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<https://doi.org/10.5109/7407634>

出版情報：九州大学大学院農学研究院紀要. 71 (1), pp.25-34, 2026-02-27. Faculty of Agriculture, Kyushu University

バージョン：

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Ecological Risk Assessment of Surface Water Through Heavy Metal Contamination in the Fish Spawning Tetulia River Estuary of Bangladesh

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(Received September 26, 2025 and accepted November 5, 2025)

Estuaries worldwide have been severely degraded and become reservoirs for many types of pollutants, such as heavy metals. Hilsa shad (*Tenulosa ilisha*) is Bangladesh's most important single-species fishery that contributes to 12% of total catch and employment for millions of people. An important natural breeding area for hilsa in Bangladesh, the Tetulia River, is the subject of this study's evaluation of heavy metal pollution. Surface water samples were collected during four periods July, August 23, February, and March 24 to analyze the concentrations of seven trace elements (Cd, Cr, Mn, Fe, Ni, Cu, and Pb) and assess metal toxicity. In the dry season, the average concentrations of Cu, Cr, Ni, Cd, Mn, Fe, and Pb were 0.06, 0.09, 0.06, 0.08, 0.30, 3.93, and 0.19 mg/L, respectively, while in the wet season, they were 0.05, 0.18, 0.05, 0.07, 0.17, 3.20, and 0.08 mg/L, respectively. The concentrations of Cr, Cd, Fe, and Pb exceeded the recommended safe limits for drinking water and freshwater aquatic life protection. The ecological risk index indicated contamination levels ranging from low to high. This study highlights the need for effective policies to safeguard valuable, productive, and diverse coastal ecosystems, particularly concerning water pollution. Further investigation to explore specific source of metals in coastal areas are warranted.

Key words: estuary, tetulia river, water quality, toxic elements, ecological risk

INTRODUCTION

Water is a fundamental necessity for all life forms on Earth (Bytyci *et al.*, 2018). The primary sources of water include rivers, estuaries, glaciers, rainwater, and groundwater. Seawater is significantly diluted by freshwater from land drainage in an estuary, a semi-enclosed coastal water feature that remains directly connected to the open sea (Hasan *et al.*, 2022a). Estuarine ecosystems are dynamic, highly productive environments that support rich biodiversity. Due to their high productivity and nutrient abundance, many fish and shellfish species rely on estuaries for spawning, feeding, nursing, and migration (Chowdhury *et al.*, 2011). Despite its significance, water remains one of the most poorly managed resources globally and is under serious threat from various human activities (Islam *et al.*, 2013). Rivers, in particular, play a crucial role in receiving and transporting pollutants from both point sources and nonpoint sources (including urban runoff, agriculture, and atmospheric deposition). These pollutants accumulate in fish, posing significant health risks to humans (Salam *et al.*, 2021;

Tenebe *et al.*, 2017). The issue is especially severe in developing countries like Bangladesh (Hossain *et al.*, 2019). Industrial effluents often contain hazardous toxic elements such as cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), and lead (Pb) (Lambert *et al.*, 2000). The increasing prevalence of these pollutants in water systems raises global concerns, particularly in regions with inadequate environmental regulations, such as Bangladesh (Hossain *et al.*, 2022).

Heavy metals (HMs) in aquatic ecosystems are a major global concern due to their harmful effects and potential for bioaccumulation (Hossain *et al.*, 2022). Toxic compounds, originating from both natural and human activities, are introduced into aquatic environments and subsequently absorbed by aquatic organisms. Even at low concentrations, trace metals can be detrimental to the health of both aquatic species and humans (Hossain *et al.*, 2022). These pollutants can severely impact aquatic biodiversity and disrupt ecosystems. The anadromous fish known as Hilsa (*Tenualosa ilisha*) or Indian shad travels from the Bay of Bengal to the rivers Tetulia, Padma, and Meghna, as well as its tributaries, to reproduce and nurse (Bhaumik and Sharma, 2011). The hilsa fishery plays a vital role in Bangladesh's economy, providing livelihoods for 2.5 million fishermen. It accounts for 12% of the country's total fish production and contributes approximately 1% to the national GDP, with an annual market value of \$1.3 billion (Dutta *et al.*, 2021). Hilsa prefers freshwater environments with salinity levels below 0.1 psu for spawning and nursery activities. With the recent rise in hilsa production, concerns over heavy metal contamination and metal-based pollutants in aquatic environments have become increasingly significant in the fishery industry (Islam *et al.*, 2014).

