ASSESSMENT OF SEASONAL HEAVY METAL POLLUTION AT THE ESTUARIES OF SOME SELECTED CANALS FEEDING THE RIVER KARNAPHULI

By

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Declaration

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Dedicated

to

Late Professor Engr. M. Ali Ashraf

List of Publications

Journal Article

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Declaration by the Supervisor

This is to certify that Ariful Islam has carried out this research work under my supervision, and that he has fulfilled the relevant Academic Ordinance of the Chittagong University of Engineering and Technology, so that he is qualified to submit the following Thesis in the application for the degree of MASTER of PHILOSOPHY in Chemistry. Furthermore, the Thesis complies with the PLAGIARISM and ACADEMIC INTEGRITY regulation of CUET.

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Abstract

The main goal of this study was to evaluate the sessional variation of heavy metals concentration in surface water and sediments at the estuaries of major cannals (locally known as khal) feeding to Karnaphuli river and their associated health risks. Additionally, some important physico-chemical parameters of surface water were also studied to assess the present environmental loads at the study points. Ten major khals, which serve as the natural drainage to the Karnaphuli river were chosen for collecting the surface water and sediments samples; among them six from the Chattogram city side and four from the opposite side of Karnaphuli river. Concentrations of eight heavy metals, like Cu, Cr, Cd, Pb, Ni, Mn, As and Zn in surface water and sediment samples during the wet and dry seasons were determined using flame atomic absorption spectroscopy (FAAS). Beside these, some important physico-chemical parameters, such as temperature, pH, DO, BOD, COD, TDS, EC, salinity and hardness of surface water were measured using portable multi-analyzer and standard methods, where applicable. Some of the studied parameters at some locations showed higher values than the limits recommended by WHO, especially in the dry season. The values of all parameters, except temperature were cosideably higher in the wet season than in dry season. The average concentrations of Cu, Cr, Cd, Pb, Ni, Mn, As and Zn in surface water samples during wet were found 57.48 ± 7.07, 52.79 ± 5.63, 14.94 ± 3.15, 52.15 ± 5.41, 34.34 ± 3.89, 64.90 ± 10.31, 9.40 ± 1.55 and 60.37 ± 6.77 μg/L and in dry season the concentrations were 65.24 ± 9.40, 62.50 ± 6.52, 22.20 ± 4.41, 72.24 ± 9.14, 38.28 ± 5.34, 69.90 ± 11.13, 15.03 ± 3.53 and 75.03 ± 9.78 μg/L respectively. Again, the average concentrations of those heavy metals in surface sediments samples were 38.84 ± 3.50, 46.92 ± 3.84, 2.18 ± 0.42, 42.98 ± 3.97, 43.39 ± 3.55, 1.34 ± 0.19 and 91.93 ± 7.72 mg/kg in wet season and 51.13 ± 2.88, 59.23 ± 1.65, 2.52 ± 0.14, 61.05 ± 4.09,

49.66 ± 5.70, 58.55 ± 8.112, 21 ± 0.74 and 104.44 ± 5.02 mg/kg respectively in dry season. The average concentration of Cu, Cr, Cd, Pb and Ni in sediments were found higher than the limit recommended by USEPA, 2019. However, the study also found that the concentration of heavy metals in both water and sediment samples were found higher in the dry season than that of wet season at most of the locations.

The metal pollution index (MPI) shows that water of all the studied feeding khals are highly polluted in both wet and dry seasons. Potential carcinogenic and non-carcinogenic health risks through dermal contact were found within the acceptable limit recommended by USEPA for lifetime exposure to the surface water. Most of the environmental indices calculated, like enrichment factor (EF), degree of contamination ($\boldsymbol{C}_d$), pollution load index (PLI), geoaccumulation index ($\mathbf{I}_{geo}$), potential ecological index (PERI) and nemerow pollution index (P_N) for heavy metals in surface sediments showed no potential risk; although the contamination factor (CF) and modified contamination degree (mC_d) indicate that the sediments of the studied khals became moderately and highly contaminated respectively with heavy metals. Pearson's correlation coefficient was applied to find out the association between pollutants in the investigated samples. The results showed that physiochemical parameters of surface water, and concentration of heavy metals in surface water and sediments are influenced by seasonal water flows. Moreover, heavy metals showed variation from one location to others, and it was considerably higher in the industrial sites than that of municipal waste discharge sites.

The obtained comprehensive data for physico-chemical parameters of surface water, and toxic heavy metals in the surface water and sediments at the estuaries of studied khals feeding to Karnaphuli river may help the policy maker for making effective legislation to minimize the ecological risks of the river through proper monitoring, controlling and protection.

বিমূর্ত

বর্তমান গবেষণা কার্যের প্রধান লক্ষ্য ছিল ভিন্ন ঋতুতে কর্ণফুলি নদীতে পতিত হওয়া খালসমূহের সংযোগস্থলের পানি এবং তাদের তলদেশের উপরিভাগের তলানীর মধ্যে উপস্থিত ভারী ধাতুসমূহের ঘনত্বের পার্থক্য নির্ধারণ এবং স্থানীয় জনগণের উপর এর স্বাস্থ্য ঝুঁকি মূল্যায়ন করা। উপরন্তু, নমুনা সংগ্রহের স্থানসমূহে পরিবেশগত ভার বুঝার জন্য উপরিতলের পানির কিছু গুরুত্বপূর্ণ ভৌত-রাসায়নিক নিয়ামক পরিমাপ করা হয়েছিল। যে খালগুলোর মাধ্যমে দুই পাড়ের পানি প্রাকৃতিকভাবে কর্ণফুলি নদীতে নিষ্কাশিত হয় সেগুলোর প্রধান দশটিকে এ গবেষণাকার্যের জন্য নির্বাচন করা হয়েছিল; যেগুলোর মধ্যে ছয়টি চট্টগ্রাম শহর পার্শ্ব থেকে এবং চারটি ছিল তার বিপরীত তীর এলাকা থেকে। ফ্লেম এটোমিক অ্যাবসর্বশন স্পেকট্রসকপি (FAAS) এর মাধ্যমে বর্ষা ও শুষ্ক মৌসুমে পানি এবং তলানির নমুনাসমূহে আটটি ভারী ধাতু, যেমন Cu, Cr, Cd, Pb, Ni, Mn, As এবং Zn এর ঘনত্ব নির্নয় করা হয়েছিল। পাশাপাশি, সংগৃহীত পানির নমুনাসমূহের কিছু গুরুত্বপূর্ণ ভৌত-রাসায়নিক নিয়ামক, যেমন তাপমাত্রা, pH, DO, BOD, COD, TDS, EC, লবনাক্ততা ও খরত্ব প্রযোজ্য ক্ষেত্রে বহনযোগ্য মাল্টি-এনালাইজার এবং আদর্শ পদ্ধতি অনুসরণ করে পরিমাপ করা হয়েছিল। বেশ কিছু লোকেশনে কয়েকটি নিয়ামকের মান WHO কর্তৃক নির্ধারিত সীমার উর্ধ্বে ছিল, বিশেষ করে শুষ্ক মৌসুমে এ প্রবনতা পরিলক্ষিত হয়েছে। বর্ষা মৌসুমের তুলনায় শুষ্ক মৌসুমে পানির তাপমাত্রা ব্যতীত অন্যান্য নিয়ামকের মান যথেষ্ট পরিমাণে বেশী ছিল। বর্ষা মৌসুমে পানির উপরিতলস্থ নমুনাসমূহে পরিমাপকৃত Cu, Cr, Cd, Pb, Ni, Mn, As এবং Zn এর গড় ঘনত্ব ছিল যথাক্রমে ৫৭.৪৮ ± ৭.০৭, ৫২.৭৯ ± ৫.৬৩, ১৪.৯৪ ± ৩.১৫, ৫২.১৫ ± ৫.৪১, ৩৪.৩৪ ± ৩.৮৯, ৬৪.৯০ ± ১০.৩১, ৯.৪০ ± ১.৫৫ এবং ৬০.৩৭ ± ৬.৭৭ μg/L, আবার শুষ্ক মৌসুমে ঐসকল ধাতুর গড় মান ছিল, যথাক্রমে ৬৫.২৪ ± ৯.৪০, ৬২.৫০ ± ৬.৫২, ২২.২০ ± ৪.৪১, ৭২.২৪ ± ৯.১৪, ৩৮.২৮ ± ৫.৩৪, ৬৯.৯০ ± ১১.১৩, ১৫.০৩ ± ৩.৫৩ এবং ৭৫.০৩ ± ৯.৭৮ μg/L। পানির নমুনাসমূহের সংগ্রহস্থল থেকে সংগৃহীত তলানীর নমুনাসমূহে উল্লিখিত ভারী ধাতুসমূহের গড় ঘনত্ব ছিল যথাক্রমে ৩৮.৮৪ ± ৩.৫০, ৪৬.৯২ ± ৩.৮৪, ২.১৮ ± ০.৪২, ৪২.৯৮ ± ৩.৯৭, ৪৩.৩৯ ± ৩.৫৫, ১.৩৪ ± ০.১৯ এবং ৯১.৯৩ ± ৭.৭২ mg/Kg, যেখানে শুষ্ক মৌসুমে এ সকল মান যথাক্রমে ৫১.১৩ ± ২.৮৮, ৫৯.২৩ ± ১.৬৫, ২.৫২ ± ০.১৪, ৬১.০৫ ± ৪.০৯, ৪৯.৬৬ ± ৫.৭০, ৫৮.৫৫ ± ৮.১১২, ২১ ± ০.৭৪ এবং ১০৪.৪৪ ± ৫.০২ mg/Kg ছিল। উভয় মৌসুমে তলানী নমুনাসমূহে Cu, Cr, Cd, Pb এবং Ni এর গড় ঘনত্ব USEPA, 2019 এ উল্লেখিত নির্ধারিত সীমার চেয়ে বেশী পরিলক্ষিত হয়েছে। এ গবেষণায় আরো দেখা গেছে যে, প্রায় সকল নমুনা স্থানে বর্ষা মৌসুমের

তুলনায় শুষ্ক মৌসুমে পানি এবং তলানী নমুনাসমূহে মূল্যায়িত ভারী ধাতুসমূহের ঘনত্ব লক্ষণীয়ভাবে বেশী ছিল।

হিসাবকৃত মেটাল পল্যুশন ইনডেক্স (MPI) উভয় মৌসুমে মূল্যায়নকৃত খালসমূহের পানির প্রবল দূষণ নির্দেশ করে। সারাজীবন ধরে ত্বকে সংস্পর্শের মাধ্যমে এ পানির কার্সিনোজেনিক এবং নন- কার্সিনোজেনিক ঝুঁকি USEPA কর্তৃক নির্ধারিত গ্রহণযোগ্য সীমার মধ্যে রয়েছে। তলানীর নমুনাসমূহে উপস্থিত ভারী ধাতুসমূহের ক্ষেত্রে হিসাবকৃত অধিকাংশ পরিবেশগত সূচক, যেমন এনরিচমেন্ট ফ্যাক্টর (EF), ডিগ্রি অব কন্টামিনেশন (C_d), পল্যুশন লোড ইনডেক্স (PLI), জিওঅ্যাক্যুমুলেশন ইনডেক্স (I_{geo}), পটেনশিয়াল ইকোলজিক্যাল ইনডেক্স (PERI) এবং নেমেরো পল্যুশন ইনডেক্স (P_N) গুলো পরিবেশগত ঝুকি দেখায়নি বা কম ঝুকি দেখিয়েছে; যদিও কন্টামিনেশন ফ্যাক্টর (CF) এবং মোডিফায়েড কন্টামিনেশন ডিগ্রি (mC_d) নির্দেশ করে যে, মূল্যায়নকৃত খালসমূহের তলানী ঐ সকল ভারী ধাতু দ্বারা যথাক্রমে মাঝারি এবং অত্যন্ত দূষিত। গবেষণাটির ফলাফল দেখিয়েছে যে, পরীক্ষাধীন খালসমুহের পানির ভৌত-রাসায়নিক নিয়ামক, এবং পানি ও তাদের তলদেশের উপরিভাগের তলানীতে উপস্থিত ভারী ধাতুর পরিমাণ মৌসুমী পানি প্রবাহ দ্বারা প্রভাবিত। অধিকন্তু, মূল্যায়নকৃত খালসমুহের একটি থেকে অন্যটিতে ভারী ধাতুর পরিমাণের মধ্যে তারতম্য পাওয়া গেছে এবং যা ছিল শহর এলাকার বর্জ্য বহনকারী খালসমুহের তুলনায় কল-কারখানার বর্জ্য বহনকারী খালসমুহের ক্ষেত্রে যথেষ্ট পরিমাণে বেশী। এ গবেষণায় মূল্যায়নাধীন খালসমূহের পানির ভৌত-রাসায়নিক নিয়ামক, এবং পানি ও খালসমূহের তলানীতে উপস্থিত ভারী ধাতুর পরিমাণ সংক্রান্ত প্রাপ্ত ফলাফল কর্ণফুলী নদীর পরিবেশগত ঝুঁকি হ্রাস করতে সংশ্লিষ্ট নীতি নির্ধারকদেরকে পর্যবেক্ষণ, নিয়ন্ত্রণ ও সুরক্ষা বিষয়ক আইন প্রনয়ণে সহায়ক হবে।

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List of Abbreviations of Technical Symbols and Terms

AAS	Atomic Absorption Spectrophotometer
AEDE	Annual Effective Dose Equivalent
ATP	Adenosine Triphosphate
APHA	American Public Health Association
ATSDR	Agency for Toxic Substances and Disease Registry
BCSIR	Bangladesh Council of Scientific and Industrial Research
CCCB	Commercial Capital City of Bangladesh
CDI_{derm}	Chronic daily intake via dermal contact
CF	Contamination Factor
CMC	Criteria of maximum concentration
CRM	Certified reference materials
DoE	Department of Environment
DPHE	Department of Public Health Engineering
ECR	Environment Conservation Rules
EF	Enrichment Factor
ε_f	Efficiency
ERL	Effects Range Low
ERM	Effects Range Median
EPA	Environmental Protection Agency
H_{ext}	External Hazard Index
HI_{derm}	Hazard Index via dermal contact
HQ_{derm}	Hazard quotient via dermal contact
IAEA	International Atomic Energy Agency
ICRP	International Commission on Radiological Protection
IPCS	International Programme on Chemical Safety
I_{geo}	Geoaccumulation Index
MAC	Maximum allowable concentration
mg/L	milligrams per liter
mg/Kg	miligrams per Kilogram
MPI	Metal pollution index

μS/cm	Microsiemens per Centimeter
μg/L	Microgram per Liter
NOAA	National Oceanic and Atmospheric Administration
NCRP	National Council on Radiation Protection
NIST	National Institute of Standards and Technology
NYSDEC	New York State Department of Environmental Conservation
PCA	Personal Computer analyzer
PLI	Pollution Load Index
PERI	Potential Ecological Risk Index
$PI_{Nemerow}$	Nemerow Pollution Index
Ppt	Parts per thousand
Ppm	Parts per million
Ppb	Parts per billion
SF	Slope Factor
SQGs	Sediment Quality Guidelines
UNSCEAR	United Nations Scientific Committee on the Effects of Atomic Radiation
USGS	United States Geological Survey
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

Chapter 1: INTRODUCTION

1.1 Background

Chattogram is the second largest city, Prime Sea Port, and the heart of all commercial and business activities in Bangladesh. That's why Chattogram is called the commercial capital city of Bangladesh (CCCB, 2018). Chattogram is located on the bank of Karnaphuli river which originates in the Lushai highlands of Mizoram, is the largest and most important river in Chattogram and the Chattogram hill tracts (Uddin et al., 2019). All import and export activities are performed based on the port of Chattogram. This river port is known as the lifeline of the economic activities of the country due to its increasing trade demand. It is a matter of great concern that this lifeline river of Chattogram is affected severely by many ways. A number of mills, factories, and industries are situated both side on the bank of the Karnaphuli river. All wastes from these mills, factories, and industries are drained into the Karnaphuli river and continuously deposited on its bottom layer. There are also some local shipbreaking yards at the river site.

The origin of riverine contamination in Chattogram is attributed not only to industrial discharges but also to the influx of municipal and domestic waste transported through the city's extensive sewage and drainage infrastructure. The continuous input of these anthropogenic pollutants contributes significantly to seasonal variations in water quality. Within aquatic ecosystems, sediments serve as fundamental repositories for nutrients and contaminants. Seasonal discrepancies in pollution levels are more pronounced during the winter months compared to the summer, largely due to alterations in hydrodynamic conditions, sediment transport mechanisms, local geomorphological transformations, and

physicochemical properties of sediments. These factors collectively exert greater influence during the dry season, amplifying pollutant retention and distribution. The higher the exchange capacity of the sediment, the greater sediment pollution is the river.

Riverbed sediments contain toxic heavy metals in multiple physicochemical states, including dissolved ions, colloidal suspensions, particulate matter, and forms bound to sediment particles (Weiner, 2008). The mobility and distribution of these metals in aquatic systems are governed by various geochemical interactions such as adsorption, precipitation, and dissolution (Abdel & Elchaghaby, 2007). These processes significantly influence the metals' ecological availability and potential uptake by aquatic biota (Nouri et al., 2011). After long periods of deposition, heavy metals are mixed with river precipitate to sediment via various mechanisms such as sedimentation, complexation, and adsorption of clay particles, and accumulate in high concentrations in the food chain (Sinha and Paul, 2014). Heavy metal concentrations in sediments are typically higher than the concentrations in water. Furthermore, heavy metal deposition in sediment may be re-enriched into the water column through resuspension, desorption, oxidation, or reduction processes, making it more hazardous to the aquatic environment and human health (Dong et al., 2012; Zhao et al., 2013). When high concentrations of these metals accumulate in sediments, they pose a threat to both the aquatic ecosystem and human health (Islam et al., 2015b; Ahmed et al., 2015). As a result, determining heavy metal concentrations in the sediments is a useful method for assessing anthropogenic and industrial impacts, as well as the risks posed by wastewater and waste discharges in rivers (Saleem et al., 2015).

