industrial owners, and relevant authorities for further development as they continue to plan potential future corrective actions. Finally, a biological treatment process combined with the conventional treatment process could be adopted, and more research should be considered for developing an efficient treatment plant for achieving Sustainable Development Goal 6 (Clean Water and Sanitation).

## RECOMMENDATIONS

This study observed a terrifying situation prevailing around the CETP discharge areas caused by the discharge of improperly treated effluent into the nearby surface and groundwater. The study carefully analyzed the findings extracted from the experimental results and, finally, made some recommendations that would be helpful in reducing environmental degradation regarding CETP effluent discharge.

The recommendations are as follows:

1. Advanced leather manufacturing technologies should be introduced to decrease BOD, COD, Na, and Cr load and less water used in the production processes.
2. Modern and effective ETP comprised of combined treatment (i.e., coagulation, flocculation, adsorption, membrane filtration, advanced oxidation, and biological) facilities should be accommodated in the CETP.
3. Advanced oxidation and biological treatment should be adopted to remove organic pollutants from the effluent photocatalytic.
4. Wastewater recycling systems or re-use effluent water from processing should be introduced to ensure sustainable water resource management.
5. Capacity of the CETP and public awareness should be increased and proper monitoring should be ensured to maintain the surface and groundwater quality standards for effluent discharge.

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# **APPENDICES**

## **Appendix I:**

### **LIST OF PUBLICATIONS**

1. Monira U., & Mostafa M. G. (2023). Leather industrial effluent and environmental concerns: a review. *Sustainable Water Resources Management (Springer)*, 9 (6): 1-14. IF 2.4.
2. Monira U., Sattar G. S., & Mostafa M. G. (2023). Characterization of Tannery Effluent and Efficiency Assessment of Central Effluent Treatment Plant (CETP) at Savar in Bangladesh. *Asian Journal of Science and Applied Technology (AJSAT)*, 12 (1): 48-53.
3. Monira U., Sattar G. S., & Mostafa M. G. (2023). Characterization and Removal Efficiency of Central Effluent Treatment Plant (CETP). *Journal of Sustainability and Environmental Management (JOSEM)*, 2 (1): 42 – 50.
4. Monira U., Sattar G. S., & Mostafa M. G. (2022). Characterization of Tannery Effluent of Savar Tannery Estate in Bangladesh. *BAUET*, 3 (2): 67-76.
5. Monira U., Sattar G. S., & Mostafa M. G. (2024). Assessment of Surface Water Quality Using the Water Quality Index (*WQI*), and Multivariate Statistical Analysis (MSA), around Tannery Industry Effluent Discharge Areas. *H<sub>2</sub>Open (UK)* 7 (2): 130-162. IF 2.15.

## Characterization of Tannery Effluent of Savar Tannery Estate in Bangladesh

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**Abstract:** Tannery industrial effluents comprise a huge volume of chemical composites, including toxic chemicals. The study aimed to analyze various physicochemical parameters of the composite tannery industrial effluents of Savar Tannery Industrial Zone. All the physicochemical parameters of the effluents were measured using the standard methods of analysis. The mean concentration of total suspended solids (TSS), total dissolved solids (TDS), and pH of the effluents were 1756, 6817, and 8.2 mg/L, respectively. The average value of dissolved oxygen (DO), biological oxygen demand (BOD), and chemical oxygen demand (COD) were 0.6, 553 mg/L, and 1646 mg/L, respectively. The average electrical conductivity (EC) was 10996  $\mu\text{S}/\text{cm}$ , and the concentration of anions, including  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{PO}_4^{3-}$  and  $\text{Cl}^-$  were 60.18, 1560, 1200, 28.3, and 2417 mg/L, respectively. The concentration of the cations of the tannery effluents was in the following order:  $\text{Na} > \text{Ca} > \text{Cr} > \text{Cu} > \text{Zn}$ . The BOD and COD ratio revealed that the tannery effluents were less biodegradable. The study observed that the tannery industrial effluents should be treated before discharging into surface water bodies.

**Keywords:** BOD<sub>5</sub>; COD; Composite; CETP; Effluents; Tannery.

### 1. Introduction

The tannery industry is one of the most pollution-generating sectors in Bangladesh. During leather processing, in almost all steps substantial amounts of chemicals are used [1]. About 90 percent of tannery companies in Bangladesh adopt the chrome tanning method since it is simple to use and gives the leather great characteristics. The tanning process is entirely a wet process that uses a lot of water and wastes it unevenly 90% of it was discharged as effluent [2]. Tannery effluents contain huge amounts of organic and inorganic pollutants including glossily colored chemicals, sodium chloride, sulfate, chromium salts, toxic metallic compounds, physiologically oxidizable tanning constituents, and vast amounts of rotten suspended debris [3,4]. The soaking step of the tanning process, which is the most polluting, accounts for 50–55 percent of the tanning industry's overall pollution burden. Protein, hair, skin, and emulsified fats are taken from the hides during the liming stage and then discharged into the effluent, enhancing the total solids content. Sulfides, ammonium salts, and calcium salts were present in the effluents from the tanning, de-liming, and bating operations and the effluent is somewhat alkaline. Sulfates, sodium bicarbonate, chlorides, sulphuric acid, and chrome are found in chrome and pickling tanning effluents. Numerous studies showed that the effluents from beam house procedures have a huge amount of whole solids content [5,6]. There is 20 percent of the chemicals used in the tanning procedure are fascinated by leather, with the rest being discharged as effluent [7,8]. Chrome salts, dyestuff residues, fat liquoring agents, systems, and other organic debris are the principal contaminants of the post-tanning process [9]. Vapors from degreasing and

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## Leather industrial effluent and environmental concerns: a review

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### Abstract

The tannery industry is one of the most pollution-generating and environmentally unfriendly industries in the world. The study aimed to assess the current state of physicochemical features of leather effluent and explore environmental pollution concerns for human health. It consolidated all the available data on leather effluent characterization collected from various journals, newspapers, and websites of about 100 papers published in the last 30 years. The review analysis illustrated that almost every tannery industry uses notable amounts of chemicals to transfer animal hides into leather. Beam house operations produce 75% of the total chemical oxygen demand (COD) and biological oxygen demand (BOD) load, and tanning operations produce 70% of the total chrome load in the effluent of a complete leather process. About 40% of the unused chromium salts were discharged as the final tannery effluents, and 30% of leather industrial effluents contained chromium (VI). The result showed that the values of some physicochemical parameters of the Asian and African countries for leather industrial effluent, such as electrical conductivity (EC), BOD, COD, total dissolved solids (TDS), total suspended solids (TSS), chromium (Cr), and sodium (Na), are significantly higher than the tolerance limits for industrial effluent discharged into land surface or public sewers. The pollutants cause harmful effects on water, soil, plants, and human health. A modern and effective Effluent Treatment Plant (ETP) of combined treatment facilities should be adopted in leather industries to reduce environmental pollution due to untreated leather industrial effluents. Hence, it is imperative to take the necessary oversight and curative measures to reduce pollution and enhance environmental sustainability for the world, particularly in developing countries.

**Keywords** Biological oxygen demand (BOD) · Chemical oxygen demand (COD) · Leather · Effluent · Pollution

### Introduction

Environmental pollution is becoming a universal issue, and untreated industrial effluent discharge is one of the essential causes of water contamination that adds a significant amount of pollutants to the environment. Industrial wastewater discharge poses a serious risk to human health, because it contaminates nearby soil, water, and storm drains (Saha et al. 2021a; Sayed and Mostafa 2021). Lower and upper-middle-income countries, such as Bangladesh, India, China, Turkey, Brazil, Ethiopia, and Pakistan, rely heavily on their leather industries (Leta et al. 2004; Kurt et al. 2007; Verma et al. 2008; Haydar and Aziz 2009; Lofrano et al. 2013; Chowdhury et al. 2013; Wang et al. 2014). The leather industry produces 22,700.5 million square feet (or 2108.94 million

square meters) (FAO 2008) per year, with a global trade value of US\$100 billion (UNIDO 2010). The United States, Germany, and other European nations are the major importers, whereas India, China, Pakistan, and Egypt are the main exporters since the early 1970s (Saxena et al. 2017; Roy 2012). Most of the regions in and surrounding tanneries are believed to have extremely high levels of groundwater pollution (Mondal et al. 2005; Sajil Kumar 2013). In 2020, China produced the most leather worldwide. The growing demand for leather and leather products is increasing gradually.