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In Bangladesh, the Padma–Meghna–Tetulia freshwater river system serves as a crucial breeding ground for the anadromous *Tenualosa ilisha*. These brood fish migrate from marine waters into these rivers for spawning, after which they spend their nursery and juvenile stages in freshwater and estuarine environments. The Tetulia River estuary, in particular, plays a vital role as a breeding, feeding, and nursery habitat for various aquatic species, including hilsa, in connection with the Bay of Bengal. However, nearly all rivers in the country are heavily polluted with heavy metals due to human activities, primarily the unregulated discharge of untreated industrial effluents (Ustaoglu and Islam, 2020). Therefore, assessing surface water quality and heavy metal pollution levels is essential for protecting both the environment and public health. While some studies have examined different biological aspects of the Tetulia River (Rakib *et al.*, 2022; Hossain *et al.*, 2015), none have specifically investigated contamination levels or the ecological risk index (ERI) of toxic elements in this estuary. Thus, the present study aims to assess the contamination levels of potential toxic elements and determine the water quality index in relation to the ecological risk index (ERI) within the Tetulia River estuary, a key spawning and nursery habitat for hilsa.

MATERIALS AND METHODS

Study area and sample collection

Water samples were collected on four occasions July, August 23, and February and March 24 to cover both the dry and wet seasons. For this study, samples were taken from four different locations: Kalaiya, Hazir Hat, Char Kajal, and Lalua (Fig. 1). Water samples were taken from the surface using a 1.5 L water sampler (Wildco–1520) at a depth of 0–0.5 m, which is considered the euphotic layer. Following collection, the water was acidified by adding 1 mL of 65% HNO₃ acid, subsequently passed through a vacuum filtration system's Whatman GF/F (0.45 µm) filter paper without delay. The filtered samples were stored in a refrigerated, dark environment until laboratory analysis. An atomic absorption spectrometer was used to test the amounts of heavy metals (PerkinElmer, PinAAcle 9000H, USA) at the Department of Agroforestry and Environment Laboratory, Faculty of Forestry and Environment, Gazipur Agricultural University, Bangladesh.

Trace element evaluation index (TEI)

The TEI was calculated according to Edet and Offiong, 2002.

$$TEI = \sum T_c/T_{max} \dots\dots\dots (1)$$

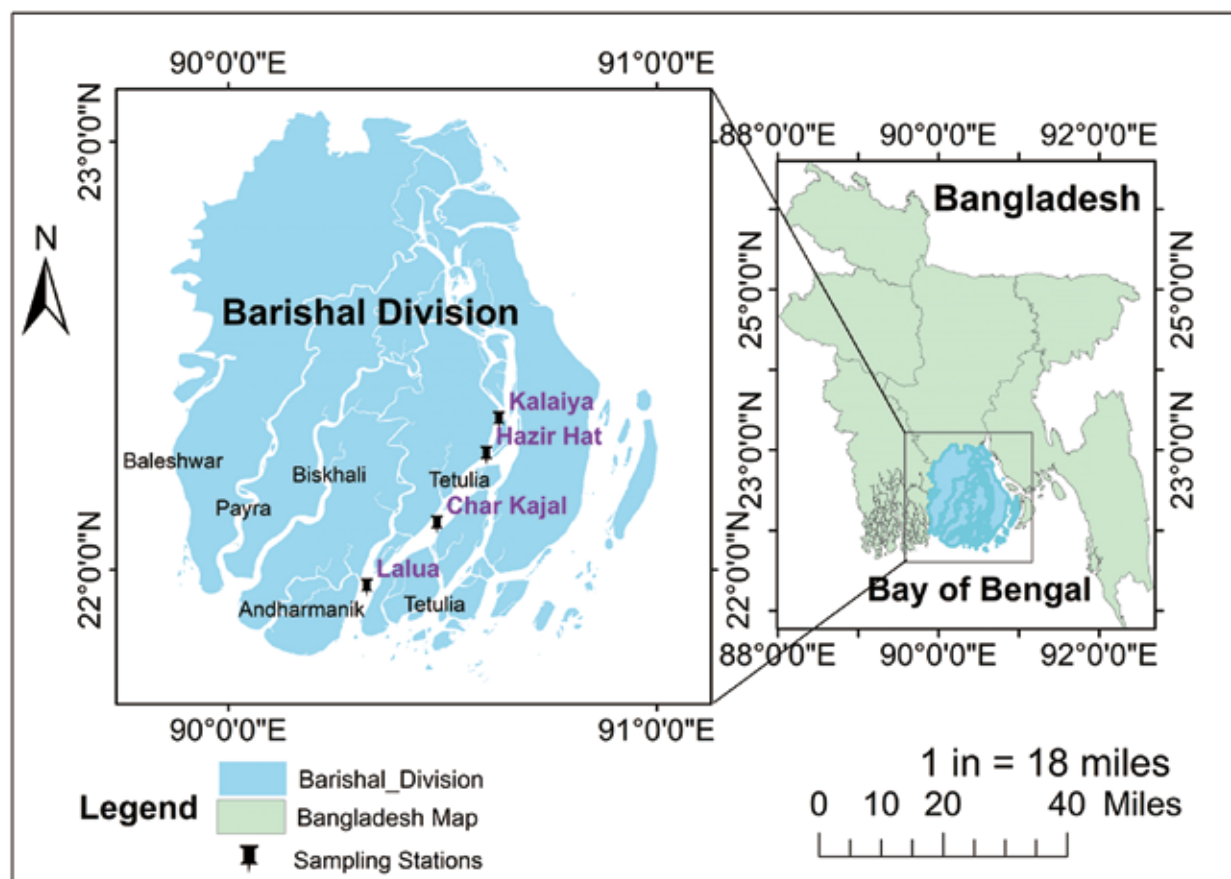


Fig. 1. Sampling location of the study area.