1.2 Present State of the Problem

The Karnaphuli River plays a significant ecological and hydrological importance, as it strongly affects both water quality and sediment composition within the

region. In recent years, the condition of the estuarine environment has been declining rapidly, primarily due to intensified industrial operations, expanding urban infrastructure, and increased human-induced pressures (Wang et al., 2014; Jiang-Qi et al., 2013). Fluctuations in the river's chemical profile and sediment dynamics are largely attributed to the ongoing input of various pollutants, which interact with natural biogeochemical cycles and sedimentary processes (Singare et al., 2011). The quality of sediments and water in the river estuary is polluted by seasonal deposition of pollutants and river fluctuations. Various natural forces—including wave dynamics, tidal movements, water flow, salinity variations, rainfall, and diffusion—facilitate the transfer of detrital materials into the river's water column and underlying sediments (Jorcin, 2000). Additionally, sediment input into the Karnaphuli River is influenced by factors such as ground subsidence, surface erosion, organic matter decay, and the transport of particulate matter by both wind and surface runoff. Suspended and dissolved materials formed a reservoir for pollutants and toxic heavy metals at the bottom of the water column. (Ahmed and Reazuddin et al., 2000) reported that the presence of heavy metals in river sediments have a direct impact on fish physiology, which may enter human body through ingestion/food chain. The availability of fish is rapidly decreasing as pollution levels rise. The health status of fishing communities is severely affected, resulting in significant socioeconomic challenges (Rashid et al., 2012). In Chattogram, wastewater from multiple sources including the Nasirabad industrial area, chemical, leather, textile, and steel re-rolling industries is discharged into the city's surface drainage network, which ultimately drains into the Karnaphuli River. Most of these industrial facilities are concentrated in the Kalurghat region, where several fertilizer manufacturing plants also release their effluents into drainage canals that flow into the river. This impacts on the drinking water supply in Chattogram by contaminating water at the Mohara water treatment plant's intake zone (BKH, 1995).

Sediments become contaminated by heavy metals and hazardous substances through sources like wastewater discharge, vehicle emissions, runoff, brick kiln activities, and leachates from urban and agricultural areas (Ahmad et al., 2010; Chen et al., 2012). To evaluate their environmental impact, indices such as CF, EF, Igeo, PLI, and PERI are used, considering metal concentration, bioavailability, and toxicity (Yao et al., 2009; Yu et al., 2011). Heavy metal contamination in sediments is assessed using indices like enrichment factor, geoaccumulation index, contamination factor, pollution load index, and ecological risk index (Hou et al., 2014; Zhang et al., 2011; Islam et al., 2018; Yang et al., 2009; Huang et al., 2013). Bangladesh faces increasing heavy metal pollution in aquatic environments, posing health risks. The aim of this study is to estimate the levels of heavy metals in surface sediments in two different seasons to assess the pollution state of the Karnaphuli river estuary's selected khals. The outcomes of the present research are to estimate the risk of pollution caused by seasonal heavy metals in sediments of selected canals that flow into the Karnaphuli river, as well as to establish a comprehensive baseline data set that will help the government establish effective legislation for regular aquatic monitoring. Statistical model was developed to assess the distribution of heavy metals in surface sediments during summer and winter seasons. The findings of this study will also be beneficial to future researchers.

1.3 Aim of the Present Study

The aim of the present study is to assess the pollution status of the selected khals of Karnaphuli river estuary by estimating the levels of heavy metals in water and surface sediments in two different seasons.

1.4 Objectives of the Present Study

The overall objectives of the present study were to assess the water quality in terms of physicochemical properties and heavy metals contamination in water

and surface sediments at the estuaries of selected khals feeding to Karnaphuli river.

1.4.1 Specific Objectives

The major objectives of the present study were -

i. to evaluate the physicochemical properties of surface water at the estuaries of some selected khals feeding the Karnaphuli river in two different seasons.

ii. to assess the seasonal heavy metals contamination and its spatial distribution in surface water and sediments at the estuaries of the selected khals feeding the river Karnaphuli.

iii. to estimate the different pollution indices for assessing the ecological and health risk due to the water and sediments contamination in comparison with the recommended water quality guidelines.

1.5 Relevance and Justification

The Karnaphuli River is the primary waterway in Chattogram, Bangladesh, navigable to Rangamati and essential for transporting cotton and timber. An upstream hydroelectric project supplies power to key industries and supports irrigation over extensive farmland (Britannica, 2008). Furthermore, the river is the major source of fishes of the habitats living on the Karnaphuli riverbank area.

River water, sediments and biota are the three major reservoirs of heavy metals in the aquatic environment. Water and sediments quality determine the health of an aquatic ecosystem. Karnaphuli river estuary, flowing through Chattogram city receives a huge amount of domestic and industrial wastes and sewages (Islam et al., 2017). Monitoring the environmental status of Karnaphuli river and its tributaries is very important for their ecological and economical services provided to city areas (Islam et al., 2017). After considering all perspectives it has

been designed to conduct the research on the assessment of seasonal heavy metal pollution at the estuaries of some selected khals feeding the Karnaphuli river.

The results of the present study will give an indication on the extent of heavy metal contamination in the Karnafuli River. Recommendations for improvement would be made based on the results. Results of this research may also unearth new ideas concerning heavy metals from river water and sediments and may trigger other related research in years to come. The results will also contribute to preserve the environment and its natural resources like fishes, water, grasslands, vegetation, and animals for future generations.

1.6 Thesis Outline

This thesis report is comprised with five chapters.

Chapter 1 contains the introduction, research gap, aims and objectives and outcomes of the study.

Chapter 2 reviews background literature relating the present research work.

Chapter 3 describes the sampling locations, instrumental analytical procedures and mathematical formulas used in different calculations.

Chapter 4 presents the results obtained and relevant discussion.

Chapter 5 concludes the present research work and gives hints about the future work in the relevant topic that can be carried out.

The references and data sheets as indices appeared at the end of this report.

Chapter 2: LITERATURE REVIEW

2.1 River System in Bangladesh

Bangladesh is located in the deltaic or low-lying region, where it is formed by the confluence of three powerful river systems: the Ganga-Padma, the Brahmaputra-Jamuna, and the Barak-Meghna. This unique geographical area comprises about 8% of the country's land, and it is distinguished by the presence of perennial streams, beals, and estuaries (Paul & Haq, 2010). Bangladesh's river network includes numerous waterways, with 56 rivers originating outside the country, notably the Ganges, Brahmaputra, and Meghna. The rest mainly consist of tributaries that flow into larger and medium-sized river systems. Rivers in Bangladesh are typically grouped into major rivers such as the Ganges-Padma, Brahmaputra-Jamuna, and Barak-Meghna and smaller rivers, including border tributaries and distributaries (Paul & Haq, 2010). The river Karnaphuli is the largest and a significant river in the regions of Chittagong and the Chittagong Hill Tracts. It originates from the South Lushai Hills, a tall range of hills in Assam, India, situated at Latitude 23° 53' N and Longitude 92° 27' E. The Karnaphuli river enters the Chittagong region, flowing from the west and southwest, and ultimately empties into the Bay of Bengal at Patenga, with its coordinates being 22° 14' N and 91° 47' E (Sarwar et al., 2010). The river flows past the city of Chittagong on its right bank, approximately 16 km away from the river's outlet. Before reaching its destination, it traverses through mountainous wilderness, forming a narrow loop at Rangamati and then following a winding path, which includes two notable loops, the Dhuliachhari and the Kaptai. Just before entering the Kaptai loop, there is a hydroelectric dam.

2.2 Pollution in Karnaphuli River

The Karnaphuli estuary plays a significant role in various aspects, such as facilitating navigation, transportation, fishing, docking facilities, and industrial usage of river water (Siddique and Akter, 2012) Furthermore, it is employed for port operations, fishing, and industrial applications, particularly for cooling and processing needs (Sarkar, 1998). However, pollution levels in the Karnaphuli river Estuary are steadily rising and exceeding safe thresholds, negatively impacting coastal fisheries and the local population (Forkan, 2003). Water pollution arises when external substances, whether of natural or other origins, combine with water, leading to the pollution of water sources. This pollution can be harmful to living organisms due to its toxic nature and its impact on reducing the normal oxygen levels in water. Additionally, it can have undesirable aesthetic effects and contribute to the proliferation of epidemic diseases. (Pandey,1997). Numerous canals, tributaries, and small rivers flow into this river, significantly influencing the hydrobiology of the Karnaphuli river by introducing a substantial volume of polluted water, solid waste, and sewage (Hossain et al., 2006). Despite being a modern facility with appropriate waste management systems, (Hossain et al., 1992) noted that the Karnaphuli estuary is still experiencing pollution from the discharge of its effluents. Approximately 800 industrial establishments are situated along or in close proximity to the Karnaphuli river's banks within various industrial zones, including Kalurghat, Nasirabad, Sagarika, and Anawara. This includes facilities like an oil refinery, oil company depots, and ship-breaking activities (ADB, 2004). It is clear that significant quantities of harmful pollutants in the rivers and the Bay of Bengal pose a threat to aquatic ecosystems, especially fish populations. Numerous instances of specific yet severe environmental issues, such as fish die-offs, have been documented by the Department of Environment (DoE), various institutions, and local fishermen (Bhouyain, 1983).

2.3 Physicochemical Parameters of River Water

2.3.1 Dissolved Oxygen (DO)

Dissolved oxygen (DO) is a vital indicator for assessing surface water health, reflecting the oxygen available to aquatic organisms (Abdul Aziz & Ishtiaq, 2014; Harvey et al., 2011). Oxygen levels in water result from inputs like atmospheric exchange and photosynthesis and are reduced by respiration and organic matter decay (Best et al., 2007). DO concentrations typically decrease with rising temperature and salinity (Varanka, 2016). It also plays a key role in nutrient cycling and can influence the release of phosphorus from sediments under low-oxygen conditions, thereby impacting water quality in rivers and streams (Harris et al., 2015; Spears et al., 2007). Sarwar et al. (2010) reported DO levels below Bangladesh's environmental standards (DoE, 1997).

2.3.2 Biochemical Oxygen Demand (BOD)

The Biochemical Oxygen Demand (BOD) stands as a frequently employed standard for assessing water quality, furnishing information on the readily biodegradable portion of the organic load in water (Jouanneau et al., 2014). The BOD test measures the dissolved oxygen consumed by aerobic biological organisms in a water sample to decompose organic material at a designated temperature over a specified duration, typically requiring a five-day incubation period (BOD_5) at 20°C. BOD_5 at 20°C serves as a reliable proxy for assessing the extent of organic water pollution. Oxygen plays a crucial role in sustaining aquatic life and plants in rivers. In the absence of freely dissolved oxygen, rivers and lakes become inhospitable for most aquatic organisms. Consequently, organic pollutants that rely on oxygen for decomposition can have the most immediate and impactful effects on the ecology of these environments (Lee et al., 1999). BOD originates from sources such as sediments, plant debris, animal waste, industrial discharges, wastewater treatment plants, agricultural

operations, malfunctioning septic systems, and urban runoff. Factors affecting dissolved oxygen also influence BOD. The measurement compares initial dissolved oxygen levels to those after five days. Sarwar et al. (2010) found BOD values above the Bangladesh standard (DoE, 1997)

.2.3.3 Chemical Oxygen Demand (COD)

COD is a measure employed to evaluate the contamination levels in both surface and groundwater (Khan et al., 2015). COD represents the oxygen demand required by dissolved substances, commonly utilized to characterize the concentration of organic matter. It serves as a crucial parameter in assessing water quality, indicating the depletion of dissolved oxygen. Elevated COD values lead to a substantial reduction in dissolved oxygen content, posing a threat to aquatic life. Traditional methods for COD evaluation, however, involve the time-intensive procedure of refluxing samples to achieve thorough oxidation (Lee et al., 1999). BOD emerges as a pivotal factor influencing COD levels. The interdependence of COD and BOD is evident, involving a chemical oxidation and reaction process triggered by microorganisms breaking down organic matter into a more stable state. Consequently, heightened microbial growth results in increased oxygen consumption, leading to reduced dissolved oxygen levels and an elevated BOD. A higher COD values than Bangladesh standard (DoE, 1997) was reported in a study (Sarwar et al., 2010).

2.3.4 Total Dissolved Solids (TDS)

Total dissolved solids (TDS) consist of substances fully dissolved in water, measured as residue after evaporation of filtered samples. TDS correlates closely with electrical conductivity, allowing one to be estimated from the other (Mosin, 2013). Elevated TDS levels reflect increased salts and minerals, often causing poor taste (Mohsin et al., 2013). Typically, TDS in mg/L is about half the electrical conductivity in μS/cm (Stone et al., 2013; Mosimanegape, 2016). Sarwar et al.

(2010) found TDS values exceeding Bangladesh's environmental standards (DoE, 1997).

2.3.5 pH

The pH level of water reflects the concentration of hydrogen ions, determining whether a solution is acidic, neutral, or alkaline, with 7 as the neutral midpoint on a scale of 0 to 14 (Mosimanegape, 2016). WHO (1986) reported that prolonged exposure to solutions with pH values between 10 and 12.5 may result in gastrointestinal irritation and swelling of hair strands (Taruna & Alankarita, 2013). In chemical terms, pH is defined as the negative logarithm of hydrogen ion activity in a solution (Varanka, 2016; Wetzel, 2001). In low pH environments (1–6), surface waters are typically rich in carbonic acid and dissolved carbon dioxide, while higher pH conditions (8–14) are associated with elevated concentrations of bicarbonates and carbonates (Allan & Castillo, 2007). Although some degree of acidity may occur naturally, anthropogenic inputs can significantly contribute to the acidification of surface waters (Falkenmark et al., 2003). Like nutrient analysis, pH assessment is a key component in evaluating the ecological health of freshwater systems (Toivonen et al., 2013). In a previous investigation, Sarwar et al. (2010) reported that the pH of the Karnaphuli River fell within the range recommended by the Department of Environment, Bangladesh (DoE, 1997).

2.3.6 Electrical Conductivity (EC)

Generally, electrical conductivity (EC) assesses a solution's ionic activity, allowing it to conduct current (Mohsin et al., 2013). Electrical conductivity (EC) is widely used as a proxy for estimating the presence of dissolved ionic substances in water (Anhwange et al., 2012; Mohsin et al., 2013; Mosimanegape, 2016). In general, an increase in ionic concentration results in elevated EC values. In a previous study, Sarwar et al. (2010) observed EC levels exceeding the

national standards outlined by the Department of Environment, Bangladesh (DoE, 1997).

2.3.7 Salinity

Saline water intrusion poses a frequent risk to freshwater reservoirs such as aquifers. Additionally, the elevated levels of salt and minerals in saline water can adversely affect various animal and plant species (Thompson, 2014). The coastal areas of Bangladesh are expected to experience frequent cyclones and storm surges due to the significant elevation in astronomical tides and rising sea levels (Seal & Baten, 2012). Research indicates that a sea level rise of 88 cm results in a 5 parts per thousand (ppt) increase in saline water intrusion, reaching 40 km inland from the Tetulia freshwater river in the Meghna estuary (Shamsuddoha & Chowdhury, 2007). The heightened pressure exerted by saline water on the freshwater region reduces the accessibility of fresh water in the coastal zone. This leads to the consumption of contaminated water, resulting in waterborne illnesses like cholera and diarrhea among the population. Additionally, the scarcity of fresh water contributes to an increase in malnutrition problems, as food production declines (Sarwar, 2005).

2.3.8 Total Hardness

Total hardness in surface waters represents the combined concentration of divalent metal ions, primarily calcium (Ca^{2+}) and magnesium (Mg^{2+}), present in dissolved form (Gajendran, 2011). Temporary hardness is attributed to bicarbonates and carbonates of calcium and magnesium, while permanent hardness is influenced by sulphates, chlorides, and other anions (Aher & Deshpande, 2011; Uchchariya & Saksena, 2012). The sources of these ions include diverse rock formations, runoff from agricultural lands, discharges from industrial activities, and sewage inputs (Gupta et al., 2009). Additionally, hardness in surface waters arises from the breakdown of carbon dioxide by soil

microorganisms, which then dissolves in percolating rainwater to release carbonates (Gajendran, 2011).

2.3.9 Temperature

Temperature is a critical and highly responsive parameter shaping the physical, chemical, and biological dynamics of riverine ecosystems (Hannah et al., 2008). Fluctuations in thermal conditions influence fish species by altering their habitat distribution (Heinle et al., 2020), growth patterns (Coulter et al., 2016), and breeding activities (Tornabene et al., 2020). The future is expected to bring elevated stream temperatures due to anticipated rises in air temperatures (Vliet et al., 2011). This escalation could have adverse effects on stream ecosystems, including the deterioration of fish habitats and an increased probability of algal blooms (Benyahya et al., 2007). Many watershed management strategies and regulatory standards prioritize the preservation of Temperature as a fundamental goal (Liu et al., 2017). Sarwar et al. (2010) found T°C values in between the Bangladesh standard (DoE, 1997).

2.4 Sources and Uses of Heavy Metals

Heavy metals are elemental metals naturally present in the Earth's crust, characterized by high atomic mass and densities generally above 5 g/cm^3 (Jaishankar et al., 2014; Tchounwou et al., 2012). These elements are dispersed widely across environmental compartments including surface water, sediments, soil, vegetation, aquatic organisms, and humans. While certain metals like iron and zinc are essential micronutrients integral to biological functions (Sukdeo, 2010; Jaishankar et al., 2014), their accumulation beyond natural background concentrations poses significant ecological and health risks (Moodley et al., 2014).

In aquatic ecosystems, heavy metals occur in multiple chemical species—such as dissolved ions, particulate matter, or those adsorbed to sediment and organic

matrices—which influence their transport dynamics, bioavailability, and toxicity (de Souza Machado et al., 2016). The comprehensive quantification of heavy metals generally involves acid digestion to release metals embedded within mineral lattices or bound to sediment particles and organic substances (Guéguen & Dominik, 2003; Namieśnik & Rabajczyk, 2010). The fraction deemed bioavailable represents those metals accessible for uptake by organisms, capable of bioaccumulation and biomagnification through trophic levels. Due to their non-biodegradable nature, heavy metals can persist in aquatic environments for extended periods, even after cessation of pollutant inputs (Javed & Usmani, 2017).

Sources of heavy metals include both natural geochemical processes and anthropogenic activities. Naturally, weathering of rocks, volcanic eruptions, and magmatic differentiation release these metals into soil and water systems (Ali et al., 2019; Bradl, 2005). Human-induced inputs predominantly derive from mining, manufacturing, urban runoff, and agricultural practices (Wuana & Okieimen, 2011). Industrial emissions discharge metals through effluents and atmospheric fallout, while urban contributions emerge from vehicle exhaust, residential waste, and landfill leachates (Chen et al., 2005; Ferreira et al., 2016; Brand et al., 2018). Agricultural applications of fertilizers and pesticides also introduce heavy metals into soils, which can be mobilized into aquatic ecosystems via surface runoff (Wuana & Okieimen, 2011).