The tannery industry is one of the most polluting industrial sectors in developing nations, particularly Bangladesh. In the process of turning animal hides into leather, nearly every tannery industry uses significant amounts of chemicals (Dargo et al. 2014). About 90% of tannery industries worldwide adopt the chrome tanning method, since it is easy to use and gives the leather excellent properties. The tanning method is essentially entirely a wet process that absorbs substantial volumes of water and releases roughly 90% of the used water as effluent (Chowdhury et al. 2013). Tannery

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## Characterization and Removal Efficiency of Central Effluent Treatment Plant (CETP)

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**Abstract:** Tannery industries are one of the most pollution-generating industries in the world. Tannery wastewater is usually characterized by high BOD, COD, TDS, and TSS and a high percentage of dissolved organic and inorganic matter. The central effluent treatment plant (CETP) of industry plays a vital role in sustainable industrial waste management and saves different lives from harmful effects. The study aimed to analyze various physicochemical parameters of the composite tannery influent and effluent as well as the removal efficiency of the CETP of the Savar Tannery Industrial Zone in Bangladesh. It was carried out at Savar Upazila, situated in the northwest part of Dhaka, Bangladesh. The samples were collected three times (pre-monsoon, monsoon, and post-monsoon) in a year, from monsoon 2021 to pre-monsoon 2022. The major water quality parameters for the influents and effluents included pH, BOD, COD, TDS, TSS,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{Cl}^-$ , Na, Ca, Cr, Fe, Cu, Zn, and Pb. Most of the parameters, especially BOD, COD, TDS, and TSS after treatment, exceeded the standard permissible limits of effluent discharge prescribed by the ISW-BDS-ECR (1997), DoE-BD, and NEQS (2000), and these values were two times higher than the permissible limit. The DO value was four times lower than the permissible limit, indicating heavily polluted water. The concentration of the cations in the tannery effluents was in the following order:  $\text{Na} > \text{Ca} > \text{Cr} > \text{Fe} > \text{Cu} > \text{Zn} > \text{Pb}$ . The analysis results illustrated that the overall removal efficiency of the CETP was about 47%. The study observed that the performance of the CETP was not satisfactory, and hence it needs further improvement in the treating capacity for sustainable industrial wastewater management.

**Keywords:** CETP, Efficiency, Effluent, Influent, Tannery

Conflicts of interest: None

Supporting agencies: None

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### 1. Introduction

Rapid industrialization and urbanization, particularly in developing nations, have increased awareness of the connection between pollution, public health, and the environment (WHO, 1982). Industries produce a lot of effluents, depending on the type of industry, and may contain a variety of hazardous compounds, including acids, bases, metals, organic pollutants, and inorganic pollutants (Islam and Mostafa 2018). The most water-intensive industries in the world are leather, pulp, and paper mills, fertilizer, textile and dyeing, sugar, chemicals, and petroleum refineries (Shakil and Mostafa 2021; Rahim and Mostafa, 2021 and Mostafa 2018). Lower and upper-middle-income countries, like Bangladesh, India, Pakistan, China, Brazil, and Ethiopia rely heavily on their leather industries (Chowdhury et al. 2013). At present, the

leather industry is one of the most polluting industries in Bangladesh. The leather industry wastewater is characterized by its high BOD, high COD, total dissolved solids, total suspended solids, and a high percentage of dissolved organic and inorganic matter (Akan et al. 2009; Monira and Mostafa 2022). So, this untreated wastewater will create problems for the environment. The purity, beauty, attractiveness, and sustainability of the environment are primarily affected by population growth and industrialization (Islam and Mostafa 2022). The quality of soil, surface water, and groundwater has systematically deteriorated by the release of untreated or not properly treated industrial effluents into the ecosystem (Islam and Mostafa 2020). The environment is threatened by the entry of numerous contaminants such as heavy metals and other organic and inorganic hazardous components in soil, surface water, and groundwater aquifers (Shakil and Mostafa 2020; Islam and Mostafa

## Characterization of Tannery Effluent and Efficiency Assessment of Central Effluent Treatment Plant (CETP) at Savar in Bangladesh

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**Abstract** - The industry discharges a large volume of effluent, many of which contain lots of chemicals and toxic substances that have the potential to cause distress to the environment. The study focused on analyzing various physicochemical parameters of the effluent discharge from the Central Effluent Treatment Plant (CETP) at the Savar Tannery Industrial Zone. The effluent was collected four times (pre-monsoon, monsoon, and post-monsoon) a year, from 2021-2022. The effluent was inspected for vital water quality parameters, such as pH, COD, BOD, TDS, TSS,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{Cl}^-$ , Na, Ca, Cr, Fe, Cu, Zn, and Pb. Most of the parameters exceed the standard permissible limit of the Department of Environment, Bangladesh (DoE, BD), NQES, and ISW-BDS for inland water. The mean concentrations of COD, BOD, TSS, and Cr were 337, 97.5, 209, and 6.1 mg/L, and these values were far above the permissible limit with a removal efficiency of 51%. The study observed that industrial discharge of improperly treated effluent deteriorates the surface water quality and causes huge threats to aquatic life and sustainable water resource management.

**Keywords:** CETP, Effluent, Heavy Metals, Pollutants, Tannery

### I. INTRODUCTION

Rapid industrialization and urbanization, particularly in developing nations, have increased awareness between pollution, public health, and the environment (WHO, 1982). Industries produce a lot of effluents, depending on the type of industry. The most water-intensive industries in the world are leather, textiles, pulp, paper mills, fertilizer, dyeing, sugar, chemicals, and petroleum refineries (Shakil and Mostafa, 2021a, b; Islam and Mostafa, 2018 and 2021; Monira *et al.*, 2022). Lower and upper-middle-income countries, like Bangladesh, India, Pakistan, and China, rely heavily on their leather industries (Chowdhury *et al.*, 2013). At present, the leather industry is one of the most polluting industries in the world. The leather industry wastewater is characterized by its high BOD, COD, TDS, and TSS and a high percentage of dissolved organic and inorganic matter (Akan *et al.*, 2009). So, this untreated wastewater will create problems for the environment. The quality of soil, surface water, and groundwater was systematically deteriorated by the release of untreated or improperly treated industrial effluent into the environment (Islam and Mostafa 2020). Untreated wastewater must be properly treated before discharging into the environment. In this context, an effective effluent treatment plant plays an important role in maintaining surface and groundwater quality as well as the

environment. Generally, a common effluent treatment plant (CETP) is designed to help industries better control pollution. For this reason, an efficient effluent treatment plant is very necessary for its liquid waste management. The Central Effluent Treatment Plant (CETP) has been established at the Savar tannery estate, aiming to reduce pollution in the nearby areas of the city. The industries discharge the effluent through a pipeline, and it enters the CETP for treatment. After the treatment, it releases from the CETP and falls into the Dhaleshwari river. The samples were collected after the treatment by the CETP, just before falling into the Dhaleshwari River.

The CETP can process about 25,000 m<sup>3</sup> of liquid waste per day. But 40,000 m<sup>3</sup> of waste is produced by the tanners inside the estate every day (Monira *et al.*, 2022; Hossain *et al.*, 2019). The warning that about 15,000 cubic meters of untreated waste are currently being dumped into the nearby Dhaleshwari River is quite depressing. Concerns about the efficient operation of the CETP and other supporting elements like the dumping yard and chrome recovery section in ensuring environmental compliance have consequently developed as a burning problem of the relocation process from Hazaribagh to Hemayetpur. About 155 tannery industries have been transferred from Hazaribagh, Dhaka, to the Savar Tannery Estate at Hemayetpur to save the Buriganga river from further pollution, and 132 industries are now active in the production of leather goods (Mollik, 2022). Heavy metals, chromium, and other organic and inorganic substances that are discharged into the river pollute the river near the CETP. So, the efficiency of the Savar CETP is questionable. As of now, there are no details on the impact of tannery industrial effluent on the aquatic life at the Savar tannery estate. The study focused to analyze the discharge effluent from the CETP of the Savar Industrial zone in Bangladesh and its impacts on aquatic life.

### II. MATERIALS AND METHODS

#### A. Study Area

The study zone is located in the tannery industrial estate at Savar Upazila, situated in the northwest part of Dhaka city, Bangladesh. It is located at 23°51'30"N 90°16'00"E / 23.8583°N 90.2667°E / 23.8583; 90.2667. Fig. 1 shows the sampling location of the study zone.

## 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<sup>-</sup>, Na<sup>+</sup>, and NO<sub>3</sub>-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

## Appendix-II: Standard curves for heavy metals, and anions

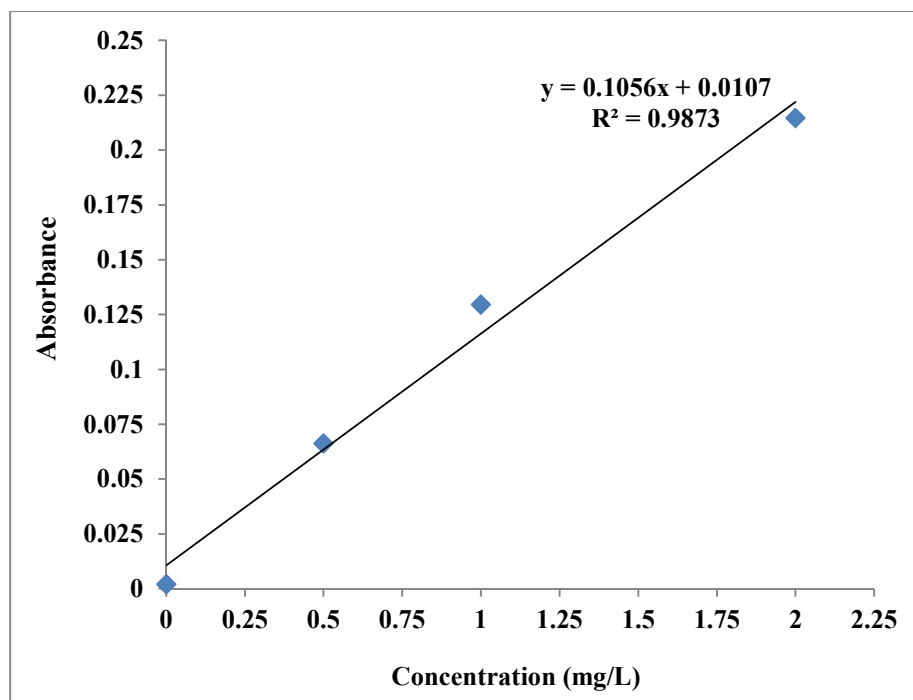


Figure 1: Standard curve of Chromium (Cr)