Where T_c represents the observed concentration of the i^{th} parameter, and T_{max} denotes its maximum permissible limit. The maximum allowable concentrations for Cd, Cr, Mn, Fe, Ni, Cu, and Pb are 0.003, 0.05, 0.5, 0.3, 0.07, 2.0, and 0.01 mg/L, respectively (WHO, 2011). The Trace Element Index (TEI) is categorized as follows: low (<10), medium (10–20), and high (>20).

Pollution index and ecological risk assessment

$$ERI = \sum RI = \sum Ti \cdot PI \dots\dots\dots (2)$$

$$PI = Cs/Cb \dots\dots\dots (3)$$

Each heavy metal's potential ecological risk factor is represented by RI, the toxic–response factor by Ti , and the pollution index by PI. The heavy metal concentration in the sample is denoted by C_s , whereas the comparable background values are represented by C_b . Cd, Cr, Mn, Fe, Ni, Cu, and Pb all have background values of 0.01, 0.05, 0.1, 1, 1, 1, and 0.05, respectively, according to references (DoE, 1997; Wedepohl, 1995). Cd has a toxic–response factor of 30, Cr has a factor of 2, Mn has a factor of 1, Fe has a value of 2.7, and Ni, Cu, and Pb each have a factor of 5 (Taiwo *et al.*, 2019). Ecological risk indexes are classified according to the following: an ERI below 150 indicates low ecological danger, an ERI between 150 and 300 shows moderate ecological risk, an ERI between 300 and 600 indicates considerable ecological risk, and an ERI beyond 600 recommends a very high ecological risk (Taiwo *et al.*, 2019; Proshad *et al.*, 2020).

Statistical analyses

Multivariate statistical analysis of spatiotemporal variations in the Tetulia River estuary was conducted using R version 4.0.3 (Pinheiro *et al.*, 2020). Descriptive statistics, including mean, range, and standard deviation, was calculated for all variables. The 'heatmaply' software was used to conduct boxplot analysis (Galili *et al.*, 2018). The links among heavy metals was examined using Principal Component Analysis (PCA).

RESULTS

Figs. 2, 3 and Table 1 shows the average concentrations of trace elements (TEs) in water samples taken from the Tetulia River in Bangladesh. The TE concentrations varied significantly between the seasons and sampling locations. While the dry season had an opposite sequence of average TE concentrations, as shown in Table 1, the order of importance during the rainy season was as follows: Fe > Cr > Mn > Pb > Cd > Cu > Ni. According to Table 1, Figures 2 and 3, the average concentration of Cu in surface water was 0.05 mg/L during the rainy season and 0.06 mg/L during the dry season. During the wet season, the concentrations of dissolved Cr varied between 0.05 and 0.32 mg/L, while during the dry season, they ranged from 0.008 to 0.29 mg/L (Table 1, Figs. 2 and 3). Surface water Ni concentrations were consistently higher at the Kalaiya station during both the dry and wet seasons, with the dry season averaging 0.06 mg/L and the wet season 0.05 mg/L.

The average Cd concentration in surface water was 0.08 mg/L during the dry season and 0.07 mg/L during the wet season. For Mn, the mean concentration in surface water was 0.17 mg/L in the wet season and increased to 0.30 mg/L in the dry season (Table 1). Notably, Fe levels were elevated in the dry season, reaching 3.93 mg/L, compared to 3.20 mg/L in the wet season. The mean Pb concentration in surface water was recorded at 0.19 mg/L during the dry season and 0.08 mg/L in the wet season (Table 1). While the concentrations of Cr, Cu, Ni, Cd, Mn, Fe, and Pb were generally higher in the dry season, Cr levels were found to be greater in the wet season. Spatially, Cu and Ni concentrations exhibited significant variation ($p < 0.05$), whereas Cr, Mn, Fe, and Pb showed significant temporal differences ($p < 0.05$).

Principal Component Analysis (PCA) revealed that four principal components accounted for 92.2 % of the total variance in the environmental variables (Fig. 4). PC1, which explained 50.2 % of the total variance, was

Table 1. Mean concentrations of trace elements (mg/L) in surface water samples from the Tetulia River in Bangladesh

	Cu	Cr	Ni	Cd	Mn	Fe	Pb
Dry Season							
Char kajal	0.04	0.07	0.04	0.07	0.26	3.47	0.16
Hazir hat	0.03	0.09	0.06	0.05	0.28	3.83	0.12
Kalaiya	0.17	0.12	0.14	0.16	0.35	4.45	0.38
Lalua	0.02	0.09	0.02	0.04	0.31	3.97	0.12
Mean	0.06	0.09	0.06	0.08	0.30	3.93	0.19
Wet Season							
Char kajal	0.02	0.18	0.03	0.03	0.09	3.08	0.06
Hazir hat	0.03	0.16	0.04	0.04	0.12	3.10	0.05
Kalaiya	0.07	0.21	0.12	0.18	0.23	3.18	0.14
Lalua	0.08	0.17	0.02	0.04	0.24	3.44	0.05
Mean	0.05	0.18	0.05	0.07	0.17	3.20	0.08