The toxicological profiles of heavy metals vary widely. Metals such as vanadium, chromium, manganese, iron, and nickel are essential at trace levels but can induce toxicity upon bioaccumulation (Hogan, 2010). Conversely, several metals heavier than rare earth elements, typically non-essential for biological processes, exhibit significant toxicity even at minimal concentrations, resulting in long-term environmental and health concerns (Hogan, 2010).

Mining and industrial activities often elevate heavy metal concentrations in estuarine and coastal sediments well above natural background levels, leading to marked ecological hazards (Binnig, 2001). Seasonal fluctuations in metal concentrations are frequently documented, with elevated levels generally observed during dry periods such as winter, influenced by hydrological cycles and anthropogenic discharges (Dey et al., 2015).

2.5 Heavy Metal Pollution of River Water and Sediments

Heavy metal concentrations in estuaries and marine sediments are notably high due to the preferential shift of heavy metals from the dissolved to the particulate phase. Consequently, concentrations in sediments are frequently many orders of magnitude higher than those in the overlying water. The presence of high and potentially hazardous heavy metal concentrations in sediments is concerning because they can settle and accumulate there. In regions where conditions favor bioavailability, even a small fraction of sediment-bound metals taken up by organisms can have significant toxicological effects. Furthermore, elevated metal levels in pore water within sediments can greatly impact sediment toxicity. The disappearance of sensitive species or the emergence of resistance mechanisms, such as effective excretory mechanisms in organisms, in response to metal-polluted sediments can serve as indicators of the harmful consequences. According to Binning and Baird (2001), many of these metals have no recognized biological role in the marine environment, but their interactions with other chemical species can render them more hazardous. Heavy metals are naturally occurring substances in the environment, but the rapid expansion of human activities has led to their levels exceeding natural concentrations, resulting in severe consequences for living organisms, as noted by Cheung et al. (2003). Heavy metals pose a threat to living organisms because they persist in the

environment and tend to accumulate within organisms over time, according to Verma and Dwivedi (2013).

Trace elements are elements that occur naturally in low concentrations, typically ranging from parts per billion (ppb) to less than 10 parts per million (ppm) in various environments, as explained by Tchounwou et al. (2012). These trace elements are crucial for life processes, and both plants and animals have various mechanisms for accumulating sufficient quantities of trace elements from their surroundings, as described by Mann et al. (2011). Even though heavy metals can be found in trace amounts, they are still toxic, even at low concentrations, because of their tendency to bioaccumulate in biological organisms over time (Sukdeo, 2010). This is possible due to their ability to be transported by various environmental media, enabling them to bioaccumulate and biomagnify in aquatic organisms and food webs (Sukdeo, 2010). As Verma and Dwivedi (2013) outline, bioaccumulation refers to the gradual buildup of elements in biological organisms over time, leading to higher concentrations within the organism compared to the element's concentration in the environment. These elements accumulate in living organisms through ingestion from their surroundings and are retained more rapidly than they are broken down or excreted (Verma and Dwivedi, 2013). Bioaccumulation of elements is influenced by the chemical availability of elements in the environment and the organism's capacity to ingest and excrete those (Mann et al., 2011).

Biomagnification, as described by Mann et al. (2011), is the process by which pollutants are transferred to organisms through the food they consume, resulting in higher concentrations within the consumer compared to the source. Biomagnification occurs along food chains, with pollutant levels increasing as they move up various trophic levels (Sukdeo, 2010). This is because successive trophic levels consume larger quantities of contaminated food, leading to the higher-order consumers receiving greater amounts of the pollutant (Sukdeo,

2010). The following explains the origins of heavy metals and how their increased presence impacts the well-being of aquatic organisms:

2.6 Effects of Heavy Metal Contamination of River Water and Sediments

Heavy metals tend to concentrate in estuarine and marine sediments due to their tendency to transition from dissolved forms in water to particulate matter that settles on the seabed. This process causes sediment metal concentrations to be significantly higher than those in the surrounding water column. The persistence and accumulation of these metals in sediments pose ecological risks, especially in conditions that enhance their bioavailability to aquatic organisms, where even minor uptake may result in toxic effects. Moreover, elevated levels of metals in sediment pore waters can further intensify toxicity within benthic habitats. Biological responses such as the loss of vulnerable species or the development of detoxification mechanisms, like enhanced metal excretion, highlight the impact of metal contamination in sediments (Binning & Baird, 2001). While many heavy metals do not serve any biological function in marine environments, their chemical interactions can increase their toxicity. Though naturally occurring, human activities have substantially raised environmental concentrations of these metals, threatening aquatic life (Cheung et al., 2003). Their environmental longevity and tendency to bioaccumulate render heavy metals especially harmful pollutants (Verma & Dwivedi, 2013).

Trace elements exist naturally in very low concentrations, typically measured in parts per billion to low parts per million, and play essential roles in biological functions. Both flora and fauna have evolved mechanisms to absorb necessary amounts from their environment (Tchounwou et al., 2012; Mann et al., 2011). Despite their importance at trace levels, heavy metals can be toxic even in small amounts because of their capacity to build up within organisms over time. These metals are transported through various environmental pathways, enabling their

accumulation and magnification through aquatic food webs (Sukdeo, 2010). Bioaccumulation is the process by which organisms gradually accumulate metals to levels exceeding those in their surroundings, driven by uptake rates surpassing elimination (Verma & Dwivedi, 2013; Mann et al., 2011).

Biomagnification refers to the increase in contaminant concentrations as pollutants ascend the food chain, resulting in top predators harboring higher metal burdens than lower trophic levels, due to the consumption of contaminated prey (Mann et al., 2011; Sukdeo, 2010).

The subsequent discussion focuses on the origins of heavy metals and their impacts on aquatic organisms and ecosystem health.

2.6.1 Copper (Cu)

Copper (Cu) is an element widely distributed across natural environments, occurring in soils, rocks, aquatic systems, air, vegetation, and fauna (Hardy et al., 2008). Its natural release occurs primarily through the weathering and dissolution of copper-containing minerals and native copper sources. Anthropogenic inputs include discharges from wastewater treatment plants, corrosion of copper plumbing infrastructure, use of copper-based agrochemicals such as fungicides and pesticides, and atmospheric deposition originating from mining, metallurgical processes, coal combustion, and steel manufacturing (DWAF, 1996).

Functioning as a vital trace nutrient, copper participates in numerous physiological and biochemical activities within both plant and animal systems (Tchounwou et al., 2012). In aquatic vertebrates like fish, copper is a critical component of enzymes involved in neural function and hemoglobin production (Woody & O'Neal, 2012). Nonetheless, elevated copper concentrations are detrimental, especially to aquatic organisms, where it is recognized as one of the most toxic heavy metals (Woody & O'Neal, 2012).

Copper exists in several oxidation states—0, I, II, and III—with the divalent form Cu(II) being the most toxic to aquatic life (DWAF, 1996). Environmental parameters such as water hardness, dissolved oxygen, and the presence of co-occurring metals influence copper's toxicity, generally increasing under conditions of soft water and low oxygen (DWAF, 1996). Excess copper exposure can lead to compromised immune defenses, altered migratory behavior, respiratory distress, and neurological dysfunction in fish (Woody & O'Neal, 2012). Additionally, copper can inhibit nitrogen fixation by cyanobacteria even at low levels, thereby affecting ecosystem productivity (DWAF, 1996). The Sediment Quality Guidelines established by NOAA (1999) indicate threshold concentrations for copper with an Effects Range Low (ERL) at 34 mg/kg and an Effects Range Median (ERM) at 270 mg/kg.

2.6.2 Chromium (Cr)

Chromium (Cr), commonly found in the Earth's crust and frequently occurring as crocoite (PbCrO4), exists predominantly in trivalent (Cr^{3+}) and hexavalent (Cr^{6+}) forms, with the latter being more soluble and toxic across a wide pH range. The relative abundance of these species in aquatic environments is governed by redox potential and pH, which also modulate their toxicity levels.

Natural sources contribute minor amounts of chromium through weathering of chromium-bearing minerals. However, elevated chromium contamination in water bodies primarily originates from industrial discharges associated with metal finishing, pulp and paper manufacturing, steel welding, chromate production, and related operations. These activities commonly release the more hazardous hexavalent chromium, recognized for its carcinogenic properties.

Chromium adversely affects plant physiology by impairing root development and seed germination. While adult fish exhibit some tolerance, juveniles are more

susceptible to chromium-induced growth inhibition. Invertebrates and algae typically show higher sensitivity to chromium exposure.

According to sediment quality criteria established by NOAA, the threshold effect concentration (Effects Range Low) for chromium is 81 mg/kg, while the median effect concentration (Effects Range Median) is 370 mg/kg. Water quality guidelines recommend maximum allowable dissolved chromium concentrations of 7 μg/L for hexavalent chromium and 12 μg/L for trivalent chromium to safeguard aquatic organisms.

2.6.3 Cadmium (Cd)

Cadmium (Cd) is a heavy metal naturally present in the Earth's crust, with an average concentration near 0.2 mg/kg (DWAF, 1996). It can contaminate drinking water through industrial effluents and by leaching from polyethylene pipes and containers (Fakhri et al., 2014). Major anthropogenic sources include industries involved in alloy production, paints, batteries, plastics manufacturing, and mining operations (Tchounwou et al., 2012). Agricultural activities also contribute to cadmium pollution via the use of fertilizers and pesticides containing Cd, which may enter aquatic systems through surface runoff (DWAF, 1996).

Cadmium strongly adheres to clay particles and organic materials, allowing it to remain in soils and sediments for extended periods, often decades (Estifanos, 2006; Jaishankar et al., 2014). Cd is toxic even at low concentrations, affecting a wide range of organisms (Levit, 2010). Plants absorb cadmium, leading to its accumulation and transfer through food chains, potentially impacting higher trophic levels (Jaishankar et al., 2014). Due to its chemical similarity to zinc, cadmium can replace zinc in enzymes, impairing their activity and causing harmful physiological effects in plants and animals (DWAF, 1996; Jaishankar et al., 2014).

In aquatic environments, cadmium bioaccumulates in macrophytes, plankton, invertebrates, and fish species (DWAF, 1996). In fish, Cd tends to concentrate in organs such as gills, liver, and kidneys, causing toxic effects (Levit, 2010). Exposure to cadmium is associated with iron deficiency, liver disorders, and neurological damage in aquatic fauna (Levit, 2010). The toxicity of cadmium is influenced by its chemical form, which is affected by water conditions including pH, temperature, and the presence of other chemical species (DWAF, 1996).

According to NOAA's Sediment Quality Guidelines (1999), the Effects Range Low (ERL) and Effects Range Median (ERM) values for cadmium in sediments are 1.2 mg/kg and 9.6 mg/kg, respectively, which are used to evaluate ecological risks related to sediment contamination.

2.6.4 Lead (Pb)

Lead (Pb) is naturally present in small amounts in the Earth's crust, primarily from the breakdown of sulfide minerals (Tchounwou et al., 2012; DWAF, 1996). Elevated concentrations are mainly caused by human activities, including mining, burning of fossil fuels, battery and paint production, and discharge from industrial and municipal wastewater (DWAF, 1996; Lee et al., 2019).

Pb occurs in both organic and inorganic forms, with the organic forms being more harmful to aquatic organisms (Kumar et al., 2020). The most common form accumulating in aquatic life is Pb(II) (DWAF, 1996). Acidic conditions (low pH) enhance Pb's bioavailability, negatively impacting aquatic plants by reducing root development, photosynthesis, and seed germination, and causing cellular damage (Nas & Ali, 2018). In aquatic animals, lead accumulation induces oxidative damage and nervous system dysfunction (Lee et al., 2019). Additionally, Pb exposure can cause mucus formation on fish gills, impairing respiration and increasing mortality risk (DWAF, 1996). The toxicity of Pb is influenced by water hardness, which affects its uptake in organisms (DWAF,

1996). According to NOAA's Sediment Quality Guidelines (1999), Pb concentrations above 46.7 mg/kg (ERL) pose ecological concerns, with 218 mg/kg (ERM) indicating more severe effects.

2.6.5 Nickel (Ni)

Nickel (Ni) is a metal that naturally occurs in the environment but usually in small amounts (Wuana & Okieimen, 2011). It mostly appears in the form called nickel (II), which is stable in water with a pH between 5 and 7 (Javed & Usmani, 2017). Nickel is found in soil, plants, and water, with oceans being the largest natural source (Ahmad & Ashraf, 2012). Human activities like mining, electroplating, metal finishing, burning fossil fuels, and power plant emissions increase nickel pollution (Wuana & Okieimen, 2011).

Nickel is important for some plants, especially legumes, because it helps enzymes that process nitrogen (Ahmad & Ashraf, 2012). However, too much nickel can harm plants by slowing their growth, reducing root and shoot size, and lowering seed germination (Ahmad & Ashraf, 2012). In animals, high nickel levels may cause cancer and reduce growth of microorganisms (Wuana & Okieimen, 2011). According to NOAA's guidelines (1999), nickel in sediments above 20.9 mg/kg can start to cause harm, and levels over 51.6 mg/kg are more dangerous.

2.6.6 Manganese (Mn)

Manganese (Mn) is among the most abundant metals in the Earth's crust, commonly found in association with iron. It is crucial for the physiological health of both humans and animals, with small amounts from dietary sources being essential. However, prolonged exposure to higher levels can be harmful, as its toxicity varies based on factors like the route of exposure, chemical form, age, sex, and species. The nervous system is the most affected, and long-term exposure can lead to manganism, a condition marked by symptoms such as

muscle weakness, tremors, a lack of facial expression, and psychological issues (EPA, 2004; Kohl & Medlar, 2007; Calkins, 2009).

Although Mn is naturally found in surface and groundwater and in soils that wash into these sources, human activities greatly contribute to its environmental presence. Significant sources include coal and wood burning, iron and steel production, and power plants. Additionally, industrial waste, landfill leaching, and underground injections introduce manganese into water systems. Potassium permanganate is also used in water treatment to eliminate contaminants like manganese and iron (EPA, 2004; Calkins, 2009). The World Health Organization has established a limit of 0.4 mg/L for Mn in drinking water (Calkins, 2009).

2.6.7 Arsenic (As)

Arsenic (As) is a naturally found metalloid present in the Earth's crust and ranks as the twentieth most common element. It appears in both inorganic and organic forms, with inorganic arsenic being more harmful to living organisms and the environment (Jaishankar et al., 2014). Natural releases of arsenic come from processes like volcanic eruptions and soil weathering, whereas human activities contribute through industrial production, especially in manufacturing agricultural chemicals such as pesticides and herbicides (Tchounwou et al., 2012). Additional sources include mining, metal processing, and the fabrication of glass and ceramics (DWAF, 1996).

In aquatic systems, arsenic predominantly exists in oxidation states III and V, depending on factors like pH and redox conditions (DWAF, 1996; Abbas et al., 2018). Both forms are toxic, with arsenic recognized as a carcinogen affecting plants and animals even at low concentrations. The severity of arsenic's effects varies based on its chemical state, environmental context, and organism susceptibility (Pather, 2014).

Exposure to arsenic can impair the growth and reproductive capacity of fish and invertebrates and disrupt fish migratory behavior. In plants, arsenate (As V) exhibits greater toxicity than arsenite (As III), impeding nutrient absorption, stunting growth, and interfering with ATP production and vital metabolic functions (Finnegan & Chen, 2012; Abbas et al., 2018). Regulatory sediment limits recommend an Effects Range Low (ERL) of 8.2 mg/kg and an Effects Range Median (ERM) of 70 mg/kg for arsenic (NOAA, 1999). For water quality, the maximum allowable concentration of dissolved arsenic is set at 10 μg/L (DWAF, 1996).

2.6.8 Zinc (Zn)

Zinc (Zn) is commonly found in the environment—in the air, soil, water, and food (Hardy et al., 2008). It comes naturally from the breaking down of rocks and minerals (Wuana & Okieimen, 2011). Human activities like mining, burning coal and waste, steel making, and using zinc in fertilizers and pesticides add more zinc to nature (Wuana & Okieimen, 2011).

Zinc is important for plants because it helps them grow, carry out photosynthesis, and fight diseases (Rudani et al., 2018). When plants don't get enough zinc, they don't grow well. Too much zinc, however, can harm their metabolism and roots and reduce photosynthesis in water plants like algae (Rout & Das, 2009; DWAF, 1996).

In animals, zinc is needed for many body processes such as breathing at the cellular level, breaking down proteins and fats, and keeping cells healthy (Akram et al., 2019). Fish with low zinc levels grow slowly, become weaker, lose weight, get cataracts, and have skin and fin damage (Akram et al., 2019). While zinc is necessary in small amounts, high levels are harmful to fish and other water creatures (DWAF, 1996). Zinc builds up in fish and increases as it moves up the food chain, which can harm predators (Wuana & Okieimen, 2011). Zinc can also coat fish gills, making it hard for them to breathe and sometimes causing death

(DWAF, 1996). Lower zinc toxicity can slow shell growth, reduce oxygen use, and hurt young animals' development (DWAF, 1996). The NOAA guidelines say zinc in sediment above 150 mg/kg may start causing problems, and above 410 mg/kg is more dangerous.

Chapter 3: EXPERIMENTAL

3.1 Study Area

There are about 35 feeding khals from Potenga to Kalurghat Bridge along both side Karnaphuli river. Among them ten major khals from Shah Amanat International Airport area to Kalurghat Bridge were selected in this study. The khals were selected based on the flow of water discharge, neighbouring industrial or other polluting activities at their upstream. Various industrial, agricultural, and municipal wastes deposition are the major sources of heavy metal pollution in surface water and sediments. The influx of saline water from the Bay of Bengal significantly influences the river's physicochemical characteristics and contributes to the increased contamination of surface sediments. Figure 3.1 shows the geographical locations of ten selected khals and as well as sampling points.