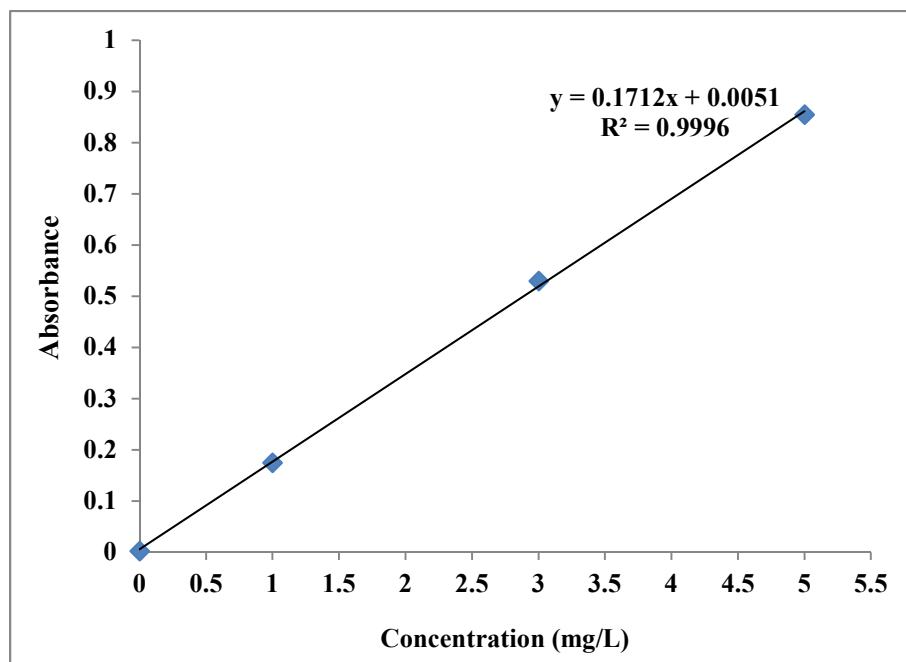
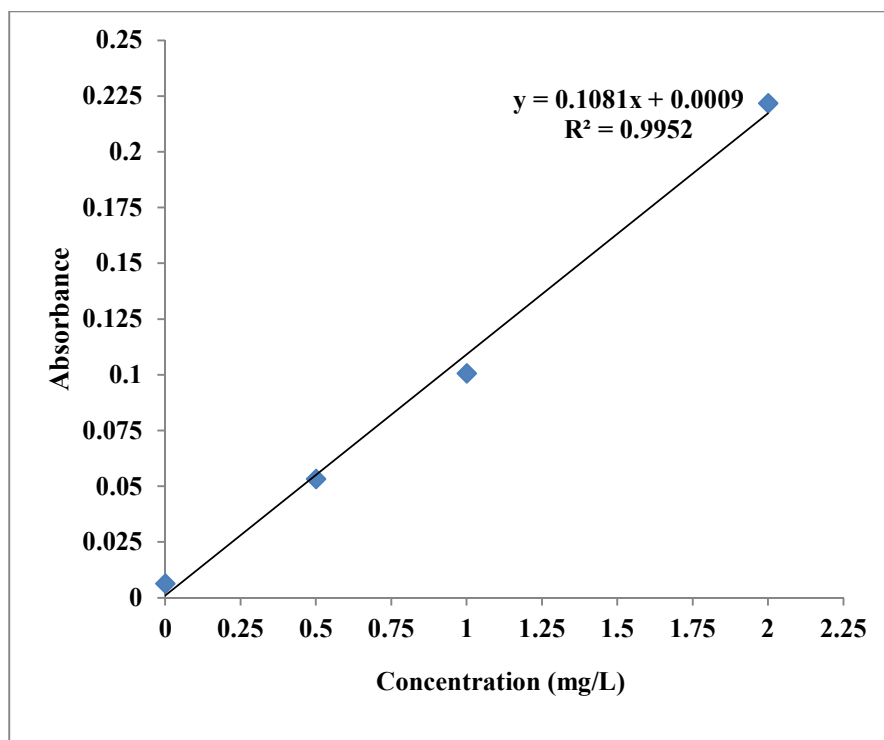
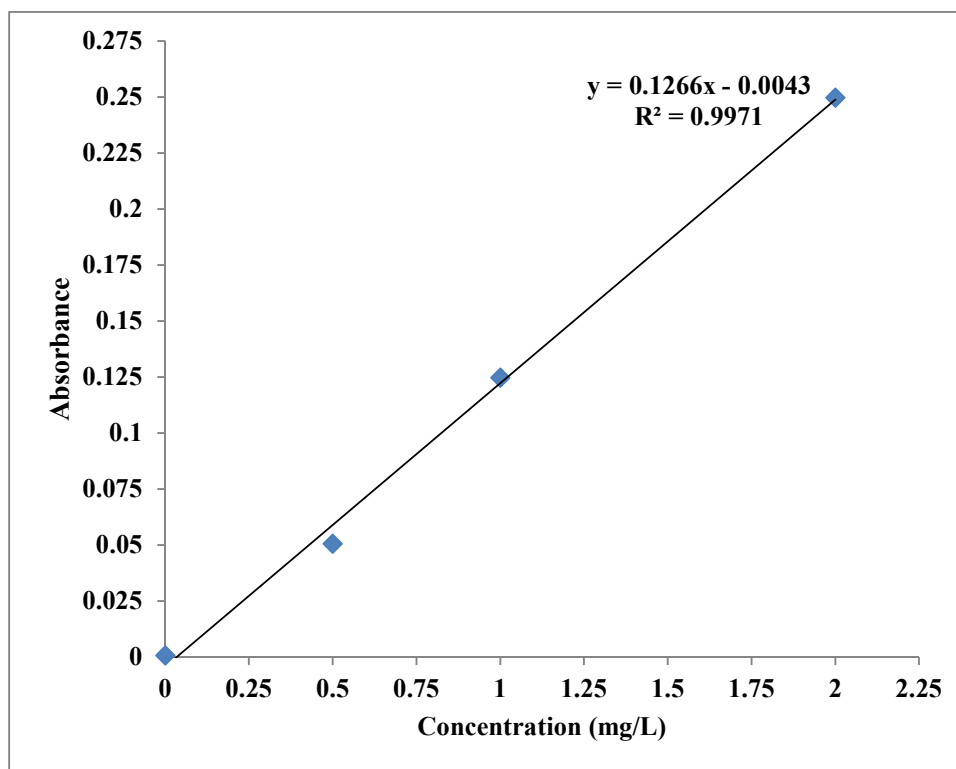


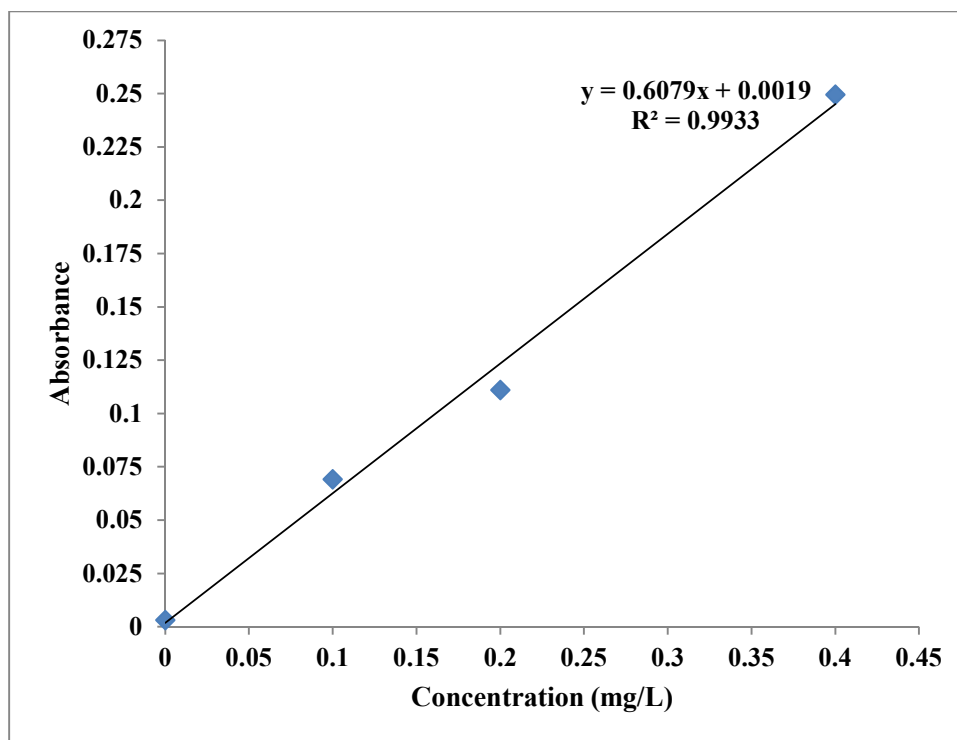
Figure 2: Standard curve of Manganese (Mn)