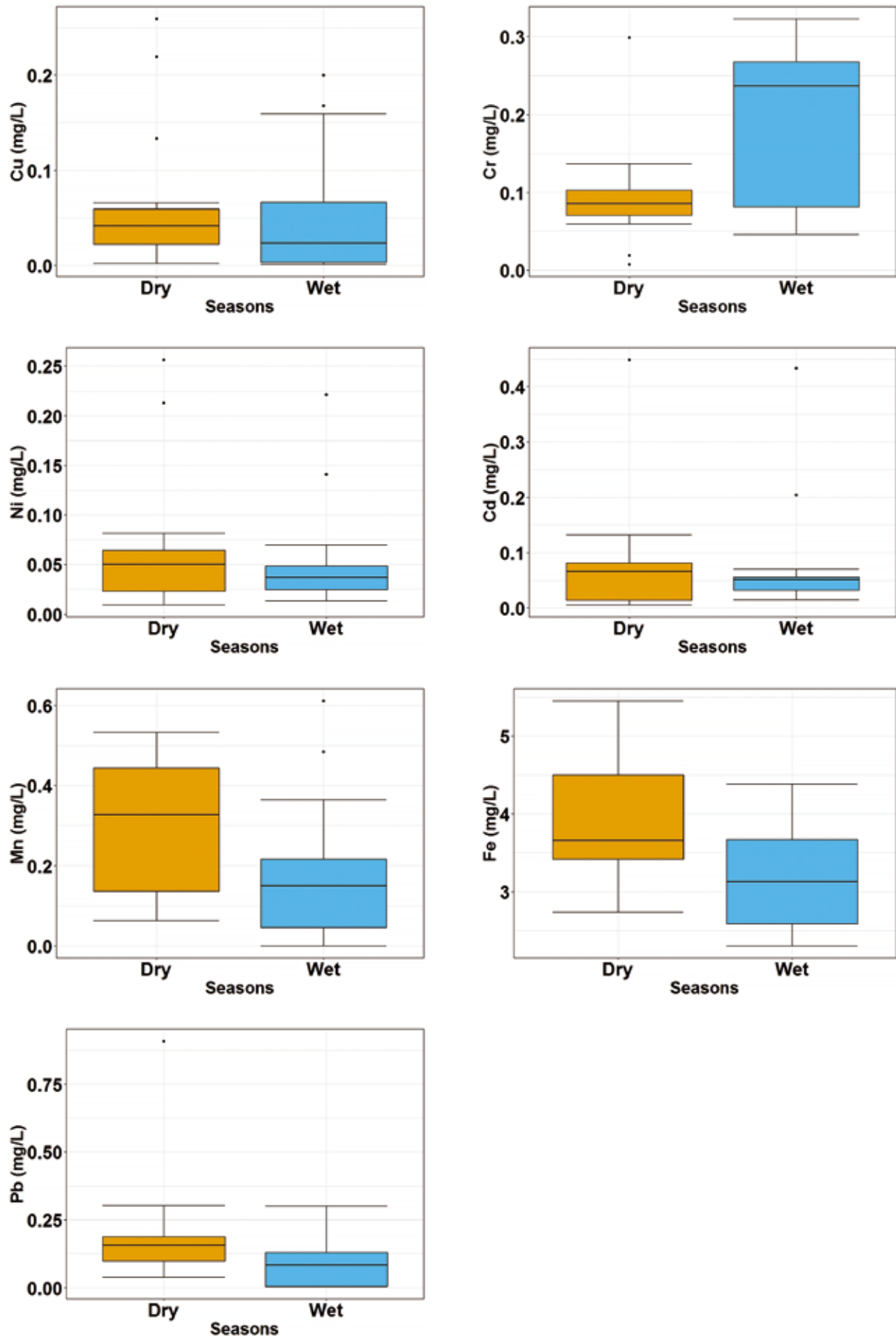


Fig. 2. Temporal variations of trace elements (mg/L) in surface water samples from the Tetulia River in Bangladesh.