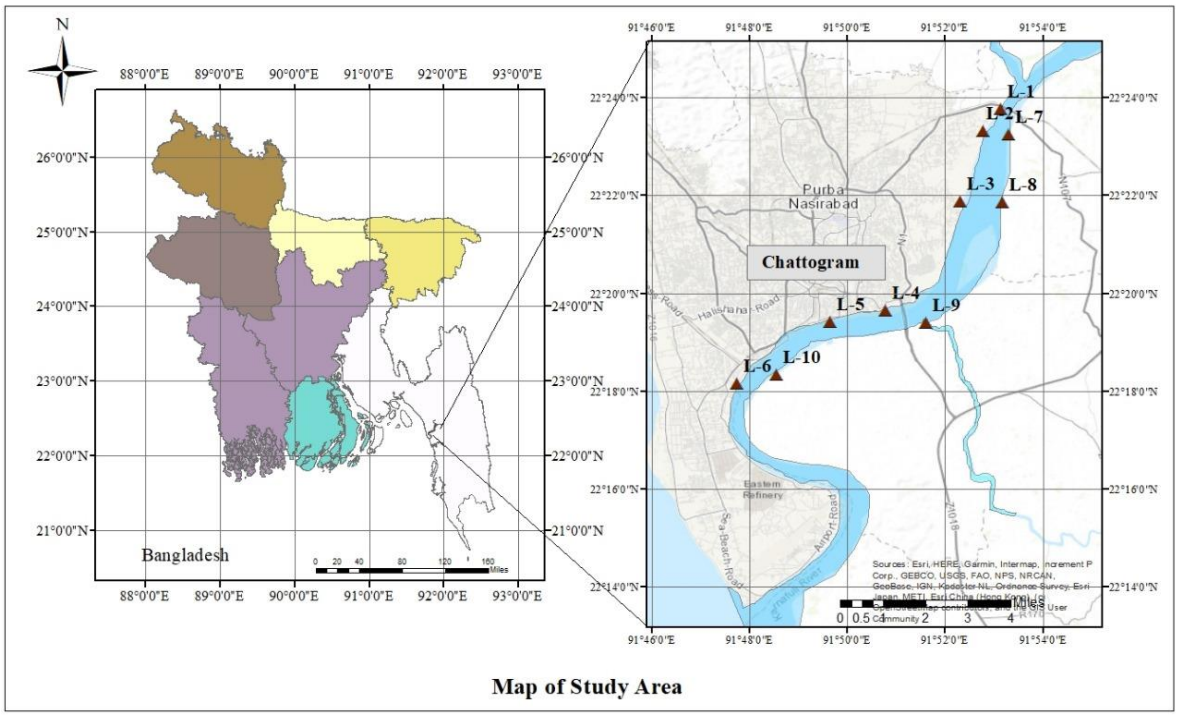


Figure 3.1. Geographical location and sampling points of ten selected khals.

Table 3.1 Geographical locations of the estuaries of ten selected khals feeding to Karnaphuli river and as well as sampling points

Sl No	Name of khals	Latitute	Longitute
L-1	West Kalurghat khal	91.885943	22.396359
L-2	Ispahani khal	91.879868	22.388722
L-3	Bolirhat khal	91.872023	22.364735
L-4	Chaktai khal	91.84665	22.327494
L-5	Custom khal	91.82769	22.323732
L-6	Mohesh khal	91.795693	22.302728
L-7	MAF newsprint khal	91.888404	22.387558
L-8	FMC dockyard khal	91.886457	22.36456
L-9	Shikolbaha khal	91.860197	22.323482
L-10	Ichanogor khal	91.818843	22.313131

3.2 Sample Collection and Preservation

3.2.1 Collection of Surface Water and Sediments

A total of 40 water and 40 surface sediments samples were collected from 10 different estuaries of selected khals feeding to Karnaphuli River during the mid of wet (July, 2019) and dry (January, 2020) seasons to observe the seasonal variation of physicochemical parameters and heavy metals concentration. Two surface water and sediments samples were collected at 50m upstream from the estuary of each khal in each season. Among them, one sample was collected from each side of each khal studied (Fig. 3.2). All samples were collected at the time of

low tide for obtaining the real sample of surface water flowing through the khals to Karnaphuli River. During the wet season (rainy), river water levels come up due to heavy rainfall, and during the dry (winter) season there is no rainfall and river water level goes down.

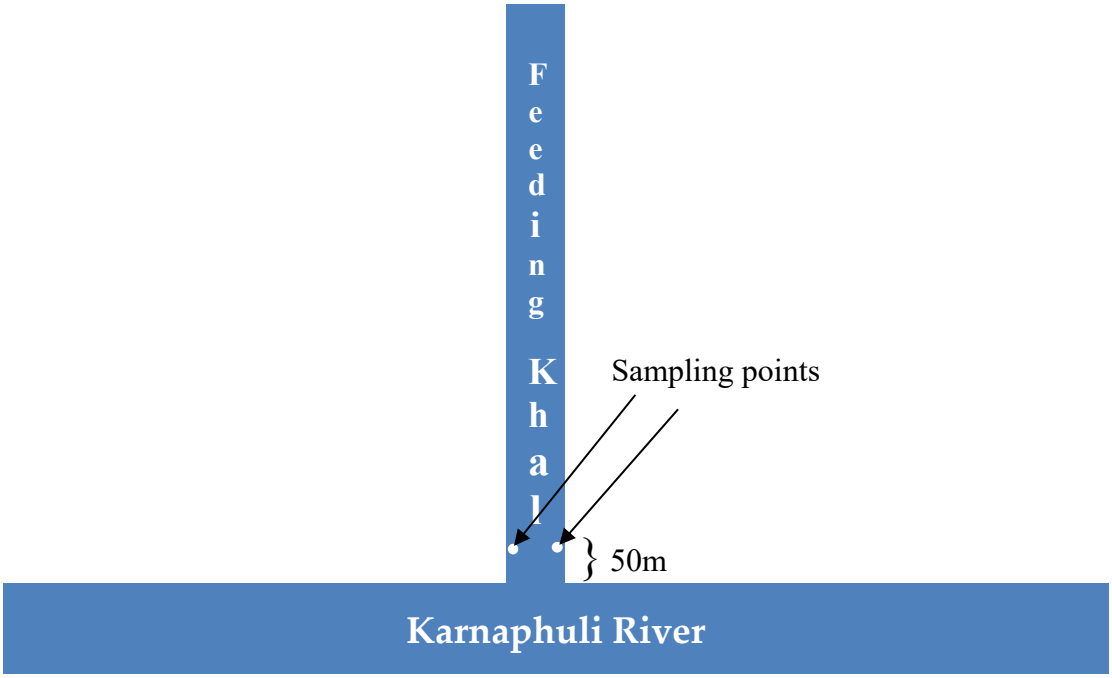


Fig. 3.2 Sampling points at the estuary of each khal feeding to the River Karnaphuli.

Wet season exhibits higher water flow in the feeding khals than in dry season which can cause the variation of physicochemical parameters and heavy metals concentration in the surface water, and as well as concentration of heavy metals in surface sediments.

3.2.2 Water Sample Preservation

Surface water sample collected from each location in a precleaned 1L plastic bottle in such a way so that no air was left in the bottle. Samples were tested as soon as possible after collection. Water temperature was measured with a digital thermometer, while dissolved oxygen was checked using a portable DO meter. pH and electrical conductivity were recorded with a digital meter. To maintain accuracy, bottles were sealed tightly, labeled, and stored in a refrigerator until

testing. The lab followed proper quality procedures (LQMS). Other tests such as BOD, COD, TDS, salinity, and total hardness were done using standard APHA (2012) methods. Each test was done triplicate, and the average result was used.

3.2.3 Sediment Sample Collection and Preservation

Sampling conducted in July 2019 (wet season) and January 2020 (dry season) following established protocols (USEPA, 2021). Sediment samples were collected from two points within the estuaries of ten selected khals that feed into the Karnaphuli River. Using a stainless-steel Ekman grab sampler, sediments were collected from the top 0–5 cm layer (Shanbehzadeh et al., 2014). This device allows water to flow through as it descends and collects sediment. At each site, sediment was collected three times and combined to form a composite sample. Immediately after collection, samples were transferred into clean, airtight, labeled plastic bags, transported to the laboratory, and stored at 4°C until further analysis.

3.3 Measurement of Physio-chemical Parameters of Water Samples

In this study, several physicochemical parameters like BOD, COD, DO, TDS, pH, EC, Salinity, Hardness and Temperature were measured to assess the physicochemical properties of the surface water samples from the estuaries of selected khals feeding to Karnaphuli river during the wet and dry seasons.

3.3.1 Temperature (TºC)

Temperature fluctuations can negatively impact aquatic life and influence other water quality factors such as pH and dissolved oxygen. Measuring temperature is one of the most fundamental ways to assess water conditions because it affects both chemical processes and biological functions in surface waters. Temperature changes alter oxygen solubility, photosynthetic activity in aquatic plants, and the metabolic rates of aquatic organisms. In this study, water temperature was

measured using a mercury-in-glass thermometer with a range from 0°C to 100°C (APHA, 1999; USEPA, 1983).

3.3.2 pH

The pH of a sample is measured electrically by employing a glass electrode alongside a reference electrode or by using a combined electrode setup. In this we use Hanna HI98107 pocket pH meter to determine water sample pH (APHA, 1999; USEPA, 1983).

3.3.3 Dissolved Oxygen (DO)

Dissolved Oxygen levels can be determined using either titration or electrochemical techniques (APHA, 1999; USEPA, 1983).

Titrimetric Method: Winkler method

The Titrimetric Principle:

Divalent manganese salts present in a solution are precipitated as divalent manganese hydroxide when treated with a strong base.

$$MnSO_4 + 2\ KOH \longrightarrow Mn\ (OH)_2 + K_2SO_4$$

Potassium iodide or potassium hydroxide is introduced, causing a pinkish-brown precipitate to form. Under alkaline conditions, the dissolved oxygen in the sample rapidly oxidizes, leading to the creation of hydroxides with valence states of three or more.

$$2Mn(OH)_2 + O_2 \longrightarrow MnO(OH)_2$$

$MnO(OH)_2$ forms a brown precipitate. Adding iodide and acid converts tetravalent hydroxides to divalent forms, releasing iodine.

$$Mn(OH)_2 + 2KI + H_2O \longrightarrow Mn(OH)_2 + I_2 + 2KOH$$

Iodine is titrated using thiosulfate solution, with starch serving as the indicator.

$$I_2 + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I^-$$

The iodine quantity measured reflects the dissolved oxygen level in the sample.

3.3.4 Biochemical Oxygen Demand (BOD)

Water samples are stored in airtight bottles and incubated at 20°C for five days. Dissolved oxygen (DO) is measured before and after incubation, and the biological oxygen demand (BOD) is calculated as the difference between these two DO values (APHA, 1999; USEPA, 1983). The initial DO was determined shortly after the dilution is made; all oxygen uptake occurring after this measurement is included in the BOD measurement (APHA, 1999; USEPA, 1983).

3.3.5 Chemical Oxygen Demand (COD)

The Closed Reflux Colorimetric method was employed to determine COD. In this method, organic matter in the water samples is fully oxidized by potassium dichromate ($K_2Cr_2O_7$) in an acidic environment containing sulfuric acid (H_2SO_4), silver sulfate (Ag_2SO_4), and mercury sulfate ($HgSO_4$). This reaction produces carbon dioxide and water. The sample is refluxed with a measured amount of potassium dichromate in sulfuric acid, and the leftover dichromate is titrated with ferrous ammonium sulfate using ferroin as an indicator. The amount of dichromate consumed corresponds to the oxygen needed to oxidize the organic substances present (APHA, 1999; USEPA, 1983).

3.3.6 Total Dissolved Solids (TDS)

TDS refers to substances fully dissolved in water that can pass through a filter. To determine TDS, a thoroughly mixed water sample is passed through a standard glass fiber filter. The filtered liquid is then evaporated in a pre-weighed container and dried at temperatures between 179°C and 181°C until its weight stabilizes. The increase in weight of the container indicates the quantity of dissolved solids present (APHA, 1999; USEPA, 1983).

Total suspended solids (TSS) are measured by drying the residue left on a pre-weighed filter after filtering a well-mixed water sample. The drying occurs at 103°C to 105°C until a constant weight is achieved. The weight gain of the filter represents the suspended solids. If filtering is slowed due to clogging by suspended particles, the difference between total solids and total dissolved solids can be used to estimate the total suspended solids (APHA, 1999; USEPA, 1983).

3.3.7 Electrical Conductivity (EC)

The specific conductance of a sample is measured by use of a self-contained conductivity meter, Wheatstone bridge-type, or equivalent. Samples are preferable analysed at 25°C If not, temperature corrections are made and results reported at 25°C. In this we used Hanna HI98319 pocket EC meter to determine water sample EC (APHA, 1999; USEPA, 1983).

3.3.8 Salinity

Salinity indicates the quantity of dissolved salts found in one kilogram of water. These salts include typical ions such as Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, Cl^{-}, SO_4^{2-}, HCO_3^{-}, and CO_3^{2-}, which may occur naturally or be introduced into the environment as pollutants. Conventionally, salinity of water is determined by volumetric method using standard $AgNO_3$ solution. The following equations are used in calculation of salinity.

$$Chlorocsity = \frac{Volume\ of\ AgNO3\ consumed\ x\ Normality\ of\ AgNO3}{Volume\ of\ the\ water\ sample}$$

$$Chlorinity = \frac{Chlorosity\ of\ water}{Density\ of\ water}$$

Considering the density of water 1, salinity is calculated in parts per thousand (ppt) using the following equation:

$$Salinity\ of\ Water\ = 0.03 + (1.805\ x\ chlorinity\ of\ water)$$

3.3.9 Hardness

The water sample is adjusted to a pH of 10.1 and placed in a conical flask. Adding an indicator like Eriochrome Black T causes the solution to turn wine red due to calcium and magnesium ions. As EDTA is gradually added during titration, it binds with these ions, displacing the indicator. When all calcium and magnesium ions are complexed with EDTA, the solution changes color to blue, signaling the titration endpoint (APHA, 1999; USEPA, 1983).

3.4 Heavy Metal Analysis of Surface Water and Sediments

We collected both sample from selected location and preserved sample for laboratory analysis.

3.4.1 Surface water Sample Preparation

Water samples were acidified immediately after collection using nitric acid to reach a pH of 2, then transported to the laboratory to prevent contamination. Glassware was thoroughly cleaned with chromic acid followed by distilled water. Analytical-grade chemicals and reagents were used throughout the study. Instrument calibration was performed using reagent blanks. For heavy metal analysis, 100 mL of each water sample was placed in a beaker and digested by adding 5 mL of concentrated nitric acid on a hot plate. After digestion, the samples were filtered through Whatman No. 42 filter paper into a 100 mL volumetric flask and diluted to volume with distilled water. Heavy metal concentrations were then measured using an Atomic Absorption Spectrometer (AAS) following standard procedures (APHA, 1995) at the Bangladesh Council of Scientific and Industrial Research (BCSIR), Dhaka.

3.4.2 Sediments Sample Preparation

Surface sediment samples were collected, placed in labeled polythene bags with location and sample codes, and air-dried at room temperature. The dried samples

were then ground and sieved through a 2 mm sieve. Throughout the process, analytical-grade chemicals and reagents were used, with reagent blanks applied to adjust instrument readings. Two grams of each prepared sediment were digested on a hot plate using 50% nitric acid. Following digestion, the mixture was filtered through Whatman No. 42 filter paper into a 100 mL volumetric flask, with residues thoroughly rinsed. Heavy metal levels in the sediments were determined using Atomic Absorption Spectroscopy (AAS) according to APHA (1995) protocols at the BCSIR laboratory in Dhaka.

3.4.3 Quality Control

All glassware, including burettes, pipettes, beakers, and volumetric flasks, was calibrated and cleaned overnight with 2% (v/v) diluted nitric acid, followed by multiple rinses with deionized water before use. Sample weights were measured using a calibrated digital balance (HR 200, maximum 210 g, precision 0.1 g; A&D Company Limited, Tokyo, Japan; Model N92, D0001). High-purity certified reference materials (CRMs) and reagents such as perchloric acid ($HClO_4$), nitric acid (HNO_3), and deionized water (Barnstead International, Model D7071, resistivity 18.2 MΩ·cm) were sourced from reputable suppliers (Scharlau, Barcelona, Spain; Sigma Aldrich, Hamburg, Germany). Instrument calibration utilized CRM stock standards (100 ± 4 mg/L) obtained from Sigma-Aldrich. To ensure accuracy and reliability, quality control procedures including spike recovery tests, duplicate measurements, independent standard verifications, and reagent blanks were implemented. Precision was verified by triplicate analyses using NIST-traceable CRMs and quality control charts with a 99% confidence limit. Calibration solutions were prepared by diluting stock standards for detection of metals and anions via Atomic Absorption Spectroscopy (AAS). The detection limits for metals Cu, Cr, Pb, Cd, Mn, Zn, Ni, and As were 0.005, 0.01, 0.001, 0.05, 0.1, 0.07, 0.00005, and 0.001 mg/L, respectively. Instrument measurements were adjusted by subtracting reagent blank values. For sediment

analysis, 2 grams of powdered sediment were digested with 70% nitric acid on a hot plate (Uddin et al., 2021), filtered through Whatman No. 42 filter paper into a 100 mL volumetric flask, and rinsed thoroughly. Heavy metal concentrations in sediment samples were quantified by AAS, following APHA (1995) protocols, at the Bangladesh Council of Scientific and Industrial Research (BCSIR) laboratory in Dhaka.

3.4.4 Chemical Reagents

Analytical-grade reagents with 99% purity were used, and ultra-pure deionized water served for all solution preparation, dilution, and cleaning procedures. Glass and plastic equipment were thoroughly rinsed and soaked overnight in 10% metal-grade nitric acid. Sample digestion utilized hydrochloric acid (37%, boiling point 122°C) and nitric acid (70%, boiling point 108°C) sourced from Merck, Germany. Nitric acid, a strong oxidizing agent, reacts with nearly all elements except gold, platinum, aluminum, boron, chromium, titanium, and zirconium. Hydrochloric acid, which is non-oxidizing, breaks down silicates and forms soluble chlorides with most elements except silver, mercury, and titanium. It also dissolves salts of weak acids like carbonates, phosphates, and borates but is ineffective against oxides of certain metals such as Al, Be, Cr, Sb, Sn, Si, Ti, and Zr.

3.4.5 Preparation of blank Solution

To ensure no contamination occurred, an acid blank was prepared and subjected to the exact digestion procedure as the samples, using identical reagent mixtures and acid ratios. Following digestion, this blank was treated as a sample and diluted at the same ratio before analysis. It was analyzed by atomic absorption spectroscopy before real samples and its values were subtracted to check the equipment's to read only exact values of the heavy metals in the samples.