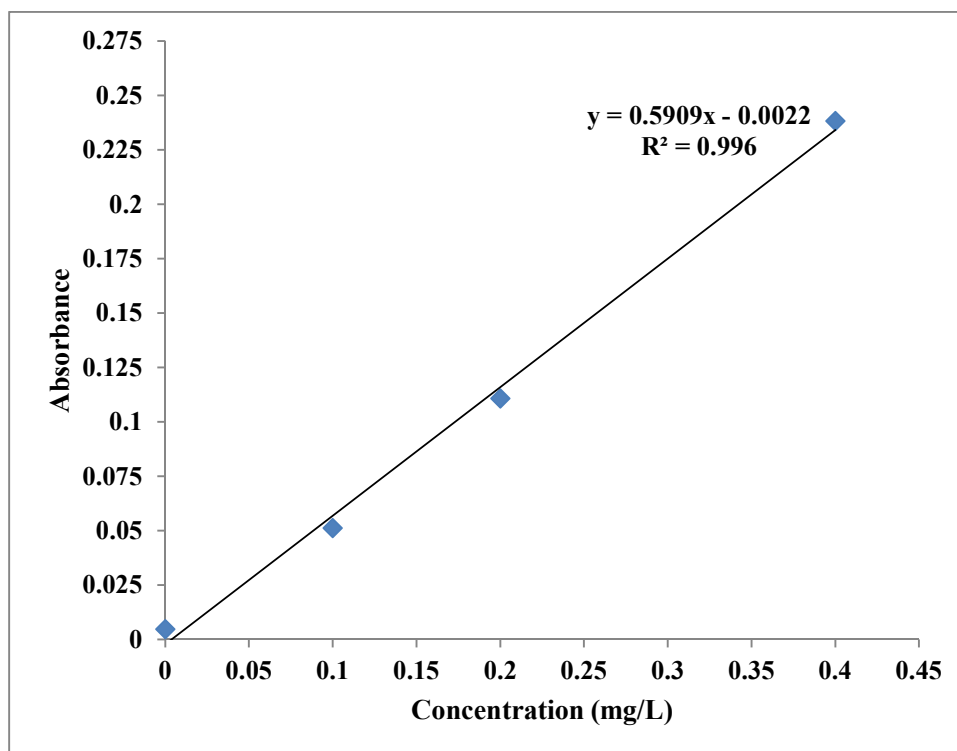
**Figure 3: Standard curve of Iron (Fe)**



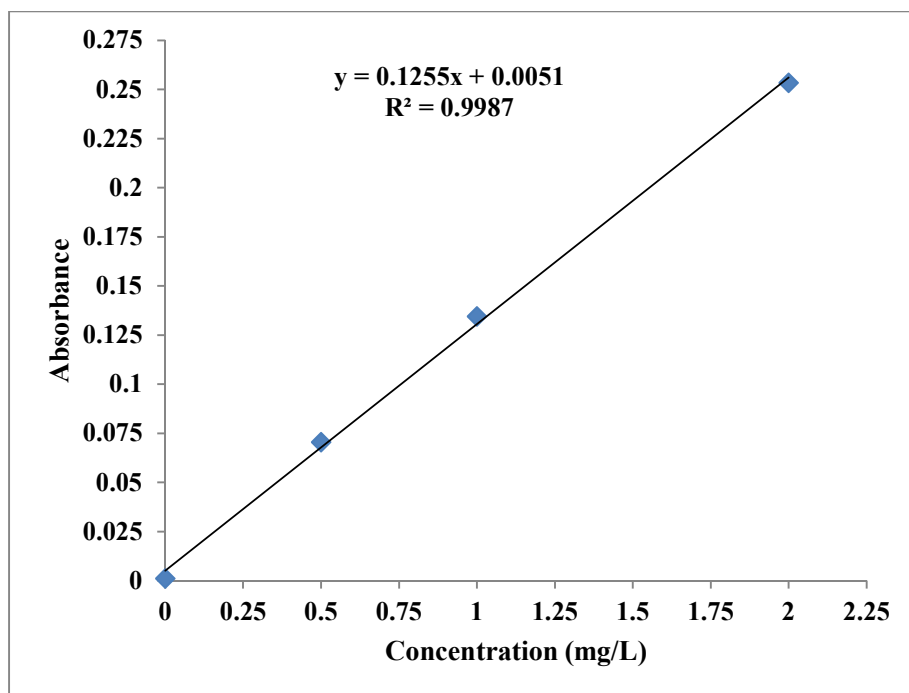
**Figure 4: Standard curve of Copper (Cu)**



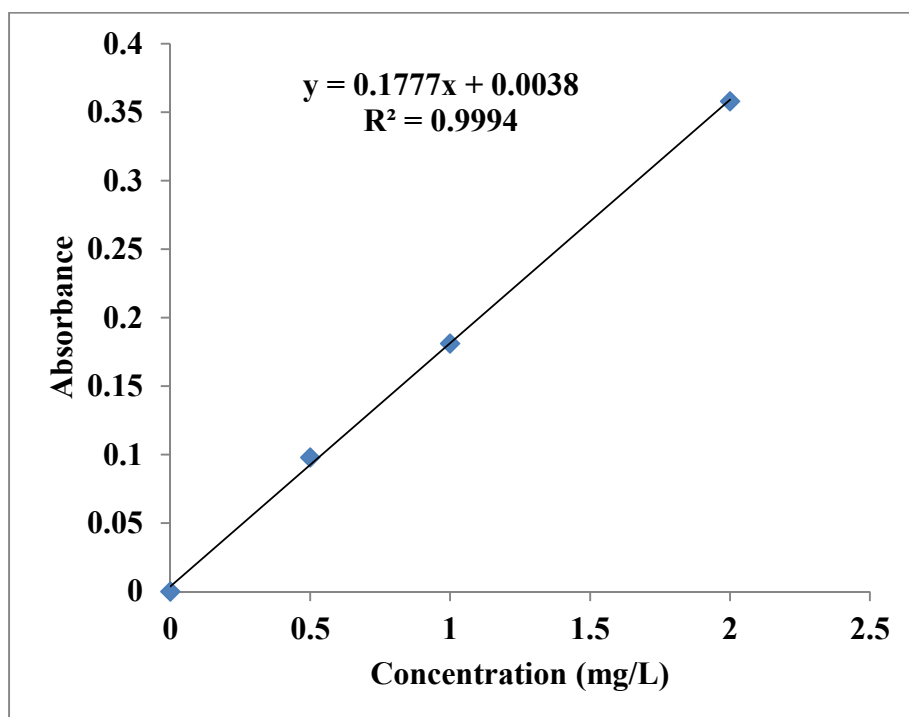
**Figure 5: Standard curve of Zinc (Zn)**



**Figure 6: Standard curve of Cadmium (Cd)**



**Figure 7: Standard curve of Lead (Pb)**



**Figure 8: Standard curve of Nitrate ion ( $\text{NO}_3^-$ )**

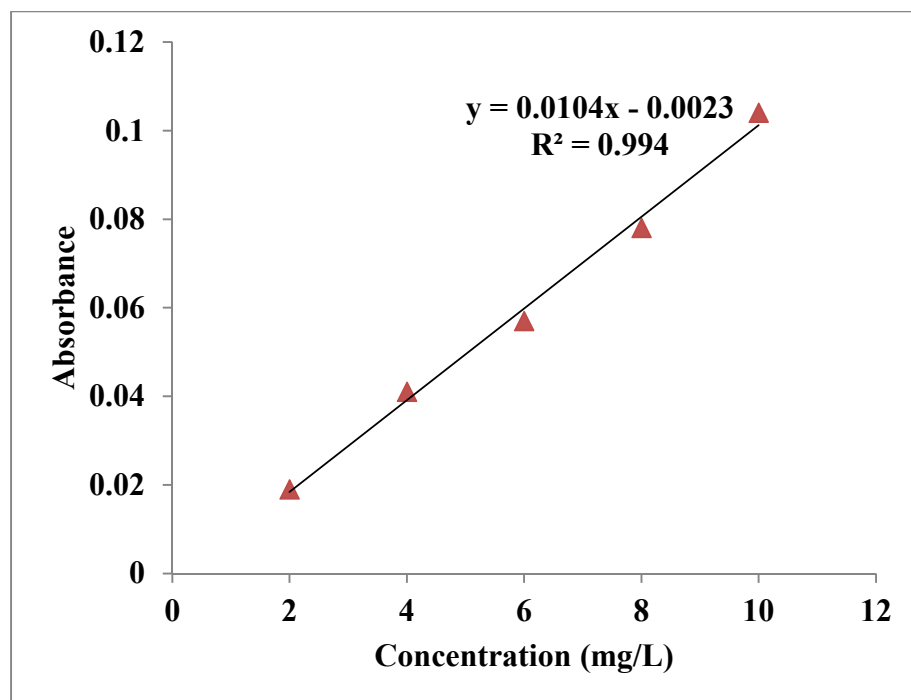


Figure 9: Standard curve of Sulfate ion ( $\text{SO}_4^{2-}$ )