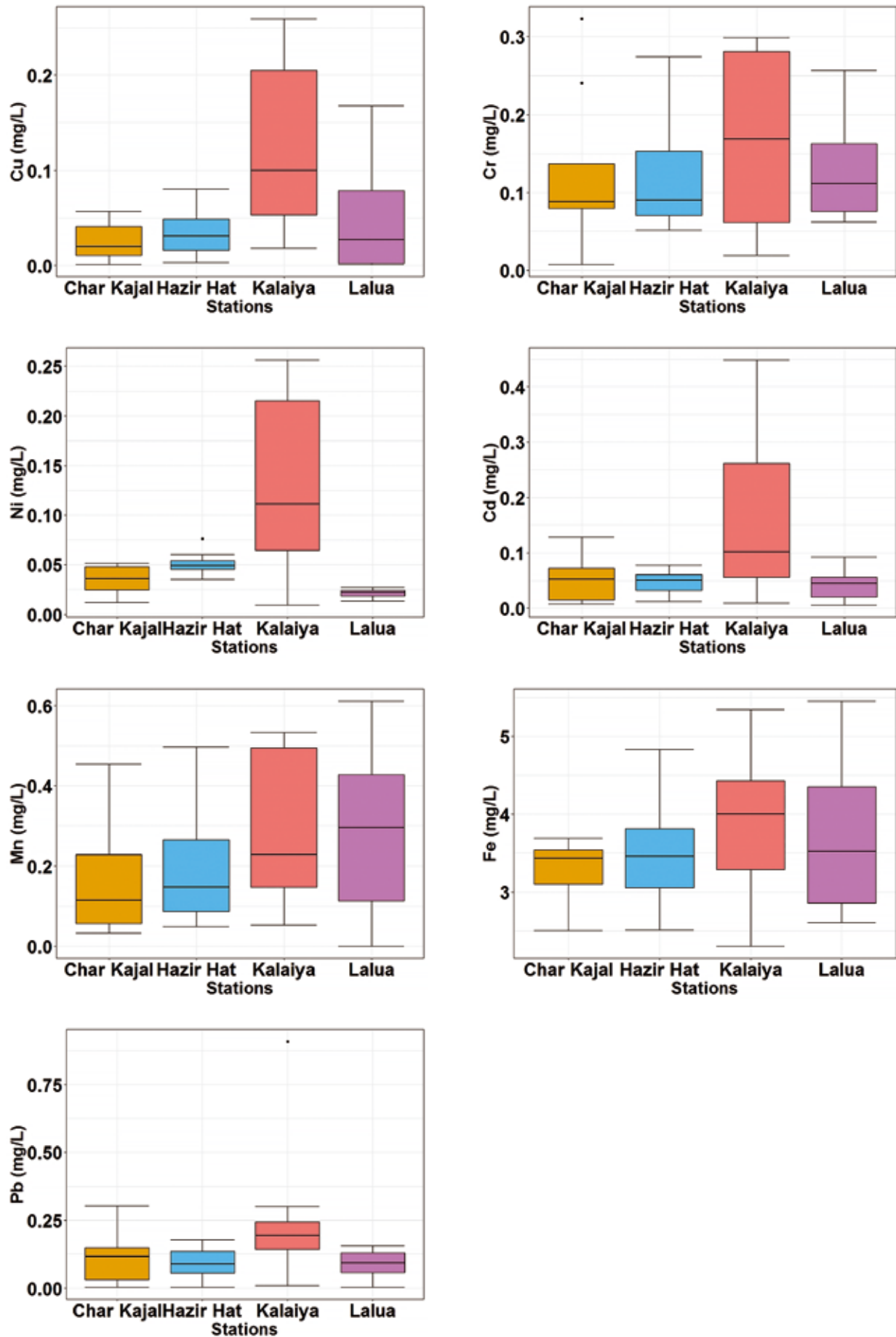


Fig. 3. Spatial variations of trace elements (mg/L) in surface water samples from the Tetulia River in Bangladesh.