3.4.6 Preparation of Stock and Standard Solutions

Atomic absorption spectroscopy users commonly obtain certified stock standards, often at 1000 ppm, for calibration purposes. Alternatively, these standards may be prepared in the laboratory from reagent-grade chemicals. In present study we used commercially available Fluka solution (1000 ppm) from Switzerland. Working standards were freshly prepared from stock solution by serial dilution.

3.4.7 Precaution Taken and Sample Preparation

A major concern during sample preparation is contamination that may occur during weighing and digestion. To minimize this risk, all glass and plastic containers were thoroughly cleaned with a 10% (v/v) acid solution followed by rinsing with deionized water. Contamination could also arise from the digestion acids or the laboratory environment. To detect any potential contamination, acid blanks were prepared and analyzed alongside the samples, ensuring the accuracy and reliability of the results.

3.5 Determination of Heavy Metal Concentration in Surface Water and Sediments

3.5.1 Aspiration of the Samples

For the analysis of a particular element in the sample the cathode lamp of that element was first fitted in the spectrometer and the efficiency bar was adjusted to the maximum value. The standards of the element which will be analysed were first run and the absorbance readings were recorded. The unknown sample was then aspirated for taking absorbance of the analyte. In case of abnormal absorbance reading, the sample was diluted with deionized water according to the requirements and then reading was taken. A blank sample was always run against the real one to subtract the contribution of the blank from the reading of

the real sample. Triplicate absorbance readings were taken for analysis of each parameter.

3.5.2 Construction of Calibration Curve

A calibration curve illustrates how an analytical method's response varies with known analyte concentrations. It enables the determination of unknown sample concentrations by comparing their measured response to those of standard solutions with predefined concentrations. Calibration involves measuring the absorbance of these standards, which, according to the Beer–Lambert Law, increases proportionally with concentration. By plotting absorbance against concentration, a linear calibration curve is obtained. The corresponding equation is shown in Figure 3.3.

$$y = mx + b \tag{1}$$

Where,

$$slope = \frac{\Delta y}{\Delta x} = m \tag{2}$$

y = absorbance (independent variable)

m = gradient of line (slope),

x = concentration (mg/L) (dependent variable)

b = y intercept

This equation is rearranged and used to calculate the unknown concentration (x) of the element from the absorbance (y) of calibration curve given by ASS for each sample. First of all from calibration curve which is a straight line (y = mx), the value of m is to be noted.

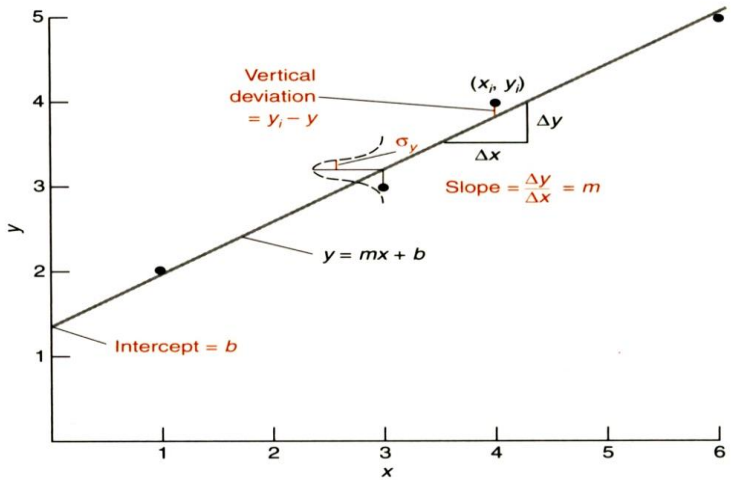


Fig. 3.3. Calibration curve

From calibration curve, we get

$$y = mx$$

$$x = y/m$$

$$= y\,(1) - y\,(2)/m \qquad (3)$$

Where, y (1) = absorbance of the sample and y (2) = absorbance of the blank and m = slope. The concentration of heavy metal is calculated using the following equation.

$$\text{Actual concentration (mg/kg)} = \frac{\text{Calculated concentration of metal in sample (mg/L)} \times \text{volume of the digested sample (mL)}}{\text{Sample weight (g)}} \qquad (4)$$

Dilution factor:

Dilution involves reducing the concentration of a solute in a solution by adding more solvent, without altering the amount of solute present. The mixture is then thoroughly stirred to ensure uniformity. The dilution factor (DF) is defined as the ratio of the final volume to the volume of the original sample, often referred to as the aliquot. The aliquot represents a measured portion taken from the initial solution. This relationship can be represented mathematically as follows:

$$\text{Dilution Factor (DF)} = \frac{\text{Volume of the diluted sample solution in mL}}{\text{Volume of the liquid taken for dilution in mL}} \quad (5)$$

For a series of dilutions, the total dilution factor is calculated by multiplying the dilution factors from each individual dilution step.

$DF_{total} = DF_1 \times DF_2 \times DF_3 \times \ldots \times DF_n$

Actual concentration with DF = Actual concentration (mg/Kg) × *Dilution factor*

Goodness of the fit

R^2 quantifies how much of the total variation in the dependent variable (y) is accounted for by the independent variable (x) in a regression model, by comparing the variance explained by the regression line to the total variance.

Multiplying R^2 by 100 gives the percentage of variability in y that can be predicted based on x.

An R^2 value of 1 indicates a perfect predictive relationship, whereas a value close to 0 implies a weak or nonexistent linear correlation.

3.6 Metal Pollution Index (MPI) of Surface Water Samples

The Metal Pollution Index (MPI) was utilized to assess the combined impact of metals on water quality, as described by Zhang et al. (2015) and Bhattacharya et al. (2015). MPI was determined by summing the ratios of measured metal concentrations to their respective maximum permissible limits (MAC), according to Equation (7). The MAC values were adopted from Bangladesh's drinking water regulations (DPHE, 2020), while the standard for nickel was sourced from the New York State Department of Environmental Conservation and USEPA criteria (USEPA, 2006).

$$\text{MPI} = \Sigma \frac{\text{Ci}}{(\text{MAC})\text{I}} \quad (7)$$

To assess human impact on metal contamination and classify water quality across sampling sites, a six-level ranking system was applied, following Bhattacharya et al. (2015). An MPI of < 0.3 represents very pure (Class I), 0.3–1.0 represents pure (Class II), 1.0–2.0 represents slightly affected (Class III), 2.0–4.0 represents moderately affected (Class IV), 4.0–6.0 represents strongly affected (Class V), and > 6.0 represents seriously affected (Class VI).

3.7 Environmental Impacts Assessment Parameters of Sediment Samples

The following parameters were calculated to assess the environmental pollution in the surface water and sediments of Karnaphuli river.

3.7.1 Enrichment Factor (EF)

The enrichment factor (EF) identifies natural versus human pollution sources and gauges contamination levels (Tamim et al., 2016; Sun et al., 2015; Datta and Subramanian, 1998).

$$\mathrm{EF} = (\mathrm{Cn}/\mathrm{Cr})\,\mathrm{Sample}/(\mathrm{Cx}/\mathrm{Cr})\mathrm{Reference} \quad (8)$$

The enrichment factor (EF) is calculated using the ratios of element concentrations in the sample (Cn) to a reference element (Cr), compared against the ratio of the same elements in a reference source (Cx/Cr). Here, Cn represents the sample concentration, Cr the reference concentration, and Cx the crustal concentration. EF values are classified as follows: no enrichment (EF < 1), low (1–3), moderate (3–5), moderately severe (5–10), high (10–25), very high (20–40), and extremely high (> 40) enrichment (Tamim et al., 2016; Sun et al., 2015; Datta and Subramanian, 1998).

3.7.2 Modified Degree of Contamination (mCd)

The modified contamination degree (mCd) can be determined by applying the following equation (9). The total number of heavy metals analysed divided by

total contamination factors for sediment samples metals (Abrahim and Parker, 2008).

$$CF = {Cn}/{Rn} \quad (9)$$

$$Cd = \sum_{k=1}^{10} CF$$

$$mCd = \sum_{k=1}^{10} CF\ /N$$

Cn represents the concentration of a heavy metal in the sample, and Rn is the reference background value (Turekian & Wedepohl, 1961; Hakanson, 1980). Contamination Factor (CF) levels are classified as: CF < 1: low; 1–3: moderate; 3–6: considerable; >6: very high

The Degree of Contamination (Cd) is the sum of CFs: Cd < 6: low; 6–12: moderate; 12–24: considerable; >24: high contamination.

The Modified Degree of Contamination (mCd) is ranked as: <1.5: unpolluted; 1.5–2: slightly polluted; 2–4: moderately polluted; 4–8: moderate to heavy polluted; 8–16: heavy polluted; 16–32: severe polluted; >32: extreme polluted (Singh et al., 2005).

3.7.3 Pollution Load Index (PLI)

The Pollution Load Index (PLI) was used to assess heavy metal contamination, following Ogbeibu et al. (2014).

$$PLI = (CF1 \times CF2 \ldots\ldots \times CFn)^{1/n} \quad (10)$$

In this equation, n refers to the total number of analyzed metals (CF_n). The contamination factor (CF) is derived by dividing the concentration of a specific metal in the sample (C_{metal}) by its respective background concentration ($C_{background}$).

PLI = 1, baseline pollutant levels; PLI>1 progressive deterioration (Mohiuddin et al., 2012).

3.7.4 Geo-accumulation Index (I_{geo})

The Geo-accumulation index (Igeo) is used to evaluate metal pollution and determine the contamination level in the samples, following the equation (11) (Muller, 1969):

$$Igeo = \log_2[{Cn}/{(1.5 \times Rn)}] \quad (11)$$

Here, Cn represents the measured concentration of a particular metal (n), while Rn is its corresponding reference value. The factor 1.5 is included to account for natural background fluctuations (Müller, 1969). The geo-accumulation index (Igeo) categorizes contamination levels as: Igeo ≤ 0: no pollution; 0 < Igeo ≤ 1: from uncontaminated to slightly polluted; 1 < Igeo ≤ 2: moderately polluted; 2 < Igeo ≤ 3: moderately to heavily polluted; 3 < Igeo ≤ 4: heavily polluted; 4 < Igeo ≤ 5: heavily to extremely polluted; Igeo > 5: extremely polluted.

3.7.5 Nemerow Pollution Index ($PI_{Nemerow}$)

The Nemerow Contamination index assesses sediment contamination by combining all measured heavy metal levels using the equation (12) (Duodu et al., 2016; Yan et al., 2016).

$$P_N = \sqrt{\frac{C_f^2}{C_{Max}^2}} \quad (12)$$

where, C_f is the average contamination factor of all metals, and C_{max} is the highest contamination factor. Pollution levels are unpolluted (P_N < 1.5), slightly polluted (1–2.5), moderate polluted (2.5–7), and heavy polluted (≥7) (Vu et al., 2017).

3.7.6 Potential Ecological Risk Index (PERI)

The potential ecological risk index was used to evaluate the contamination levels of heavy metals in surface sediment samples, as calculated using equation (13) (Hakanson 1980).

$$PERI = \sum_{i=1}^{n} E_f^i \quad \text{where, } E_f^i = C_f^i \times T_f^i \tag{13}$$

E_f^i is the potential ecological risk factor of each element; C_f^i is the Contamination factor

$$C_f^i = {Cn}/{Rn} \tag{14}$$

Here, C_n is the concentration of heavy metals in sediment, R_n is the reference value for each element, and T_f^i is the toxicity coefficient to each metal (As = 10, Cd = 30, Cr = 2, Cu = Pb = Ni = 5, Zn = Mn = 1) (Yi et al., 2011). The ecological risk factor (E_f^i) is categorized as Low ecological risk ($E_f^i < 40$), Moderate ecological risk ($40 < E_f^i \leq 80$), Appreciable ecological risk ($80 < E_f^i \leq 160$), High ecological risk ($160 < E_f^i \leq 320$), Serious ecological risk ($E_f^i > 320$). The overall Potential Ecological Risk Index (PERI) classifies risk as low (< 150), moderate (150–300), high (300–600), and very high (≥ 600) (Hakanson, 1980).

3.8 Health Risk Assessment

3.8.1 Non-carcinogenic Health Risk Assessment

Health risk assessment considered dermal contact as the primary exposure route for adults to heavy metals in surface water and sediments during daily activities like bathing and washing. Equation (18) was used to determine the exposure by dermal contact (USEPA 1989, 2004; Rovira et al., 2011; Iqbal et al., 2013).

$$CDI_{\text{derm (water)}} = \frac{C \times SA \times KC \times EF \times ED \times ET \times ABS \times CF}{BW \times AT} \tag{15}$$

where C is the concentration of heavy metal ($mg.kg^{-1}$); EF is the exposure frequency: 365 d/y (USEPA 2011a,b); ED is the exposure duration: 30 (adult) (USEPA, 2002); BW is the body weight of the individuals: 70 for adults (USEPA 1991); AT is the average time for the element: 365×ED d (non-carcinogenic elements) and 365×70 (carcinogenic elements) (USEPA, 2011a,b); SA is the skin surface area for the exposure contact: 5700 cm^2/d (adult); KC is the factor of

permeability for dermal contact: 0.001 cm/h; ET is the exposure time: 24 g/d; ABS is the fraction of dermal absorption: 0.03 (for As) and 0001 (other metals) (USEPA 2011a,b); conversion factor (CF) is 10^{-6} (USEPA, 2002).

The hazard quotient (HQ) assessed non-carcinogenic health risks from heavy metals in sediments via dermal exposure (USEPA, 2004) using the following equations:

$$\mathrm{HQderm} = \frac{\mathrm{HQderm}}{\mathrm{RfD_0}} \quad (16)$$

$$\mathrm{HIderm} = \sum_{i=1}^{n} \mathrm{HQderm} \quad (17)$$

HI represents the hazard index, while HQ_{derm} is the dermal exposure risk. RfD_0 defines safe exposure limits. Iqbal et al. (2013) state that reference doses for heavy metals in water and sediment align with dermal exposure levels. The RfD_0 value for Cu, Cr, Cd, Pb, Ni, Mn, As and Zn are 4×10^{-2}, 3×10^{-3}, 1×10^{-3}, 3.5×10^{-3}, 1.1×10^{-2}, 2.4×10^{-2}, 3×10^{-4} and 3×10^{-1}. According to Enuneku et al. (2018), when the HI is less than 1.0, it indicates that there are significant negative interactions; on the other hand, when the HI is larger than 1.0, it indicates that there is a concern for non-carcinogenic health risks.

3.8.2 Carcinogenic Health Risk Assessment

The lifetime cancer risk from exposure to polluted river water was estimated by multiplying the chronic daily intake (CDI) by the cancer slope factor (SF) (USEPA, 1991; Chen & Liao, 2006). The carcinogenic risk was calculated for each metal individually as well as combinedly for all metals using Equations (18) and (19), respectively.

$$\text{Carcinogenic Risk } (CR_i) = CDI_i \times SF_i \quad (18)$$

$$\text{Lifetime carcinogenic Risk (LCR)} = \sum_{i=0}^{n} CRi \quad (19)$$

Carcinogenic risk (CR) represents the likelihood of developing cancer over a lifetime due to exposure to carcinogenic substances. The total carcinogenic risk is

calculated by summing the individual risks from each heavy metal in the exposure pathway. The cancer slope factor (SF, mg/kg/day) quantifies the risk potency of each metal. Among the eight metals studied, As, Cd, and Cr are recognized as human carcinogens, while Pb is considered a probable carcinogen according to the International Agency for Research on Cancer (Zhang et al., 2015). The oral slope factors used were 1.5 for As, 0.0085 for Pb, 0.5 for Cr, and 15 for Cd. The acceptable lifetime cancer risk range is between 10^{-6} and 10^{-4} (Yin et al., 2015; USEPA, 2000), with values exceeding 10^{-4} indicating a significant potential carcinogenic risk (Hu et al., 2017; USEPA, 2010a, b).

Chapter 4: RESULTS AND DISCUSSION

4.1. Physicochemical Parameters of Surface Water

The physicochemical parameters, such as Temparature, pH, DO, BOD, COD, TDS, EC, salinity and hardness were measured

4.1.1 Comparison of Physicochemical Parameters of Surface Water

Physicochemical parameters, like Temparature, pH, DO, BOD, COD, TDS, EC, salinity and hardness of surface water samples at the estuaries of selected khals feeding to Karnaphuli river during wet and dry seasons are compared and summarised in Table 4.1.

The range of Temparature, pH, DO, BOD, COD, TDS, EC, salinity and hardness of the surface water samples during the wet season were found 28 - 30 °C, 6.50 - 7.95, 0.85 - 5.85 ppm, 5.3 - 47.8 ppm, 10.5 - 86.04 ppm, 85 - 1530 ppm, 127 - 2870 $mScm^{-1}$, 0.01 - 1.55 ppt, 77.5 - 948 ppm, with mean values of 29.4 ± 0.21°C, 7.40 ± 0.16, 4.57 ± 0.57ppm, 11.9 ± 4.07 ppm, 22.11 ± 7.25ppm, 429.9 ± 146.43ppm, 883.80 ± 295.20 mS/cm, 0.32 ± 0.19 ppt and 314.5±96.01ppm and respectively (Table 4.1). Similarly, the table shows that during the dry season the ranges of those physicochemical parameters were 24.8 - 28.3°C, 6.8 - 8.3, 0.85 - 5.85 ppm, 6.20 - 134.50 ppm, 13.95 - 278 ppm, 111 - 1815 ppm, 289 - 3587.5 mS/cm, 0.035 - 2.80 ppt, 24.90 ± 12.42 ppm with mean values of 27.2 ± 0.34 0°C, 7.51 ± 0.13, 3.40 ± 0.55 ppm, 24.92 ± 8.55 ppm, 54.12 ± 25.47 ppm, 582.70 ± 168.04 ppm, 1305.80 ± 378.66 mS/cm, 0.50 ± 0.30 ppt, 492.5 ± 127.69 ppm and respectively.

Table 4.1: Comparison of physicochemical parameters of surface water samples with the values recommended by WHO, 2015 and ECR, 2023.