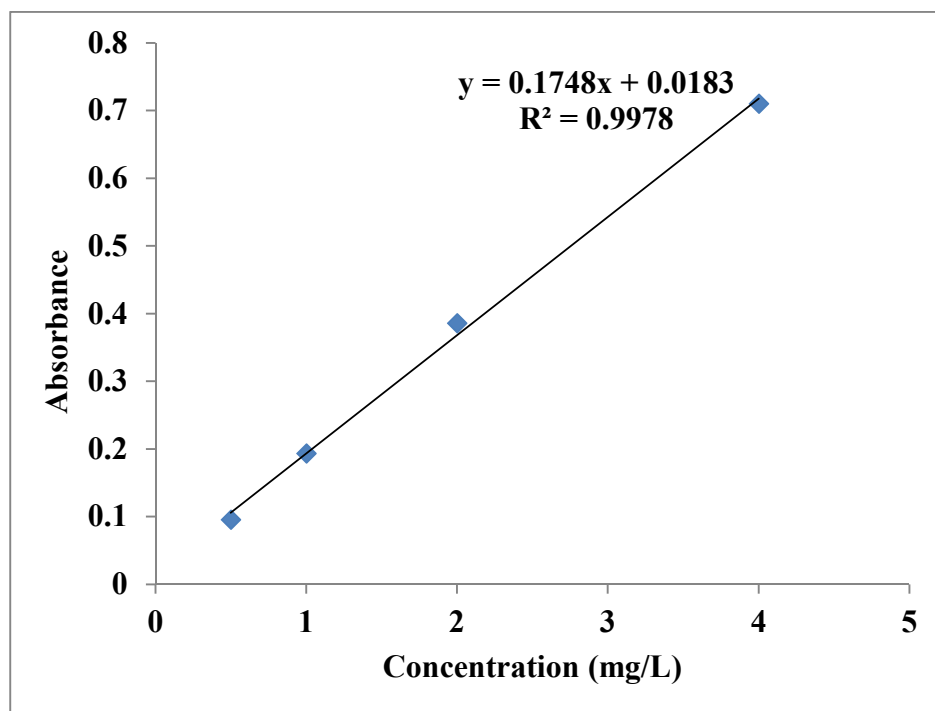


Figure 10: Standard curve of Phosphate ion ( $\text{PO}_4^{3-}$ )

**Appendix –III:**  
**Physicochemical characterization**

**Table 1: Physicochemical parameters of the CETP influent and Effluent**

| Parameters                 |          | Monsoon<br>(2021) | Post-<br>mon.<br>(2022) | Pre-<br>mon.<br>(2022) | Monsoon<br>(2022) | Post-<br>mon.<br>(2023) | Pre-<br>mon.<br>(2023) |
|----------------------------|----------|-------------------|-------------------------|------------------------|-------------------|-------------------------|------------------------|
| pH                         | Influent | 7.3               | 8.9                     | 8.9                    | 8.8               | 8.9                     | 8.8                    |
|                            | Effluent | 7.4               | 6.6                     | 8.3                    | 7.5               | 6.6                     | 8.3                    |
| DO (mg/L)                  | Influent | 0.6               | 0.8                     | 0.6                    | 0.8               | 0.8                     | 0.6                    |
|                            | Effluent | 0.5               | 0.8                     | 1.2                    | 0.9               | 0.8                     | 1.2                    |
| EC( $\mu$ S/cm)            | Influent | 11900             | 10820                   | 10270                  | 14500             | 10820                   | 10270                  |
|                            | Effluent | 12700             | 9300                    | 10180                  | 9480              | 9300                    | 10180                  |
| TDS (mg/L)                 | Influent | 7378              | 6708                    | 6367                   | 7375              | 6708                    | 6367                   |
|                            | Effluent | 6437              | 6405                    | 6617                   | 6435              | 6405                    | 6617                   |
| TSS (mg/L)                 | Influent | 1866              | 1918                    | 1486                   | 1352              | 1918                    | 1486                   |
|                            | Effluent | 223               | 322                     | 82                     | 222               | 322                     | 82                     |
| BOD<br>(mg/L)              | Influent | 508               | 590                     | 560                    | 630               | 590                     | 560                    |
|                            | Effluent | 80                | 53                      | 137                    | 120               | 53                      | 137                    |
| COD<br>(mg/L)              | Influent | 1540              | 1647                    | 1750                   | 1540              | 1647                    | 1750                   |
|                            | Effluent | 313               | 208                     | 489                    | 310               | 212                     | 490                    |
| TH (mg/L)                  | Influent | 660               | 350                     | 1470                   | 772               | 350                     | 1470                   |
|                            | Effluent | 635               | 730                     | 672                    | 932               | 730                     | 672                    |
| $\text{HCO}_3^-$<br>(mg/L) | Influent | 1250              | 1050                    | 1300                   | 1250              | 1050                    | 1300                   |
|                            | Effluent | 115               | 100                     | 730                    | 115               | 100                     | 730                    |
| $\text{PO}_4^{3-}$ (mg/L)  | Influent | 26.6              | 28.7                    | 29.6                   | 26.6              | 28.7                    | 29.6                   |

|                                          |          |      |      |       |      |      |       |
|------------------------------------------|----------|------|------|-------|------|------|-------|
|                                          | Effluent | 7.5  | 7.1  | 6.9   | 7.5  | 7.1  | 6.9   |
| SO <sub>4</sub> <sup>2-</sup> (mg/L)     | Influent | 1910 | 1890 | 1900  | 1910 | 1890 | 1900  |
|                                          | Effluent | 1870 | 1830 | 1850  | 1870 | 1830 | 1850  |
| Cl <sup>-</sup> (mg/L)                   | Influent | 2350 | 2500 | 2400  | 2350 | 2500 | 2400  |
|                                          | Effluent | 2510 | 1300 | 1190  | 2510 | 1300 | 1190  |
| NO <sub>3</sub> <sup>-</sup> N<br>(mg/L) | Influent | 56.2 | 60.1 | 64.25 | 56.2 | 60.1 | 64.25 |
|                                          | Effluent | 3.25 | 4.65 | 4.1   | 3.25 | 4.65 | 4.1   |
| Na (mg/L)                                | Influent | 1691 | 1960 | 2000  | 1880 | 1960 | 2000  |
|                                          | Effluent | 1852 | 1647 | 1944  | 1810 | 1647 | 1944  |
| K (mg/L)                                 | Influent | 1.20 | 1.28 | 1.3   | 3.0  | 1.28 | 1.3   |
|                                          | Effluent | 1.0  | 1.0  | 1.0   | 2.5  | 1.0  | 1.0   |
| Ca (mg/L)                                | Influent | 185  | 232  | 238   | 227  | 232  | 238   |
|                                          | Effluent | 87   | 85   | 95    | 143  | 85   | 95    |
| Cu (mg/L)                                | Influent | 1.7  | 1.7  | 1.8   | 1.9  | 1.7  | 1.8   |
|                                          | Effluent | 0.9  | 0.95 | 0.93  | 0.98 | 0.95 | 0.93  |
| Zn (mg/L)                                | Influent | 1.7  | 1.7  | 1.8   | 1.5  | 1.7  | 1.8   |
|                                          | Effluent | 0.90 | 0.95 | 0.93  | 0.90 | 0.95 | 0.93  |
| Cr (mg/L)                                | Influent | 75.6 | 85.8 | 80.9  | 74.5 | 85.8 | 80.9  |
|                                          | Effluent | 5.8  | 6.3  | 6.4   | 5.9  | 6.3  | 6.4   |
| Fe (mg/L)                                | Influent | 2.5  | 2.7  | 2.9   | 2.6  | 2.7  | 2.9   |
|                                          | Effluent | 1.9  | 2.7  | 1.9   | 1.7  | 2.7  | 1.9   |
| Pb (mg/L)                                | Influent | 0.28 | 0.39 | 0.39  | 0.30 | 0.39 | 0.39  |
|                                          | Effluent | 0.18 | 0.29 | 0.29  | 0.20 | 0.29 | 0.29  |
| Mn (mg/L)                                | Influent | 0.6  | 0.5  | 0.6   | 0.7  | 0.5  | 0.6   |
|                                          | Effluent | 0.2  | 0.3  | 0.2   | 0.2  | 0.3  | 0.2   |

**Table 2: Physicochemical parameters of surface water around the CETP discharge area**

| Parameter       | Sampling site | Monsoon (2021) | Post-mon. (2022) | Pre-mon. (2022) | Monsoon (2022) | Post-mon. (2023) | Pre-mon. (2023) |
|-----------------|---------------|----------------|------------------|-----------------|----------------|------------------|-----------------|
| Tem ( °C)       | SW1           | 26.2           | 23.3             | 29              | 27.8           | 24.7             | 31              |
|                 | SW2           | 27             | 22.2             | 27              | 25             | 23.8             | 29              |
|                 | SW3           | 25             | 21.2             | 26.8            | 27             | 22.8             | 27.2            |
|                 | SW4           | 25             | 21.3             | 26.7            | 27             | 22.7             | 27.3            |
|                 | SW5           | 25             | 21               | 26              | 27             | 23               | 28              |
| pH              | SW1           | 6.9            | 7.5              | 7.5             | 8.7            | 7.7              | 8.5             |
|                 | SW2           | 6.5            | 7.2              | 7.8             | 8.5            | 7.4              | 8.2             |
|                 | SW3           | 6.6            | 7.1              | 7.9             | 8.4            | 7.3              | 8.3             |
|                 | SW4           | 6.7            | 7.0              | 7.8             | 8.5            | 7.6              | 8.0             |
|                 | SW5           | 6.5            | 7.1              | 8.1             | 8.3            | 7.3              | 8.3             |
| DO (mg/L)       | SW1           | 2.0            | 1.9              | 1.7             | 1.4            | 1.3              | 1.6             |
|                 | SW2           | 3.8            | 3.6              | 3.1             | 3.6            | 3.4              | 2.9             |
|                 | SW3           | 5.7            | 5.4              | 5.3             | 5.5            | 5.0              | 4.9             |
|                 | SW4           | 5.7            | 5.5              | 5.4             | 5.7            | 5.1              | 5.0             |
|                 | SW5           | 5.9            | 5.5              | 5.1             | 5.7            | 5.3              | 5.5             |
| EC (µS/cm)      | SW1           | 1850           | 2073             | 3468            | 1950           | 2027             | 3422            |
|                 | SW2           | 392            | 433              | 463             | 368            | 407              | 437             |
|                 | SW3           | 381            | 424              | 454             | 359            | 406              | 436             |
|                 | SW4           | 361            | 415              | 451.5           | 375            | 409              | 433.5           |
|                 | SW5           | 370            | 414.5            | 451.5           | 364            | 408.5            | 433.5           |
| Turbidity (NTU) | SW1           | 29             | 27.1             | 32              | 31             | 27.9             | 36              |
|                 | SW2           | 26             | 25.6             | 32.1            | 28             | 26.4             | 32.9            |
|                 | SW3           | 25.6           | 25.3             | 31.8            | 27.4           | 25.7             | 32.2            |
|                 | SW4           | 25.5           | 25.2             | 31.3            | 27.5           | 25.8             | 32.7            |