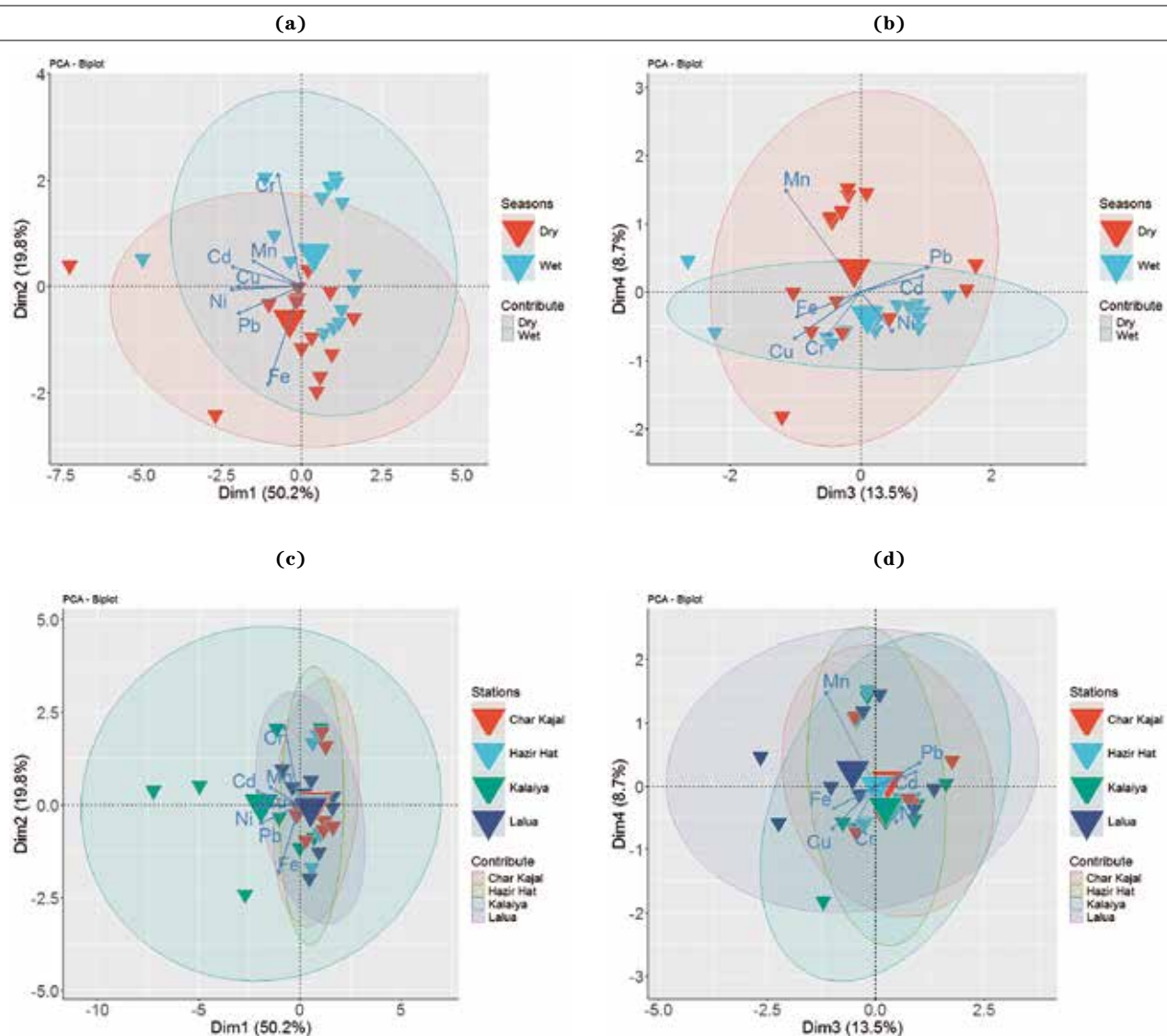


Fig. 4. Principal component analysis (PCA) for dissolved trace elements in surface water of Tetulia River, Bangladesh (a and b: seasonal (c and d: spatial).

primarily influenced by Ni, Cd, Cu, and Pb. In PC2, Mn, Pb, Cu, Fe, and Cd were the dominant factors, contributing 19.8 % to the total variance (Fig. 4). The remaining variation in PC3 and PC4 was mainly attributed to Mn, Cr, and Fe (Fig. 4). The correlation matrix illustrated the interactions among the metals. Strong positive correlations were observed between Cd and Ni ($r = 0.82$), Cd and Pb ($r = 0.79$), Ni and Pb ($r = 0.68$), and Cu and Ni ($r = 0.70$), all significant at the 0.001 level (Fig. 5). Moderate linear relationships were found between Cu and Mn ($r = 0.52$), Cu and Cd ($r = 0.51$), and Cu and Fe ($r = 0.48$) at the 0.01 significance level, while Mn and Cd ($r = 0.44$) showed a moderate correlation at the 0.05 level. Weak associations were noted between Mn and Cr, Fe, Pb, Ni; Cu and Cr; Cd and Cr, Fe; Ni and Cr, Fe; and Pb and Cr, Fe. Additionally, Cr and Fe displayed a weak to moderate negative correlation ($r = -0.32$) (Fig. 5). The ecological risk index (ERI) for potential toxic elements in Tetulia River water ranged from 125.43 to

601.59 during the wet season and from 162.29 to 547.67 in the dry season (Table 2). Based on the ERI classification by Taiwo *et al.* (2019), 25 % of the samples indicated low ecological risk, 50 % posed a moderate risk, 12 % exhibited considerable risk, and 13 % showed high ecological risk in both seasons (Table 2).

DISCUSSION

Because of their toxicity, endurance, and tendency to accumulate in living organisms, potentially hazardous substances are among the most dangerous contaminants in the natural environment (Bhuyan *et al.*, 2023). Ecosystems are particularly vulnerable to these contaminants, and their effects can be devastating (Bat *et al.*, 2022). Estuarine environments are susceptible to potential dangers posed by both naturally occurring substances and those that have been manipulated by humans. Mining, metal processing, farming, chemical