Location	Season	Physicochemical parameters								
		Temp. (°C)	pH	DO (ppm)	BOD (ppm)	COD (ppm)	TDS (ppm)	EC (mS/cm)	Salinity (ppt)	Hardness (ppm)
L-1	Wet	30.0	7.60	4.55	5.9	11.8	85	127	0.01	77.5
	Dry	28.0	7.55	2.25	7.2	13.95	111	289	0.05	95.5
L-2	Wet	30.0	6.50	1.20	47.8	86.04	471.5	652.5	0.01	388
	Dry	24.8	6.80	0.85	134.5	278	560	887.5	0.18	457.5
L-3	Wet	29.8	6.70	4.05	14.0	24.1	272.5	418.5	0.02	218
	Dry	28.3	7.50	2.40	21.1	38.5	285	677.5	0.04	274
L-4	Wet	29.0	7.80	1.80	10.0	18.5	258	635	0.05	200
	Dry	26.0	7.60	1.15	31.05	70.5	460	1052.5	0.085	530
L-5	Wet	29.0	7.80	4.45	7.1	12.75	232	555.5	0.08	196
	Dry	27.9	7.15	3.15	14.0	37	494	1741.5	0.095	438
L-6	Wet	30.0	7.50	6.10	8.75	17.35	1530	2870	1.4	948
	Dry	28.0	7.15	5.85	9.5	21	1815	3587.5	1.65	1389
L-7	Wet	30.0	7.95	5.35	6.1	10.98	155	384	0.06	126
	Dry	27.8	8.30	4.40	8.9	17.5	245	568	0.06	198
L-8	Wet	29.5	7.85	6.35	5.3	10.6	125	378.5	0.01	81
	Dry	27.4	7.95	4.05	6.6	17	177.5	442.5	0.035	126.5
L-9	Wet	28.0	7.30	5.95	8.75	18.5	205	452	0.02	138.5
	Dry	27.3	7.70	5.80	10.1	33.5	467.5	522	0.045	445
L-10	Wet	29.5	7.00	5.90	5.55	10.5	965	2365	1.55	772
	Dry	26.9	7.40	4.05	6.2	14.25	1212.5	3290	2.8	972
Range	Wet	28.0–30.0	6.50 - 7.95	1.20-6.35	5.3-47.8	10.50-86.04	85-1530	127-2870	0.01-1.55	77.5-948.0
	Dry	24.8 - 28.3	6.80 - 8.30	0.85-5.85	6.20-134.50	13.95-278	111-1815	289.0-3587.5	0.035-2.80	95.5-1389
Mean ± SE	Wet	29.48±0.21	7.40 ± 0.16	4.57 ±0.57	11.93 ±4.07	22.11 ±.25	429.90 ±146.43	883.80 ±295.20	0.32 ±0.19	314.50 ±96.01
	Dry	27.24 ± 0.34	7.51 ±0.13	3.40 ±0.55	24.92 ±12.42	54.12 ±25.47	582.75 ±168.04	1305.80 ±378.66	0.50 ±0.30	492.55 ±127.69
WHO, 2015		25	6.5-8.5	4-6	40-50	180-200	600	1000-1200	0.25	120-125
ECR, 2023		20-30	6.5-8.5	≥ 6	≤ 3	25	1000	700-1000	0.15-0.60	500

The results of different physicochemical parameters obtained in this study were compared with the values recommended by World Health Organization (WHO, 2015) and Bangladesh Environmental Conservation Rules (ECR, 2023).

The mean values of Temperature, pH and DO of surface water during both wet and dry seasons obtained in this study were found within the values recommended by WHO (2015) and ECR (2023). The BOD and COD in both seasons was found below the WHO recommended limit but higher than that of ECR (2023). Total dissolved solids (COD) in both seasons were below the set values of both standards. Mean electrical conductivity (EC) in wet season met both the standards, but the mean values of this parameter were found higher than the standard values. The salinity in wet season was below the limit recommended by WHO and ECR, but it crossed the standard values in the dry season. The mean hardness of surface was found higher than the values set by both WHO, 2015 and ECR, 2023.

Each of the studied physicochemical parameters during dry season showed higher values than in the wet season. This may be due to less water flow during the dry season, which influenced the accumulation of various compositions in the surface water samples. Another reason is the addition of municipal and industrial wastes in to the surface water. Lower values of water quality parameters during the wet season could be attributed to high dilution of runoff and unpolluted water. The variation of water quality may be influenced by changes in lithological inputs, hydrological impacts, geological feathers, cultural influences, and vegetation (Jain, 2007).

Individual contribution of studied khals, falling to the Karnaphuli river on different physicochemical parameters of water are presented in Fig. 4.1–4.10. Discussion on the contribution of the studied khals is very important as their water is discharging to the Karnaphuli river and playing an important role in polluting the river water.

Temperature (T⁰C)

The average temperature during the wet season 29.48 ± 0.14 ^{0}C was found higher than the average temperature 27.24 ± 0.24 ^{0}C in dry season at all locations. The average temperature was found higher than the recommended value 25 ^{0}C of WHO, (2015) and was fallen between the range (20 - 34) ^{0}C recommended by ECR, (2023) during both wet and dry seasons (Table 4.1). Basically the variation of weather in Bangladesh in different seasons causes the variation in temperature of surface water during the wet and dry seasons, which is reflected in all locations studied. No considerable variation of temperature was found among the locations, except location 6 in the wet season and in the case of dry season, except locations 2 (Ispahani khal) and 4 (Chaktai khal) all other location showed almost similar surface water temperature (Fig. 4.1).

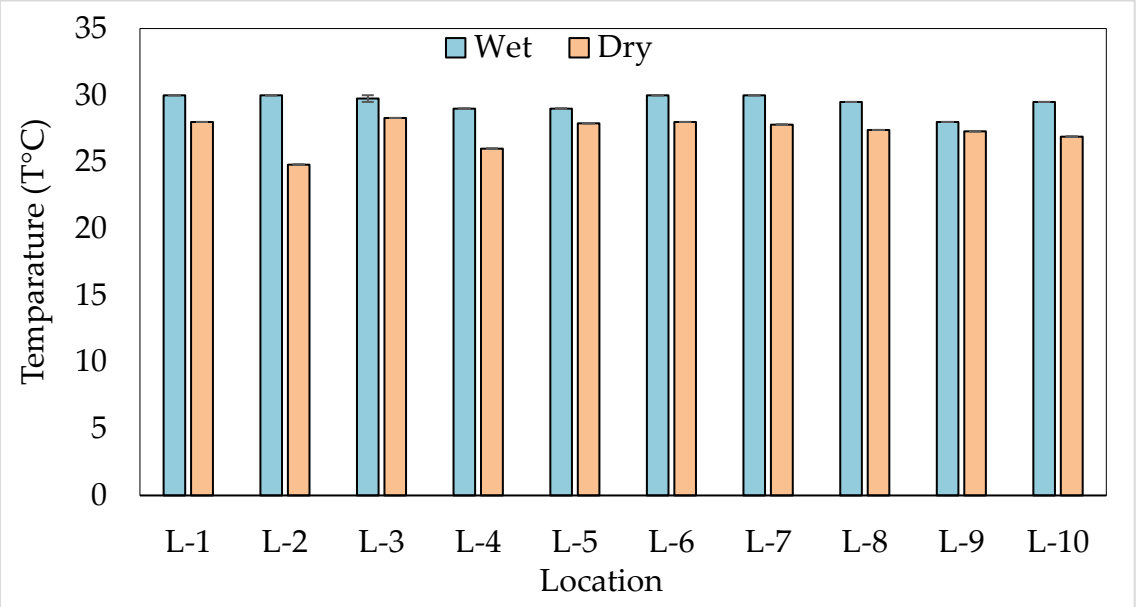


Fig. 4.1: Temperature of surface water at the estuaries of different khals feeding to Karnaphuli river during wet and dry seasons

pH

During the wet and dry season, the average pH were found 7.4 ± 0.11 and 7.51 ± 0.09 respectively, which were fallen in between the range (6.5-8.5) sat by WHO (2015) and ECR (2023) as shown in Table 4.1. No big difference in pH of surface

water during wet and dry season at different locations (Fig. 4.2). Locations 2 (Ispahani khal), 3 (Bolirhat khal) and 10 (Ichanogor khal) in wet season and locations 2 (Ispahani khal), 5 (Custom khal) and 6 (Mohesh khal) in dry season showed comparatively lower pH than others. Comparatively low pH at this three locations might be contributed from the industrial and/or municipal effluents discharged to the khals.

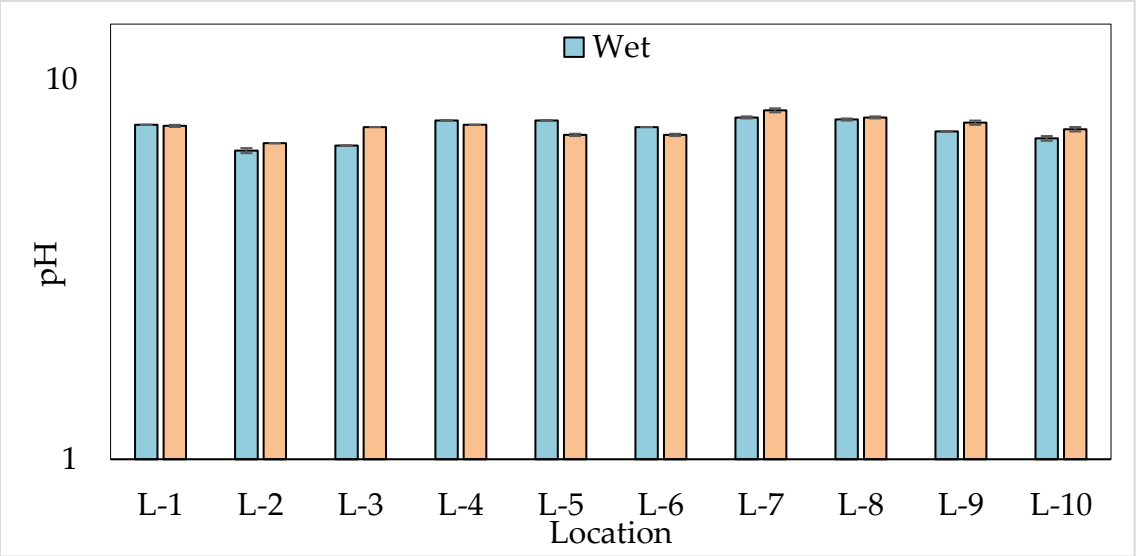


Fig. 4.2: pH values of the surface water at the estuaries of different khals feeding to Karnaphuli river during the wet and dry seasons

Dissolved Oxygen (DO)

Dissolved oxygen is one of the important water quality parameters. It is very essential metabolism of aquatic lives. The average value of DO were found 4.57 ± 0.39 ppm in wet season and 3.40 ± 0.38 ppm in dry season, which were within the recommended values (4.0-6.0 ppm) of WHO (2015) and ECR (2023) as shown in Table 4.1.

Fig. 4.3 clearly shows that surface water contains comparatively higher DO during wet season than that of dry season at all locations. This may happens to the dilution of water in khals with fresh water due to heavy rain falls in the wet season. Comparatively low DO was found at the location 1 (West Kalurghat khal), 2 (Ispahani khal), 3 (Bolirhat Khal) and 4 (Chaktai khal) during both

seasons, especially in dry season. Again, among them the DO level at location 2 and 4 was considerably low.

Ispahani khal passes through the Kalurghat industrial zone and carries the effluents from different industries and Chaktai khal carries sewage and municipal waste, and some industrial waste as well that covers a very large area of Chattogram city. Wastes from these sources may carry a huge amount of oxygen demanding organic materials that consume the dissolved oxygen in water.

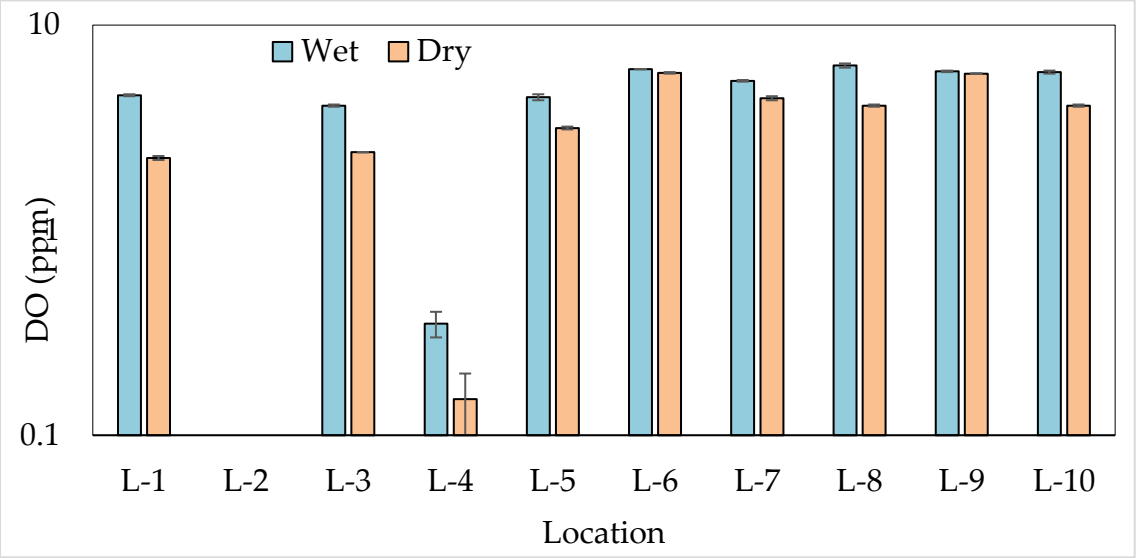


Fig. 4.3: Dissolved oxygen concentration in the surface water at the estuaries of different khals feeding to Karnaphuli river during wet and dry seasons

Biochemical Oxygen Demand (BOD)

Biochemical oxygen demand is another notable quality parameter of surface water. The average value of BOD during wet and dry season were found 11.93±2.81 ppm and 24.92 ± 8.55 ppm respectively, which were lower than the recommended values (40-50 ppm) of WHO (2015) and higher than that (5-10 ppm) of ECR (2023). BOD values were found higher in wet season than that of the dry season at almost all locations as illustrated in Fig. 4.4. BOD level at location 2 (Ispahani khal) was very high compared to rest of the locations and it

was more than a double the limitary value recommended by WHO and many fold higher than ECR recommended value. This means the water of the Ispahani khal carries extremely high quantity of oxygen demanding materials originated and discharged by different industries situated along the khal.

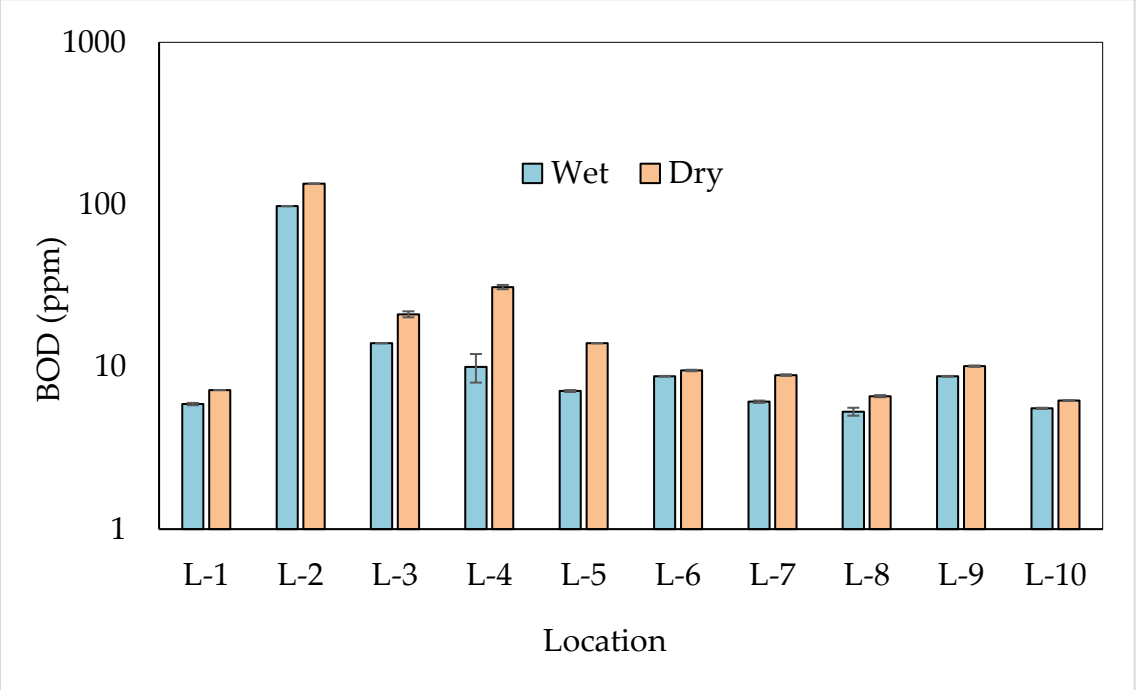


Fig. 4.4: Biochemical oxygen demand (BOD) of the surface water at the estuaries of different khals feeding to Karnaphuli river during wet and dry seasons

Chemical Oxygen Demand (COD)

The average value of chemical oxygen demand in surface water samples during wet was found lower than that of dry season, 22.11 ± 4.99 ppm and 54.12 ± 17.53 ppm respectively (Table 4.1). These average COD during wet and dry seasons was not exceed the recommended value of WHO, (2015) but exceeded the ECR, (2023) recommended value. Like BOD, a very high value of COD was recorded at location 2 (Ispahani khal), especially in dry season that certainly exceeded the highest limit recommended by both WHO and ECR. COD at other points was below the WHO recommended value, though in some cases exceeded the ECR recommended limit as presented in Fig. 4.5. The result indicates that the water

quality fairly acceptable in term COD at all study points, except the Ispahani khal (Location 2) in both season and Chaktai khal (Location 4) in dry season. Different industries located along the khal might be played an important role on the elevation of such high COD. For a certain water sample, COD is always higher than the BOD as COD measures the amount of oxygen required to chemically oxidize the organic material and inorganic nutrients, such as ammonia or nitrate, present in water; whereas COD measures the amount of oxygen required to chemically oxidize the organic materials only.