|                        |     |       |        |       |        |        |       |
|------------------------|-----|-------|--------|-------|--------|--------|-------|
|                        | SW5 | 25.6  | 25.4   | 31.8  | 27.4   | 25.6   | 32.2  |
| TSS<br>(mg/L)          | SW1 | 225   | 272    | 277   | 295    | 258    | 263   |
|                        | SW2 | 191   | 236    | 241   | 261    | 226    | 231   |
|                        | SW3 | 70.9  | 88.8   | 93.8  | 90.7   | 82.8   | 87.8  |
|                        | SW4 | 56.6  | 73.5   | 78.5  | 76.4   | 69.5   | 74.5  |
|                        | SW5 | 31.6  | 47.5   | 52.5  | 51.4   | 45.5   | 50.5  |
| TDS<br>(mg/L)          | SW1 | 1350  | 1429   | 1679  | 1110   | 1411   | 1661  |
|                        | SW2 | 785   | 851    | 925   | 675    | 925    | 915   |
|                        | SW3 | 776   | 839    | 913   | 670    | 833    | 907   |
|                        | SW4 | 761   | 818    | 892   | 663    | 814    | 880   |
|                        | SW5 | 751.8 | 806    | 882   | 661.8  | 804    | 880   |
| BOD<br>(mg/L)          | SW1 | 55    | 80     | 83    | 75     | 70     | 73    |
|                        | SW2 | 50.3  | 68     | 71    | 70.7   | 62     | 65    |
|                        | SW3 | 38.2  | 57     | 60    | 58.6   | 53     | 56    |
|                        | SW4 | 37.3  | 54.7   | 57.5  | 57.7   | 52.3   | 55.5  |
|                        | SW5 | 40    | 54.4   | 58    | 50     | 52.4   | 56    |
| COD<br>(mg/L)          | SW1 | 222   | 287    | 337   | 242    | 277    | 327   |
|                        | SW2 | 162   | 240    | 290   | 212    | 234    | 284   |
|                        | SW3 | 173   | 230    | 280   | 183    | 226    | 276   |
|                        | SW4 | 150   | 216    | 266   | 180    | 214    | 264   |
|                        | SW5 | 135   | 206    | 256   | 175    | 204    | 254   |
| TH (mg/L)              | SW1 | 180   | 305.5  | 282   | 240    | 295.5  | 272   |
|                        | SW2 | 80.3  | 179    | 155.5 | 90.7   | 173    | 149.5 |
|                        | SW3 | 63.3  | 166.8  | 143.3 | 85.3   | 162.8  | 139.3 |
|                        | SW4 | 61    | 163.5  | 140   | 83     | 161.5  | 138   |
|                        | SW5 | 62.4  | 162    | 138.5 | 78.6   | 160    | 136.5 |
| Cl <sup>-</sup> (mg/L) | SW1 | 980.4 | 1039.5 | 1080  | 1030.6 | 1011.5 | 1050  |
|                        | SW2 | 19    | 28.6   | 34.3  | 21     | 22.4   | 28.3  |
|                        | SW3 | 12.1  | 25.4   | 31.2  | 23.7   | 21.4   | 27.2  |

|                                         |     |      |       |       |       |      |      |
|-----------------------------------------|-----|------|-------|-------|-------|------|------|
|                                         | SW4 | 12.2 | 23.8  | 29.4  | 22.2  | 21.6 | 27.6 |
|                                         | SW5 | 15   | 22.6  | 28.2  | 17    | 20.4 | 26.4 |
| SO <sub>4</sub> <sup>2-</sup><br>(mg/L) | SW1 | 111  | 120.7 | 135   | 121   | 90.5 | 105  |
|                                         | SW2 | 92.1 | 94    | 108.5 | 102.7 | 80   | 94.3 |
|                                         | SW3 | 73.8 | 63.7  | 77.9  | 64.0  | 53.5 | 67.9 |
|                                         | SW4 | 69.2 | 56.9  | 71.3  | 59.5  | 50.9 | 65.1 |
|                                         | SW5 | 68.2 | 53    | 68.2  | 56.2  | 49   | 64.0 |
| NO <sub>3</sub> <sup>-</sup><br>N(mg/L) | SW1 | 9    | 14.5  | 21.7  | 11    | 9.9  | 16.5 |
|                                         | SW2 | 9.1  | 13.7  | 20.3  | 9.5   | 9.7  | 16.3 |
|                                         | SW3 | 7.1  | 11.3  | 17.9  | 9.1   | 9.3  | 15.9 |
|                                         | SW4 | 3.5  | 7.7   | 14.3  | 5.5   | 5.7  | 12.3 |
|                                         | SW5 | 0.3  | 3.6   | 10.2  | 0.5   | 1.6  | 8.2  |
| PO <sub>4</sub> <sup>3-</sup><br>(mg/L) | SW1 | 5.0  | 7.9   | 9.6   | 6.4   | 5.9  | 7.8  |
|                                         | SW2 | 5.0  | 7.3   | 8.9   | 5.4   | 5.5  | 7.5  |
|                                         | SW3 | 2.0  | 4.7   | 6.6   | 2.8   | 2.5  | 4.2  |
|                                         | SW4 | 1.8  | 4.0   | 5.9   | 2.0   | 2.2  | 3.9  |
|                                         | SW5 | .8   | 3.1   | 4.8   | 1.0   | 1.1  | 3.0  |
| HCO <sub>3</sub> <sup>-</sup><br>(mg/L) | SW1 | 186  | 217   | 349   | 194   | 183  | 311  |
|                                         | SW2 | 106  | 143   | 275   | 126   | 109  | 237  |
|                                         | SW3 | 79   | 101   | 247   | 99    | 97   | 211  |
|                                         | SW4 | 78   | 99    | 216   | 97    | 95   | 202  |
|                                         | SW5 | 65   | 84    | 202   | 81    | 82   | 188  |
| Na <sup>+</sup> (mg/L)                  | SW1 | 332  | 352   | 362   | 352   | 346  | 356  |
|                                         | SW2 | 7.7  | 10    | 16    | 9.7   | 8    | 14   |
|                                         | SW3 | 6.7  | 9     | 15    | 8.7   | 7    | 13   |
|                                         | SW4 | 6.0  | 8.3   | 14.3  | 8.0   | 6.3  | 15.3 |
|                                         | SW5 | 5.7  | 8.0   | 14    | 7.6   | 6.0  | 15   |
| K <sup>+</sup> (mg/L)                   | SW1 | 0.6  | 1.7   | 0.9   | 0.8   | 1.4  | 0.7  |
|                                         | SW2 | 0.14 | 0.9   | 0.9   | 0.16  | 0.9  | 0.7  |