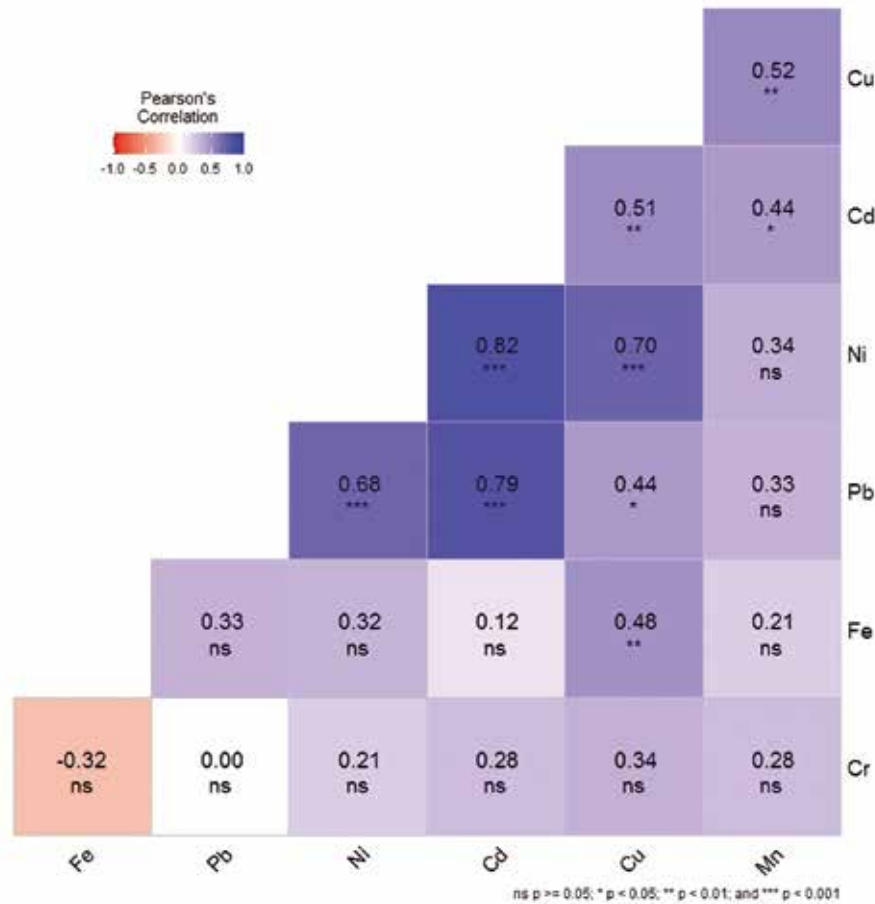


Fig. 5. Correlation analysis among the metal contents.

Table 2. Ecological risk index (ERI) of studied metal in Halda river (dry and wet seasons) in Bangladesh

Cu	Cr	Ni	Cd	Mn	Fe	Pb	ERI	Risk Level
Dry Season								
0.84	4.90	0.70	487.64	3.54	12.02	38.01	547.67	Considerable
0.15	3.47	0.29	153.21	2.84	10.35	12.20	182.56	Moderate
0.17	2.75	0.18	213.04	2.57	9.37	15.82	243.93	Moderate
0.13	3.85	0.10	132.61	3.08	10.72	11.75	162.29	Moderate
Wet Season								
0.38	8.43	0.60	566.61	2.32	8.60	14.63	601.59	High
0.18	6.73	0.21	129.09	1.27	8.39	5.84	151.74	Moderate
0.07	7.29	0.16	102.07	0.95	8.32	6.54	125.43	Low
0.41	6.82	0.10	124.74	2.44	9.30	5.63	149.47	Low

industries, domestic sewage, and urban runoff from heavily farmed areas are some of the many ways copper (Cu) gets into the environment (Yunus *et al.*, 2020; Islam *et al.*, 2014). World Health Organization (WHO) drinking water guideline levels (2011) were found to be lower in water samples collected from the Tetulia River in Bangladesh, with maximum Cu values that were lower. Industries involved in leather tanning, dye and pigment production, chrome plating, industrial welding, and wood preservation are major contributors to chro-

mium (Cr) contamination of water systems. There were worries about pollution in the Tetulia River due to Cr concentrations that were significantly higher above the recommended drinking water limits set by the WHO (2011), in contrast to Cu. For instance, the Karnafuly River in Bangladesh had chromium (Cr) levels of 0.25 mg/L, the Halda River had levels of 0.03 mg/L and the Meghna River estuary had levels of 0.02 mg/L, according to various sources (Rakib *et al.*, 2022; Islam *et al.*, 2013) (Table 3).

Table 3. Comparison of trace element concentrations (mg/L) of the Tetulia river water with other rivers of Bangladesh

Locations	Cu	Cr	Ni	Cd	Mn	Fe	Pb	References
Tetulia River estuary, Bangladesh	0.05	0.13	0.05	0.07	0.23	3.56	0.13	Current study
Karnafuly River, Bangladesh	0.05	0.25		0.01	0.12	NA	0.14	(Islam <i>et al.</i> , 2013)
Halda River, Bangladesh	1.75	0.03		0.03	0.08	0.58	0.06	(Rakib <i>et al.</i> , 2022)
Bhairab River, Bangladesh		0.03		0.001			0.02	(Ali <i>et al.</i> , 2022)
Meghna River estuary, Bangladesh		0.02		0.002			0.06	(Hasan <i>et al.</i> , 2021)