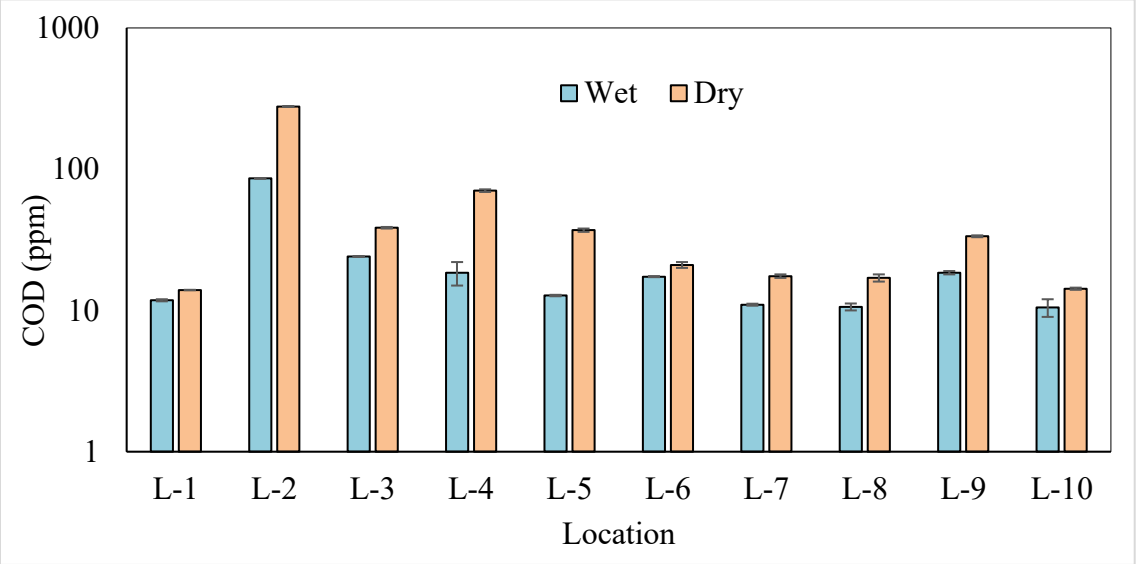


Fig. 4.5: Chemical oxygen demand of surface water at the estuaries of different khals feeding to Karnaphuli river during wet and dry seasons

Total Dissolved Solid (TDS)

The term total dissolved solids of a water body indicates the total concentration of minerals available in it. TDS also includes the dissolved organic substances in water. In the present study, the average concentration of TDS in surface water at the confluence of 10 selected khals falling to Karnofuphuli River were reported as 429.9 ± 100.82 ppm and 582.75 ± 115.70 ppm in the wet season and dry season respectively (Table 4.1). These average values in both seasons were below the WHO and ECR recommended TDS levels. Fig. 4.6 shows the individual

concentration of TDS at the confluence of different khals (Location 1-10) during the wet and dry seasons. It reveals that the concentration of TDS in surface water was higher in dry season than that of wet season at all locations studied. Exceptionally high TDS was measured at Location 6 (Mohesh khal) and Location 10 (Ichanogor khal), which were above the recommended limit; while the measured values of TDS at all other locations were below the maximum limit set by WHO and ECR. The higher values at locations 6 and 10 is due to the intrusion sea water, as they are very close to the meeting point of Karnaphuli river and the Bay of Bengal. Elevated TDS in surface can be originated from both natural and anthropogenic sources. The anthropogenic source includes, sewage discharges, industrial wastewater, sea water, agricultural and urban runoff etc.

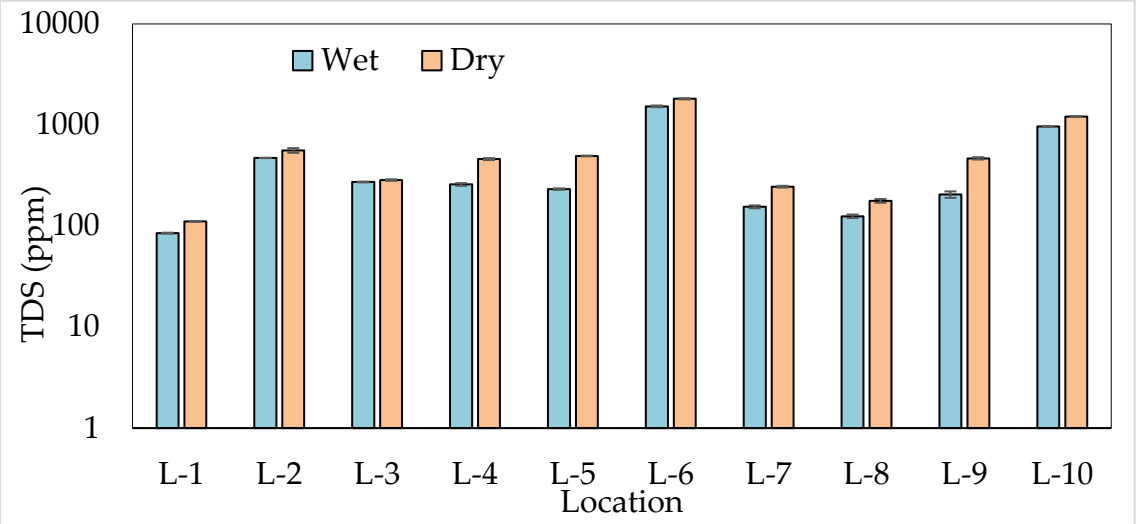


Fig. 4.6: Total dissolved solid content surface water at the estuaries of different khals feeding to Karnaphuli river during the wet and dry seasons

Electrical Conductivity (EC)

The conductivity of water directly depends on the concentration of conductive ions originated due to the presence of inorganic minerals, like chloride, sulphide, alkalis and carbonate compounds, and other dissolved salts. In this study, the average EC were found 883.8 ±203.34 ppm and 1305.8±260.62 ppm in the wet and dry season respectively. Both of the average values met the recommended limit

of WHO, 2015 and ECR (2023). A direct correlation between TDS and EC in this study that can be seen in Fig. 4.6 and 4.7. This result complies with findings reported by some other researchers (Paul & Sen, 2012; Atekwana et al., 2004; McNeil & Cox, 2000). Like TDS, EC values were also found exceptionally high Location 6 (Mohesh khal) and Location 10 (Ichanogor khal), which were far above the recommended limit in both the seasons (Fig. 4.7). The extent of conductivity in the estuaries depends on in and outflows of freshwater and seawater. Electrical conductivity was higher in dry season than in wet season at all study points, which were as usual as other parameters studied.

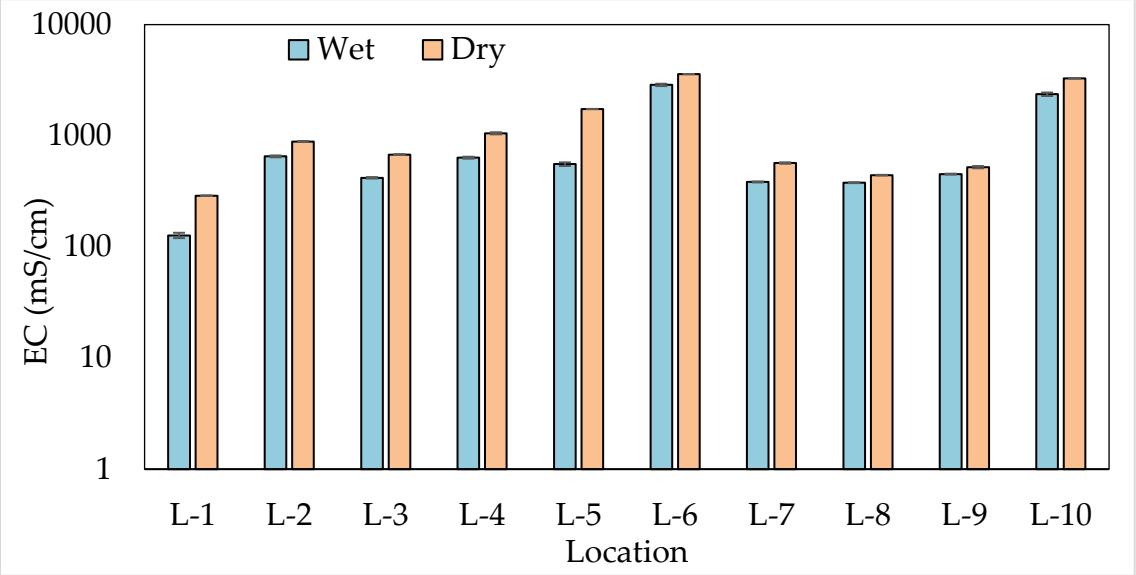


Fig. 4.7: Electrical Conductivity of surface water at the estuaries of different khals feeding to Karnaphuli river during the wet and dry seasons

Salinity

Salinity in water measures the concentration of dissolved salts in it. This water parameter is ecologically important that influence the types of organism living ia water body. The average salinity of surface water at the estuaries of selected khals falling to Katnaphuli River were found 0.32±0.19 ppt and 0.50±0.30 ppt in wet and dry seasons respectively. The average salinity in both the seasons were below the concentration recommended by WHO (2015) and ECR (2023). The average

salinity of river water of the world is about 0.12 ppt (Encyclopedia Britannica), below the recommended concentration; but the mean salinity of surface water in both the seasons were found higher than the world average in the present study. Salinity of surface water at 10 different locations individually in both wet and dry seasons are illustrated in Fig. 4.8. The salinity at all location were below the concentration recommended by WHO and ECR, except location 6 (Mohesh khal) and 10 (Ichanogor khal) in both wet and dry seasons. Salinity at this two locations during wet and dry seasons were measured as 1.40 ppt and 1.65 ppt at location 6, and 1.55 ppt and 2.80 ppt at location 10 respectively. The salinity at these two points clearly higher in dry season than in wet season. The intrusion of sea water results this high salinity, as this two khals are closer to the confluence of the Bay of Bengal among others. Fish and other aquatic organisms that live in freshwater cannot tolerate large increases in salinity. Salinity affects the dissolved oxygen levels in water. The solubility of oxygen in water decreases as salinity increases.

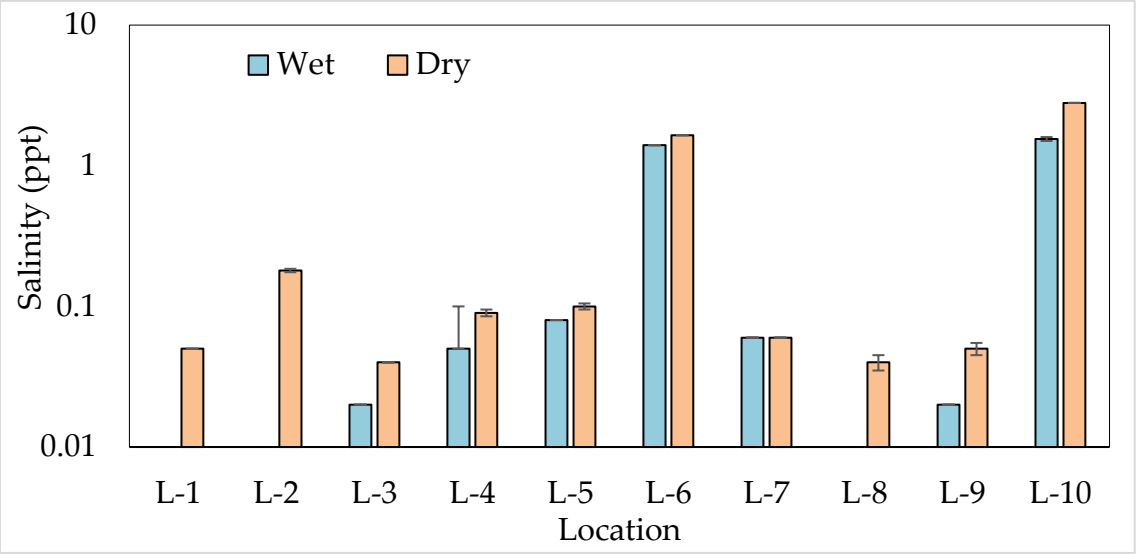


Fig. 4.8: Salinity of surface water at the estuaries of different khals feeding to Karnaphuli river during the wet and dry seasons

Hardness

Hardness is the measure of calcium and magnesium compounds, and variety of other metals. Though hardness is not a health concern it can be a nuisance. High hardness of water can cause scaling in piping, fixtures and water heaters, and poor performance of soaps and detergents. United States Geological Survey classified the hardness of water as: 0 to 60 ppm as calcium carbonate as soft; 61 to 120 ppm as moderately hard; 121 to 180 ppm as hard; and greater than 180 ppm as very hard (USGS, 2018). The observed average hardness of surface water at the estuaries of selected khals during the wet and dry seasons were 314.5±66.09 ppm and 492.55 ±87.90 ppm respectively, which are three to four times higher than the values recommended by WHO (2015) and ECR (2023). The hardness of surface water was found higher than the recommended values at almost all the points studied, especially in dry season as shown in Fig. 4.9.

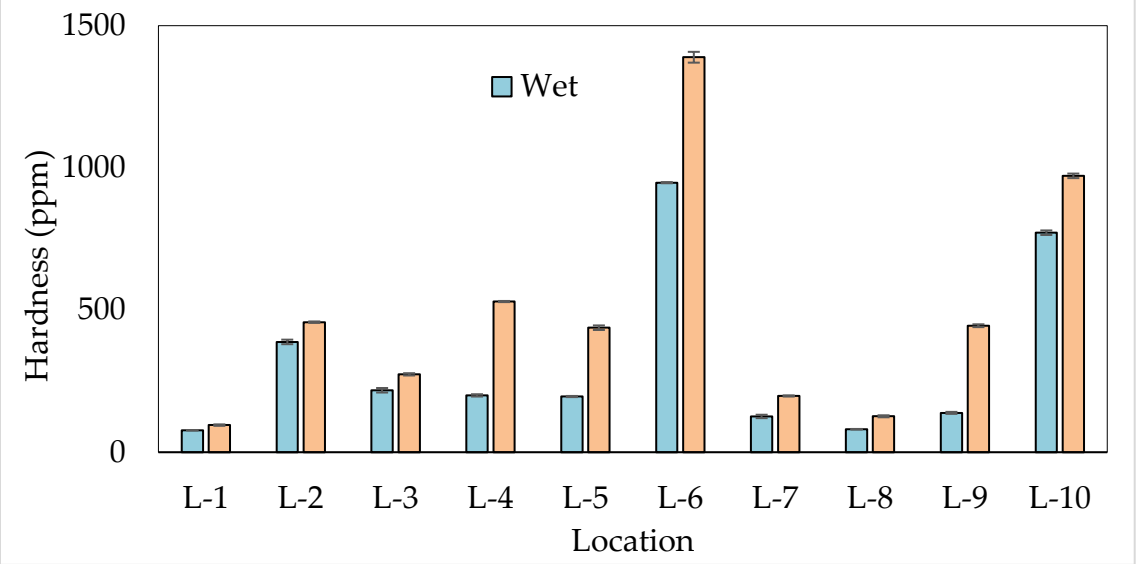


Fig. 4.9: Hardness of surface water at the estuaries of different khals feeding to Karnaphuli river during the wet and dry seasons

Hardness measured in surface water collected from Location 6 (Mohesh khal) and 10 (Ichanogor khal) showed exceptionally higher than other locations in both dry and wet seasons. Hardness found at this two locations show a good correlation with TDS, EC and salinity. During the high tide salty water from the

Bay of Bengal goes up through the Karnaphuli river and enter into the studied khals to some extent. This phenomenon results TDS, EC, salinity and hardness of the surface water higher than the expected values.

The mean values along with standard error of physicochemical parameters, like Temparature, pH, DO, BOD, COD, TDS, EC, Salinity and Hardness of surface water at the estuaries of ten selected khals feeding to Karnaphuli river during the wet and dry seasons are compared as shown in Fig. 4.10. A little variation in Temparature and pH of surface water was observed between wet and dry season. The concentration of dissolved oxygen in surface water in dry season was recorded lower than in wet season. The mean values of other parameters, like BOD, COD, TDS, EC, salinity and hardness were found higher in dry season than those of in wet season.

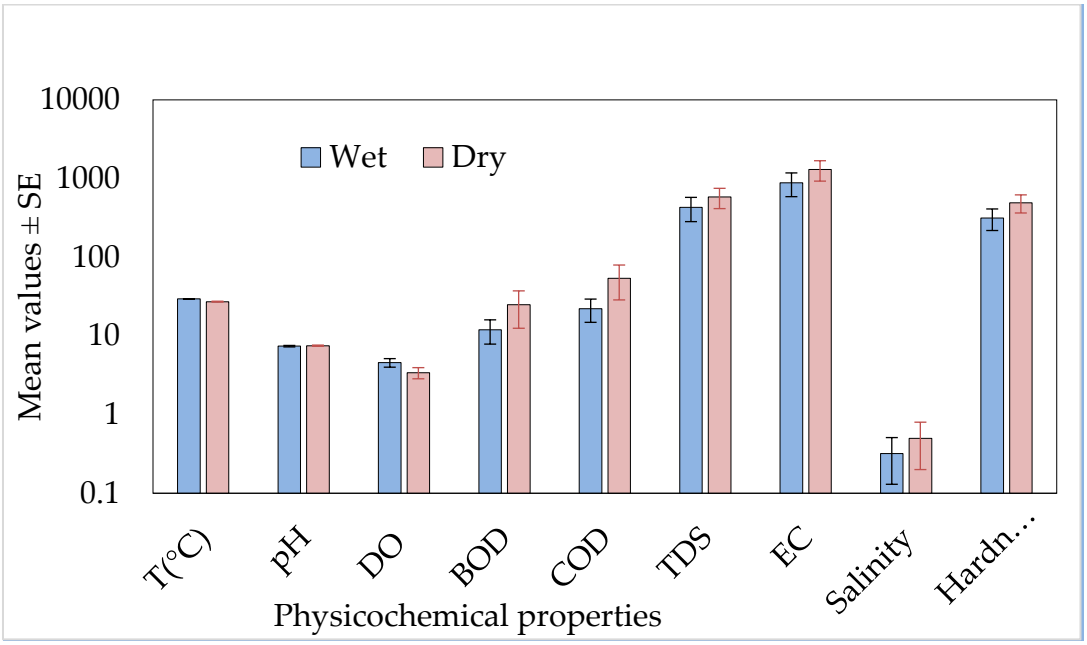


Fig. 4.10: Log base 10 graph of overall mean values of physicochemical properties of surface water during the wet and dry seasons.

A comparison of the mean concentrations of Temparature, pH, DO, BOD, COD, TDS, EC, salinity and hardness in surface water at the estuaries of different khals feeding to Karnaphuli river during the wet and dry seasons with some other

recent studies that carried out on river waters is shown in Table 4.2. The physicochemical parameters obtained in this study were found quite similar to the results reported in the previous studies.

Table 4.2 Comparison of mean values of physicochemical parameters of surface water at the estuaries of different khals feeding to Karnaphuli river during the wet and dry seasons with some other recent literatures on local and regional river water.