|                            |     |      |      |      |      |      |      |
|----------------------------|-----|------|------|------|------|------|------|
|                            | SW3 | 0.18 | 0.39 | 0.4  | 0.22 | 0.41 | 0.2  |
|                            | SW4 | 0.20 | 0.38 | 0.4  | 0.22 | 0.40 | 0.2  |
|                            | SW5 | 0.20 | 0.36 | 0.4  | 0.24 | 0.40 | 0.2  |
| Ca <sup>2+</sup> (mg/L)    | SW1 | 40.0 | 47   | 46   | 48.0 | 45   | 44   |
|                            | SW2 | 28.0 | 31.8 | 30.8 | 29.6 | 29.8 | 28.8 |
|                            | SW3 | 21.0 | 27   | 26   | 27.0 | 25   | 24   |
|                            | SW4 | 1.0  | 2.2  | 1.9  | 1.4  | 2.0  | 1.7  |
|                            | SW5 | .6   | 1.8  | 1.5  | 1.0  | 1.6  | 1.3  |
| Mg <sup>2+</sup><br>(mg/L) | SW1 | 36.9 | 46   | 52   | 37.9 | 44   | 46   |
|                            | SW2 | 21.4 | 29.9 | 34.2 | 21.8 | 28.5 | 32.2 |
|                            | SW3 | 17.2 | 25.9 | 29.9 | 17.8 | 24.3 | 28.3 |
|                            | SW4 | 11.0 | 20.4 | 24.6 | 13.0 | 18.8 | 22.6 |
|                            | SW5 | 8.5  | 17.1 | 21.5 | 9.3  | 15.9 | 19.5 |
| Fe (mg/L)                  | SW1 | 0.04 | 0.08 | 0.09 | 0.08 | 0.06 | 0.09 |
|                            | SW2 | 0.04 | 0.07 | 0.08 | 0.06 | 0.07 | 0.08 |
|                            | SW3 | 0.03 | 0.07 | 0.08 | 0.07 | 0.05 | 0.08 |
|                            | SW4 | 0.03 | 0.07 | 0.08 | 0.05 | 0.05 | 0.08 |
|                            | SW5 | 0.03 | 0.05 | 0.08 | 0.05 | 0.05 | 0.08 |
| Pb (mg/L)                  | SW1 | 1.2  | 1.9  | 2.0  | 1.4  | 1.7  | 1.8  |
|                            | SW2 | 0.05 | 0.08 | 0.09 | 0.07 | 0.06 | 0.09 |
|                            | SW3 | 0.04 | 0.07 | 0.08 | 0.06 | 0.07 | 0.08 |
|                            | SW4 | 0.04 | 0.07 | 0.08 | 0.06 | 0.07 | 0.08 |
|                            | SW5 | 0.03 | 0.07 | 0.08 | 0.05 | 0.07 | 0.08 |
| Cu (mg/L)                  | SW1 | 0.35 | 0.80 | 0.09 | 0.45 | 0.80 | 0.09 |
|                            | SW2 | 0.30 | 0.75 | 0.85 | 0.38 | 0.73 | 0.83 |
|                            | SW3 | 0.30 | 0.75 | 0.85 | 0.38 | 0.73 | 0.83 |
|                            | SW4 | 0.25 | 0.69 | 0.79 | 0.31 | 0.67 | 0.77 |
|                            | SW5 | 0.21 | 0.64 | 0.74 | 0.25 | 0.62 | 0.72 |
| Cr (mg/L)                  | SW1 | 5.0  | 5.5  | 5.6  | 5.2  | 5.1  | 5.4  |

|           |     |      |      |      |      |      |      |
|-----------|-----|------|------|------|------|------|------|
|           | SW2 | 0.30 | 0.76 | 0.84 | 0.34 | 0.72 | 0.82 |
|           | SW3 | 0.10 | 0.55 | 0.65 | 0.14 | 0.53 | 0.61 |
|           | SW4 | 0.07 | 0.18 | 0.43 | 0.11 | 0.16 | 0.43 |
|           | SW5 | 0.04 | 0.14 | 0.40 | 0.08 | 0.14 | 0.40 |
| Zn (mg/L) | SW1 | 7.0  | 9.2  | 10   | 9.0  | 9.6  | 14   |
|           | SW2 | 3.5  | 4.9  | 7.5  | 3.7  | 5.1  | 7.7  |
|           | SW3 | 1.25 | 1.6  | 1.9  | 1.35 | 1.8  | 1.7  |
|           | SW4 | 0.20 | 0.63 | 0.72 | 0.26 | 0.63 | 0.74 |
|           | SW5 | 0.09 | 0.50 | 0.60 | 0.11 | 0.50 | 0.60 |
| Mn (mg/L) | SW1 | 0.04 | 0.06 | 0.09 | 0.06 | 0.06 | 0.09 |
|           | SW2 | 0.03 | 0.05 | 0.08 | 0.05 | 0.05 | 0.08 |
|           | SW3 | 0.03 | 0.04 | 0.08 | 0.05 | 0.04 | 0.08 |
|           | SW4 | 0.02 | 0.04 | 0.08 | 0.04 | 0.04 | 0.08 |
|           | SW5 | 0.02 | 0.04 | 0.09 | 0.04 | 0.04 | 0.09 |

**Table 3: Physicochemical parameters of groundwater around the CETP discharge area**

| Parameter       | Sampling site | Monsoon (2021) | Post-mon. (2022) | Pre-mon. (2022) | Monsoon (2022) | Post-mon. (2023) | Pre-mon. (2023) |
|-----------------|---------------|----------------|------------------|-----------------|----------------|------------------|-----------------|
| Tem ( °C)       | GW1           | 25.1           | 25.6             | 26.5            | 25.3           | 25.8             | 27.1            |
|                 | GW2           | 25.0           | 25.5             | 26.8            | 25.2           | 25.7             | 26.6            |
|                 | GW3           | 24.6           | 25.2             | 26.5            | 25.0           | 25.4             | 26.3            |
|                 | GW4           | 24.6           | 24.1             | 26.4            | 24.8           | 24.3             | 26.2            |
|                 | GW5           | 24.4           | 23.9             | 26.2            | 24.6           | 24.1             | 26.0            |
| pH              | GW1           | 7.2            | 7.4              | 6.8             | 7.4            | 7.6              | 7.0             |
|                 | GW2           | 7.0            | 7.3              | 6.7             | 7.2            | 7.5              | 6.9             |
|                 | GW3           | 6.9            | 7.4              | 6.7             | 7.1            | 7.6              | 6.9             |
|                 | GW4           | 7.0            | 7.3              | 6.7             | 7.2            | 7.5              | 6.9             |
|                 | GW5           | 6.9            | 7.2              | 6.6             | 7.1            | 7.4              | 6.8             |
| DO (mg/L)       | GW1           | 4.3            | 4.0              | 4.1             | 4.3            | 4.2              | 4.3             |
|                 | GW2           | 4.2            | 4.0              | 4.2             | 4.4            | 4.2              | 4.2             |
|                 | GW3           | 4.0            | 4.2              | 4.1             | 4.0            | 4.2              | 4.3             |
|                 | GW4           | 4.4            | 4.0              | 4.3             | 4.6            | 4.2              | 4.3             |
|                 | GW5           | 4.5            | 4.0              | 4.2             | 4.5            | 4.2              | 4.4             |
| EC (µS/cm)      | GW1           | 673            | 683              | 622             | 667            | 685              | 618             |
|                 | GW2           | 663            | 679              | 614             | 667            | 679              | 616             |
|                 | GW3           | 645            | 660              | 592             | 649            | 662              | 602             |
|                 | GW4           | 644            | 656              | 594             | 644            | 660              | 594             |
|                 | GW5           | 641            | 651              | 590             | 643            | 663              | 596             |
| Turbidity (NTU) | GW1           | 4.5            | 5.0              | 4.6             | 5.1            | 5.2              | 4.4             |
|                 | GW2           | 4.5            | 4.8              | 4.3             | 4.7            | 5.0              | 4.3             |
|                 | GW3           | 4.5            | 4.8              | 4.3             | 4.5            | 4.8              | 4.1             |
|                 | GW4           | 4.3            | 4.9              | 4.2             | 4.5            | 4.9              | 4.2             |

|                        |     |      |       |       |      |       |       |
|------------------------|-----|------|-------|-------|------|-------|-------|
|                        | GW5 | 4.4  | 4.7   | 4.1   | 4.6  | 4.9   | 4.3   |
| TSS (mg/L)             | GW1 | 8.5  | 8.8   | 8.0   | 8.3  | 8.6   | 8.2   |
|                        | GW2 | 8.2  | 8.5   | 7.9   | 8.2  | 8.5   | 7.9   |
|                        | GW3 | 7.4  | 7.7   | 7.1   | 7.2  | 7.5   | 6.9   |
|                        | GW4 | 7.2  | 7.8   | 7.0   | 7.2  | 7.6   | 7.0   |
|                        | GW5 | 7.1  | 7.5   | 6.9   | 6.9  | 7.5   | 6.7   |
| TDS (mg/L)             | GW1 | 453  | 512   | 442   | 447  | 508   | 434   |
|                        | GW2 | 436  | 496   | 422   | 430  | 490   | 420   |
|                        | GW3 | 430  | 496   | 426   | 428  | 494   | 420   |
|                        | GW4 | 425  | 492   | 420   | 425  | 490   | 418   |
|                        | GW5 | 423  | 490   | 414   | 421  | 486   | 414   |
| BOD (mg/L)             | GW1 | 9.1  | 10.0  | 7.2   | 8.9  | 12.0  | 6.8   |
|                        | GW2 | 8.0  | 9.8   | 6.1   | 8.0  | 10.2  | 5.9   |
|                        | GW3 | 8.6  | 9.6   | 6.0   | 8.4  | 9.4   | 6.0   |
|                        | GW4 | 8.4  | 9.6   | 5.9   | 8.4  | 9.4   | 5.9   |
|                        | GW5 | 8.2  | 9.3   | 5.9   | 8.6  | 9.3   | 5.7   |
| COD (mg/L)             | GW1 | 16.3 | 20.2  | 15.1  | 15.7 | 18.8  | 14.9  |
|                        | GW2 | 15.1 | 19.1  | 14.0  | 14.9 | 18.9  | 14.0  |
|                        | GW3 | 15.9 | 18.2  | 14.3  | 16.1 | 17.8  | 13.7  |
|                        | GW4 | 15.0 | 17.1  | 13.2  | 15.0 | 16.9  | 12.8  |
|                        | GW5 | 14.1 | 17.4  | 13.6  | 13.9 | 17.6  | 13.4  |
| TH (mg/L)              | GW1 | 180  | 305.5 | 282   | 240  | 295.5 | 272   |
|                        | GW2 | 80.3 | 179   | 155.5 | 90.7 | 173   | 149.5 |
|                        | GW3 | 63.3 | 166.8 | 143.3 | 85.3 | 162.8 | 139.3 |
|                        | GW4 | 61   | 163.5 | 140   | 83   | 161.5 | 138   |
|                        | GW5 | 62.4 | 162   | 138.5 | 78.6 | 160   | 136.5 |
| Cl <sup>-</sup> (mg/L) | GW1 | 253  | 261   | 252   | 257  | 259   | 248   |
|                        | GW2 | 251  | 256   | 242   | 249  | 254   | 248   |
|                        | GW3 | 250  | 256   | 245   | 248  | 252   | 243   |