Shipbuilding, gas turbine production, battery factories, alloy production, electroplating, printing, and silver refineries are only a few of the human and natural sources of nickel (Ni), a non-biodegradable poisonous element that is present in wastewater (Neves *et al.*, 2020). Results showed that the highest Ni contents in Tetulia River water samples were lower than the levels recommended for human consumption by the World Health Organization (WHO) (2011). In addition to its carcinogenic characteristics, cadmium (Cd) can harm the kidneys and wreak havoc on the endocrine and reproductive systems (Islam *et al.*, 2014). There was a little increase in Cd levels during the dry season, which was probably caused by a decrease in freshwater intake, which increased concentration. Cd levels in the Tetulia River were too high, according to the World Health Organization's (2011) drinking water guidelines, suggesting heavy pollution. Specifically, the Karnafuly River had a concentration of 0.01 mg/L of Cd, the Halda River had a concentration of 0.03 mg/L, and the Meghna River estuary had a concentration of 0.002 mg/L. Although manganese (Mn) is a necessary mineral, it becomes poisonous at very high amounts. Because of its abundance in the Earth's crust, manganese (Mn) can be found in surface water in a variety of oxidation states, which are affected by factors including dissolved oxygen levels and the activity of microbes (Tobiason *et al.*, 2016). The highest manganese concentrations detected in water samples taken from the Tetulia River in Bangladesh were determined to be below the limits set by the World Health Organization's drinking water guidelines (2011). The Karnafuly River, on the other hand, had Mn values of 0.12 mg/L (Islam *et al.*, 2013), and the Halda River had lower amounts of 0.08 mg/L (Rakib *et al.*, 2022). Alternatively, the iron (Fe) levels in the Tetulia River were higher than what is considered safe for human consumption according to the World Health Organization (0.3 mg/L). The metal alloy industry's effluent discharge is probably the cause of the water's elevated Fe levels. Iron is a necessary ingredient for many biological processes, but too much of it can cause iron poisoning, which manifests as gastrointestinal distress and bloating (Fraga and Oteiza, 2002). In 2011, the Tetulia River had lead (Pb) levels that were 13.3 times greater than the World Health Organization's (WHO) recommended level of 0.01 mg/L. The Karnafuly River estuary was the subject of a comparable study that showed 0.14 mg/L of lead, but the Meghna River estuary was sampled by Hasan *et al.*, (2022b) and found 0.06 mg/L of lead. Most

of the lead in water comes from things like fertilizers, wastewater discharge, metal plating, and car exhaust (Karrari *et al.*, 2012) (Table 3).

It is worth mentioning that this precious fish species is extensively found in the Bay of Bengal, neighboring estuaries, and important riverine systems in Bangladesh (DoF, 2018). A large number of anadromous Hilsa fish from the Northern Bay of Bengal go to the waters of Bangladesh to spawn during the spawning season (Miah, 2015). Hilsa, however, can become contaminated with harmful trace metals from these spawning sites, which could harm fish and other aquatic life. Fish intake poses a concern to human health due to this pollution. There are carcinogenic and non-carcinogenic health concerns associated with these waters due to the amounts of specific metals that surpass food safety regulations, according to studies.

CONCLUSIONS

The Tetulia River, in Bangladesh's southwestern region, is an important body of water since it's the sole place where hilsa can reproduce naturally. The fast urbanization and unchecked industrial activities in emerging nations like Bangladesh are mostly to blame for the worsening river water quality caused by a variety of pollutants. The researchers in this study looked for seven trace elements that could be harmful in water samples taken from the estuary of the Tetulia River. The results showed that some of these harmful components were present in the river at concentrations higher than the prescribed safety limits, suggesting pollution that could harm the local environment. Contamination levels induced by the analyzed toxic components ranged from low to high, according to the ecological risk index (ERI) assessment. In order to preserve the Tetulia River's water quality and prevent more degradation of this economically important ecosystem, it is imperative that the appropriate authorities take immediate action to regulate and prohibit the unregulated discharge of industrial effluents into the River.

AUTHOR CONTRIBUTIONS

Jahid Hasan played a role in conceptualizing and designing the study, as well as in the preparation of materials and samples, conducting analyses, and drafting the initial manuscript. Dinesh Chandra Shaha played a role in drafting the initial manuscript. Minhaz Ahmed

played a role in conducting analyses, and drafting the initial manuscript. Muhammad Ziaul Hoque contributed to mapping the study site and participated in subsequent revisions. Md. Golam Rasul, Md. Foysul Hossain and Md. Suhag assisted in revising the manuscript. Masaru Matsumoto critically reviewed the manuscript with valuable suggestions and comments. All authors read and approved the final manuscript.

CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

FUNDING

The authors extend their thanks to the Ministry of Science and Technology, Government of the People's Republic of Bangladesh (Grant number SRG-231047), for the financial assistance.

ACKNOWLEDGMENTS

The authors are thankful to the Department of Agroforestry and Environment, Faculty of Forestry and Environment, Gazipur Agricultural University, Bangladesh for providing their laboratory facilities.

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