|                                         |     |      |      |      |      |      |      |
|-----------------------------------------|-----|------|------|------|------|------|------|
|                                         | GW4 | 249  | 253  | 244  | 247  | 253  | 242  |
|                                         | GW5 | 247  | 255  | 240  | 247  | 253  | 246  |
| SO <sub>4</sub> <sup>2-</sup><br>(mg/L) | GW1 | 27.1 | 32.1 | 24.8 | 26.9 | 31.9 | 24.6 |
|                                         | GW2 | 27.0 | 31.8 | 24.8 | 26.8 | 32.0 | 24.4 |
|                                         | GW3 | 26.1 | 31.4 | 23.9 | 25.9 | 30.6 | 23.5 |
|                                         | GW4 | 25.2 | 32.1 | 23.7 | 24.8 | 31.9 | 23.7 |
|                                         | GW5 | 24.9 | 32.0 | 23.7 | 24.9 | 31.8 | 23.5 |
| NO <sub>3</sub> <sup>-</sup><br>N(mg/L) | GW1 | 3.12 | 2.73 | 3.82 | 3.08 | 2.67 | 3.78 |
|                                         | GW2 | 2.93 | 2.53 | 3.63 | 2.91 | 2.51 | 3.61 |
|                                         | GW3 | 2.35 | 1.98 | 3.08 | 2.39 | 1.96 | 3.06 |
|                                         | GW4 | 2.36 | 1.97 | 3.06 | 2.34 | 1.93 | 3.04 |
|                                         | GW5 | 2.47 | 1.92 | 3.00 | 2.43 | 1.88 | 3.00 |
| PO <sub>4</sub> <sup>3-</sup><br>(mg/L) | GW1 | 3.8  | 4.2  | 4.6  | 3.6  | 4.0  | 4.4  |
|                                         | GW2 | 3.7  | 4.2  | 4.5  | 3.5  | 3.8  | 4.3  |
|                                         | GW3 | 3.6  | 4.3  | 4.6  | 3.4  | 3.9  | 4.2  |
|                                         | GW4 | 3.5  | 4.1  | 4.5  | 3.5  | 3.9  | 4.5  |
|                                         | GW5 | 3.5  | 4.0  | 4.5  | 3.3  | 3.8  | 4.3  |
| HCO <sub>3</sub> <sup>-</sup><br>(mg/L) | GW1 | 342  | 412  | 275  | 338  | 408  | 271  |
|                                         | GW2 | 339  | 409  | 272  | 337  | 407  | 270  |
|                                         | GW3 | 337  | 410  | 273  | 335  | 406  | 273  |
|                                         | GW4 | 338  | 405  | 276  | 338  | 403  | 274  |
|                                         | GW5 | 338  | 404  | 275  | 336  | 402  | 273  |
| Na <sup>+</sup> (mg/L)                  | GW1 | 233  | 241  | 192  | 227  | 239  | 188  |
|                                         | GW2 | 225  | 235  | 185  | 223  | 233  | 183  |
|                                         | GW3 | 224  | 236  | 186  | 220  | 234  | 184  |
|                                         | GW4 | 223  | 237  | 184  | 223  | 235  | 182  |
|                                         | GW5 | 225  | 236  | 183  | 219  | 234  | 181  |
| K <sup>+</sup> (mg/L)                   | GW1 | 0.35 | 0.7  | 0.27 | 0.25 | 0.3  | 0.23 |
|                                         | GW2 | 0.26 | 0.47 | 0.22 | 0.24 | 0.43 | 0.18 |

|                         |     |      |      |      |      |      |      |
|-------------------------|-----|------|------|------|------|------|------|
|                         | GW3 | 0.24 | 0.45 | 0.19 | 0.24 | 0.43 | 0.19 |
|                         | GW4 | 0.24 | 0.45 | 0.19 | 0.22 | 0.45 | 0.19 |
|                         | GW5 | 0.23 | 0.45 | 0.19 | 0.23 | 0.45 | 0.19 |
| Ca <sup>2+</sup> (mg/L) | GW1 | 1.3  | 1.4  | 1.2  | 1.3  | 1.4  | 1.2  |
|                         | GW2 | 1.2  | 1.5  | 1.2  | 1.2  | 1.5  | 1.2  |
|                         | GW3 | 1.2  | 1.3  | 1.1  | 1.2  | 1.3  | 1.1  |
|                         | GW4 | 1.2  | 1.3  | 1.1  | 1.2  | 1.3  | 1.1  |
|                         | GW5 | 1.2  | 1.3  | 1.1  | 1.2  | 1.3  | 1.1  |
| Mg <sup>2+</sup> (mg/L) | GW1 | 45   | 61   | 42   | 43   | 59   | 38   |
|                         | GW2 | 36   | 53   | 34   | 34   | 49   | 28   |
|                         | GW3 | 35   | 52   | 33   | 33   | 48   | 27   |
|                         | GW4 | 35   | 53   | 34   | 33   | 47   | 26   |
|                         | GW5 | 33   | 49   | 29   | 28   | 45   | 25   |
| Fe (mg/L)               | GW1 | 1.62 | 1.81 | 1.13 | 1.58 | 1.79 | 1.07 |
|                         | GW2 | 1.53 | 1.90 | 1.10 | 1.47 | 1.90 | 1.10 |
|                         | GW3 | 1.49 | 1.89 | 1.09 | 1.49 | 1.89 | 1.09 |
|                         | GW4 | 1.49 | 1.89 | 1.09 | 1.49 | 1.89 | 1.09 |
|                         | GW5 | 1.43 | 1.83 | 1.03 | 1.43 | 1.83 | 1.03 |
| Pb (mg/L)               | GW1 | 0.14 | 0.16 | 0.13 | 0.12 | 0.14 | 0.09 |
|                         | GW2 | 0.12 | 0.14 | 0.10 | 0.10 | 0.12 | 0.08 |
|                         | GW3 | 0.12 | 0.13 | 0.09 | 0.10 | 0.13 | 0.09 |
|                         | GW4 | 0.11 | 0.13 | 0.09 | 0.09 | 0.11 | 0.07 |
|                         | GW5 | 0.12 | 0.12 | 0.08 | 0.08 | 0.12 | 0.08 |
| Cu(mg/L)                | GW1 | 1.10 | 1.17 | 0.87 | 1.08 | 1.13 | 0.83 |
|                         | GW2 | 1.08 | 1.14 | 0.84 | 1.06 | 1.12 | 0.82 |
|                         | GW3 | 1.09 | 1.15 | 0.86 | 1.07 | 1.13 | 0.82 |
|                         | GW4 | 1.08 | 1.13 | 0.86 | 1.06 | 1.13 | 0.80 |
|                         | GW5 | 1.07 | 1.14 | 0.84 | 1.07 | 1.12 | 0.82 |
| Cr(mg/L)                | GW1 | 0.27 | 0.32 | 0.23 | 0.23 | 0.28 | 0.17 |

|           |     |      |      |      |      |      |      |
|-----------|-----|------|------|------|------|------|------|
|           | GW2 | 0.24 | 0.29 | 0.19 | 0.22 | 0.27 | 0.17 |
|           | GW3 | 0.23 | 0.28 | 0.18 | 0.21 | 0.26 | 0.16 |
|           | GW4 | 0.22 | 0.29 | 0.19 | 0.22 | 0.25 | 0.15 |
|           | GW5 | 0.23 | 0.21 | 0.11 | 0.19 | 0.21 | 0.11 |
| Zn (mg/L) | GW1 | 5.17 | 5.73 | 5.09 | 5.13 | 5.67 | 5.01 |
|           | GW2 | 4.98 | 5.52 | 4.88 | 4.92 | 5.48 | 4.82 |
|           | GW3 | 4.97 | 5.54 | 4.87 | 4.93 | 5.46 | 4.83 |
|           | GW4 | 4.89 | 5.41 | 4.76 | 4.81 | 5.39 | 4.74 |
|           | GW5 | 4.78 | 5.32 | 4.67 | 4.72 | 5.28 | 4.63 |
| Mn (mg/L) | GW1 | 0.33 | 0.41 | 0.23 | 0.27 | 0.39 | 0.17 |
|           | GW2 | 0.22 | 0.32 | 0.11 | 0.18 | 0.28 | 0.09 |
|           | GW3 | 0.31 | 0.43 | 0.22 | 0.29 | 0.37 | 0.18 |
|           | GW4 | 0.34 | 0.41 | 0.21 | 0.26 | 0.39 | 0.19 |
|           | GW5 | 0.23 | 0.32 | 0.12 | 0.17 | 0.28 | 0.08 |