Locations	Temp-aratur e°C)	pH	DO (ppm)	BOD (ppm)	COD (ppm)	TDS (ppm)	EC (mS/cm)	Salanity (ppt)	Hard-ness (ppm)	References
Karnaphuli (Wet season)	29.48	7.4	4.57	11.93	22.11	429.9	883.8	0.32	314.5	Present study
Karnaphuli (Dry season)	27.24	7.51	3.4	24.92	54.12	582.75	1305.8	0.50	492.55	Present study
Gomati	26.0–29.0	7.60–8.11	5.4–6.6	17.0–36.0	28.0–56.0	NS	NS	NS	124–176	Tiwari and Kishu (2016)
Meghna	26.45	8.09	9.939	NS	NS	NS	NS	9.145	498	Rahman et al., 2021
Karnaphuli	30.3	6.48	NS	NS	NS	1780	10380	0.92	NS	Hasan et al., 2021
Buriganga	NS	7.3	0.1	18	200	500	801	NS	NS	DoE (2016)
Ganga (India)	10.00–29.67	7.33–8.82	4.65–9.60	1.76–66.64	3.78–240.00	NS	NS	NS	60.65–164.22	Kumar et al., 2020
Vaiga (India)	24.0–27.0	6.8–8.6	4.32–9.57	4.5–22.6	7.2–240.0	NS	NS	NS	242–1750	Mallika et al. (2017)

4.1.2. Pearson's Correlation Coefficient Among Physicochemical Parameters

Pearson's correlation coefficient matrix among the water quality parameters, like Temparature, pH, DO, BOD, COD, TDS, EC, salinity and hardness of surface water at the estuaries of studied khals feeding to Karnaphuli river during wet and dry seasons is presented in Table 4.3.

Table 4.3 Pearson's correlation coefficient matrix among the water quality parameters in surface water samples.

Parameters	T^0C	pH	DO	BOD	COD	TDS	EC	Salinity	Hardness
T^0C	1.00								
pH	0.30	1.00							
DO	0.45	0.41	1.00						
BOD	-0.56	-0.70*	-0.70*	1.00					
COD	-0.60	-0.69*	-0.70*	**0.99****	1.00				
TDS	0.09	-0.37	0.34	-0.02	-0.02	1.00			
EC	0.12	-0.30	0.36	-0.14	-0.14	**0.97****	1.00		
Salinity	0.12	-0.26	0.40	-0.20	-0.21	**0.86****	**0.93****	1.00	
Hardness	0.02	-0.40	0.29	0.00	0.00	**0.99****	**0.97****	**0.88****	1.00

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

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

Pearson's correlation coefficients of physicochemical parameters of surface water samples evaluated using statistical software SPSS (version 23.0) are summarized in the Table 4.2. The relationship between the physicochemical parameters may offer remarkable information on their sources and pathways. Correlation analysis shows significant positive correlation between BOD-COD (r = 0.99) at $p < 0.01$ level whereas DO is significantly but inversely correlated with BOD and COD (r = -0.70, r = -0.70) at $p < 0.05$ level. pH is also significantly but inversely correlated with BOD and COD (r = -0.70, r = -0.69) at $p < 0.05$ level. Significant positive correlation was observed between EC-TDS (r = 0.97) at $p < 0.01$ level; salinity with TDS and EC (r = 0.86, r = 0.93) at $p < 0.01$ level). Hardness also showed significant positive correlation between with TDS, EC, and salinity (r = 0.99; r = 0.97 and r = 0.88) at $p < 0.01$ level. The high significant correlations between physicochemical parameters may reflect the fact that these heavy metals had similar pollution levels and similar pollution sources (Armah et al., 2010). On the other hand, the rest physicochemical parameter pairs show no significant

correlation with each other, suggesting that these physicochemical parameters are not associated with each other and lack of their identical behaviours transport in aquatic environment.

4.2. Heavy Metals in Surface Water

4.2.1 Concentration of heavy metals in surface water during wet and dry seasons

The concentrations of eight heavy metals, like Cu, Cr, Cd, Pb, Ni, Mn, As, and Zn were measured in surface water samples collected from two distinct points at the estuaries of each of the studied khals feeding into the Karnaphuli river. The data, including mean concentrations of two points during both the wet and dry seasons, are detailed in Appendices 3 and 4.

Table 4.4 summarizes the concentration ranges, mean values with standard error, and permissible limits recommended by national and international bodies, including WHO (2017; 1996), USEPA (2017-2018), and DoE (2002; 2016).

During the wet season, the highest recorded concentrations were: Cu at 92.05 μg/L, Cr at 91.90 μg/L, Cd at 29.15 μg/L, Pb at 89.88 μg/L, Ni at 57.85 μg/L, Mn at 133.75 μg/L, As at 17.30 μg/L, and Zn at 95.83 μg/L. The lowest concentrations observed were: Cu at 24.90 μg/L, Cr at 22.38 μg/L, Cd at 2.48 μg/L, Pb at 24.68 μg/L, Ni at 20.43 μg/L, Mn at 18.38 μg/L, As at 0.60 μg/L, and Zn at 28.65 μg/L. In contrast, during the dry season, the highest concentrations were: Cu at 129.98 μg/L, Cr at 119.40 μg/L, Cd at 49.65 μg/L, Pb at 131.88 μg/L, Ni at 76.30 μg/L, Mn at 142.25 μg/L, As at 39.25 μg/L, and Zn at 130.13 μg/LL, while the lowest concentrations were: Cu at 28.75 μg/L, Cr at 28.63 μg/L, Cd at 4.85 μg/L, Pb at 30.65 μg/L, Ni at 13.53 μg/L, Mn at 25.15 μg/L, As at 2.55 μg/L, and Zn at 28.90 μg/L.

During the wet season, the observed order of metal concentrations was Mn > Zn > Cu > Cr > Pb > Ni > Cd > As, with Mn showing the highest concentration and

as the lowest. The ranges and mean values for the wet season were: Cu from 24.90 to 92.05 μg/L (mean: 57.49 ± 6.87 μg/L), Cr from 22.38 to 91.90 μg/L (mean: 52.79 ± 6.32 μg/L), Cd from 2.48 to 29.15 μg/L (mean: 14.95 ± 3.34 μg/L), Pb from 30.65 to 131.88 μg/L (mean: 52.15 ± 6.93 μg/L), Ni from 20.43 to 57.85 μg/L (mean: 34.34 ± 3.81 μg/L), Mn from 18.38 to 133.75 μg/L (mean: 64.90 ± 12.44 μg/L), As from 0.6 to 17.3 μg/L (mean: 9.41 ± 1.52 μg/L), and Zn from 28.65 to 95.83 μg/L (mean: 60.37 ± 7.39 μg/L).

In the dry season, the order of metal concentrations was Zn > Pb > Mn > Cu > Cr > Ni > Cd > As, with Zn showing the highest concentration and As the lowest. The ranges and mean values for the dry season were: Cu from 7.45 to 157.4 μg/L (mean: 65.24 ± 9.40 μg/L), Cr from 21.35 to 145.7 μg/L (mean: 62.5 ± 6.52 μg/L), Cd from 3.05 to 75.95 μg/L (mean: 22.20 ± 4.41 μg/L), Pb from 9.35 to 159.3 μg/L (mean: 72.24 ± 9.14 μg/L), Ni from 6 to 109 μg/L (mean: 38.28 ± 5.34 μg/L), Mn from 3.85 to 153.80 μg/L (mean: 69.90 ± 11.13 μg/L), As from 1.95 to 72.90 μg/L (mean: 15.03 ± 3.53 μg/L), and Zn from 7.60 to 157.55 μg/L (mean: 75.03 ± 9.78 μg/L). The mean concentration of Cu in both wet and dry seasons was found below the limit recommended by WHO, USEPA and DoE. The concentration of Cr in surface water in both seasons were found a little higher than the limit set by WHO and DoE, but lower than that of USEPA. Cd and Pb concentrations were higher than all three recommended limits in both wet and dry seasons. The mean Ni concentration in both seasons were higher than WHO recommended limit, but considerably lower than USEPA and DoE recommendation.

Table 4.4 Comparison of heavy metal concentrations in the surface water samples with permissible limit recommended by WHO, USEPA and DoE.

Location	Season	Concentration (µg/L)							
		Cu	Cr	Cd	Pb	Ni	Mn	As	Zn
L-1	Wet	30.55	28.70	2.48	36.39	30.75	28.20	6.68	33.45
	Dry	40.30	36.05	5.55	42.20	38.85	36.70	6.13	40.45
L-2	Wet	24.90	52.78	3.43	24.68	41.45	39.15	9.65	46.90
	Dry	28.75	56.78	6.68	30.65	27.30	25.15	14.10	28.9
L-3	Wet	41.63	22.38	3.80	27.38	23.43	18.38	0.60	28.63
	Dry	30.48	28.63	4.85	32.38	29.03	26.88	2.55	30.63
L-4	Wet	53.28	58.85	7.48	32.03	32.58	25.03	6.03	35.23
	Dry	37.13	65.10	8.70	39.03	35.68	33.53	7.98	37.28
L-5	Wet	82.55	55.80	9.48	76.30	39.35	79.30	17.30	88.80
	Dry	91.40	67.05	15.23	93.30	39.95	87.80	39.25	91.55
L-6	Wet	68.63	44.23	25.15	89.88	20.43	117.88	13.38	65.63
	Dry	129.98	48.03	25.88	131.88	13.53	126.38	15.33	130.13
L-7	Wet	63.73	64.48	20.15	58.65	46.63	57.98	10.98	68.23
	Dry	70.08	70.73	33.15	71.98	53.63	66.48	17.93	70.23
L-8	Wet	68.90	91.90	29.15	67.65	57.85	65.65	9.48	68.40
	Dry	77.75	119.40	49.65	79.65	76.30	74.15	13.10	77.90
L-9	Wet	48.63	42.13	24.70	52.70	29.90	133.75	6.15	72.60
	Dry	91.13	58.13	40.20	126	34.35	142.25	18.20	115.75
L-10	Wet	92.05	66.65	23.63	55.88	21.05	83.65	13.80	95.83
	Dry	75.37	75.15	32.13	75.38	34.15	79.65	15.75	127.5
Range	Wet	24.90-92.05	22.38-91.90	2.48-29.15	24.68-89.88	20.43-57.85	18.38-133.75	0.60-17.30	28.65-95.83
	Dry	28.75-129.98	28.63-119.40	4.85-49.65	30.65-131.88	13.53-76.30	25.15-142.25	2.55-39.25	28.90-130.13
Mean ± SE	Wet	57.49 ± 6.87	52.79 ±6.32	14.95 ±3.34	52.15 ±6.93	34.34 ±3.81	64.90 ±12.44	9.41 ±1.52	60.37 ±7.39
	Dry	67.24 ±10.40	62.51 ±7.89	22.20 ±5.12	72.25 ±11.68	38.28 ±5.31	69.90 ±12.97	15.03 ±3.15	75.03 ±12.68
WHO, 2017; 1996		2000	50	3	10	7	100	10	3000
USEPA, 2017-2018		1300	100	2	15	100	50	50	5000
DoE, 2002, 2016		100	50	5	50	100	100	50	5000

World Health Organization (WHO, 2017; 1996),
United States of Environmental Protection Agency (USEPA, 2017-2018)
Department of Environment (DoE) Bangladesh (2002; 2016).

The mean concentration of Mn in both seasons were found higher than USEPA limit, but below the recommended limit of both WHO and DoE. The mean As

concentration crossed the WHO limit only in dry season. Zinc concentration in both seasons were observed much lower than all standard limits.

Fig. 4.11-4.19 illustrate the concentrations of Cu, Cr, Cd, Pb, Ni, Mn, As and Zn in the surface water samples collected from the estuaries of selected khals feeding to Karnaphuli river during the wet and dry seasons.

Copper (Cu):

The mean concentration of Cu in the surface water of estuaries connected to the Karnaphuli river, as detailed in Table 4.4, was recorded at 57.49 ± 6.87 μg/L during the wet season and 67.24 ± 10.40 μg/L in the dry season. Notably, these values remain within the acceptable limits established by the WHO (2017), USEPA (2017), and DoE (2016) for surface water quality. In a related study, Eliku and Leta (2018) observed significant seasonal variations in Cu concentrations, ranging from 0.82 μg/L to 1.69 μg/L in the dry season and 0.44 μg/L to 1.01 μg/L in the wet season. Their findings indicate that Cu levels exceeded the USEPA (2017) standard limit of 1.3 μg/L during the dry season.

The analysis illustrated in Fig. 4.11 shows that Cu concentrations in the surface waters of estuaries feeding into the Karnaphuli river are markedly higher during the dry season than in the wet season. This seasonal disparity is likely due to the increased dilution effect during the wet season, as higher runoff reduces Cu concentrations. Aigberua and Ayobami (2017) found similar patterns in their research, further supporting this observation.

According to Table 4.4, the highest Cu concentration during the wet season was 92.5 μg/L, recorded at the estuary of location 10 (Ichanogor Khal), while the lowest was 24.90 μg/L at location 2 (Ispahani Khal). Locations 4 through 9 also exhibited elevated concentrations, ranging from 48.63 μg/L to 82.55 μg/L, in contrast to the lower levels at locations 1 and 3, which recorded 30 μg/L and 41.63 μg/L, respectively. The notably high Cu concentrations at locations 10 (Ichanogor

Khal) and 8 (FMC Dockyard Khal) during the wet season are likely attributable to domestic and agricultural activities in these regions. This conclusion is reinforced by Fadillah et al. (2023), who identified agricultural activities, livestock manure, domestic activities, traffic, and mechanical workshops as significant sources of copper pollution.

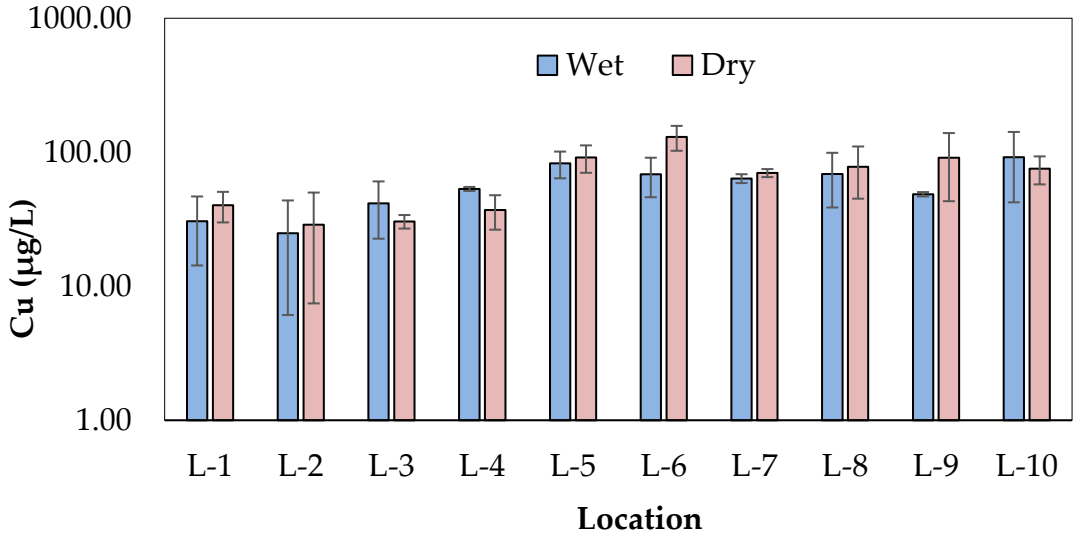


Fig 4.11: Concentration of Cu in the surface samples water during wet and dry seasons

In the dry season, the highest Cu concentration in surface water was observed at location 6 (Mohesh Khal) with 129.98 µg/L, while the lowest was at location 2 (Ispahani Khal) with 28.75 µg/L. Other locations, including 5 and 7 through 9, also showed elevated Cu concentrations, with the exception of locations 1, 3, and 4. The increased Cu levels at location 6 (Mohesh khal) and other khals (locations 5 and 7-9) are likely linked to domestic waste, Cu-based pesticides, and mechanical workshop activities common in these areas. Furthermore, the elevated Cu levels may result from processes such as sorption and desorption, contaminant leaching, and sewage leakage from urban runoff, as suggested by Kabir et al. (2020).

Chromium (Cr):

Cr, renowned for its powerful oxidizing capabilities and corrosive nature, is not only highly toxic but also extensively utilized in industries such as corrosion control, leather tanning, electroplating, and pigment production due to its effective properties (Hossain et al., 2021). According to Table 4.4, the mean concentration of Cr in the surface water of estuaries connected to the Karnaphuli river from the 10 studied khals was recorded at 52.79 ± 6.32 μg/L during the wet season and 62.51 ± 7.89 μg/L in the dry season. These Cr concentrations exceed the surface water quality standards set by WHO (2017, 1996), USEPA (2017-2018), and DoE (2002, 2016). Remarkably, Cr maintains a significant concentration in the surface waters of these estuaries across both seasons. Similarly, Lipy et al. (2021) reported substantial Cr levels during both wet and dry seasons, with mean concentrations of 2.59 μg/L and 3.35 μg/L, respectively, which were significantly higher than those in the present study and exceeded the DWSB, TRV, and WHO guidelines for surface water quality.

The data clearly indicate that the mean Cr concentration in the surface water of estuaries feeding into the Karnaphuli river is lower during the wet season than in the dry season as illustrated in Fig. 4.12. This seasonal variation could be attributed to the dilution effect from heavy rainfall and increased runoff, which likely decreases Cr concentrations during the wet season. Rakib et al. (2022) found that dissolved Cr concentrations ranged from 0.001 to 0.006 μg/L during the wet season and from 0.019 to 0.167 μg/L during the dry season, attributing the lower concentrations in the wet season to the dilution effects of large input discharges and precipitation.

Further examination of Table 4.4 reveals that among the estuaries of the 10 studied khals, the highest Cr concentration during the wet season was 91.9 μg/L at location 8 (FMC Dockyard khal), while the lowest was 22.38 μg/L at location 3 (Bolirhat khal). Nearly all other khals, except location 1 (West Kalurghat khal)

with 28.70 µg/L, exhibited higher Cr concentrations ranging from 42.13 µg/L to 66.65 µg/L. Commercially, Cr compounds are widely used in leather tanning, dyes and pigments, chrome plating, industrial welding, and wood preservation (Barnhart, 1997).

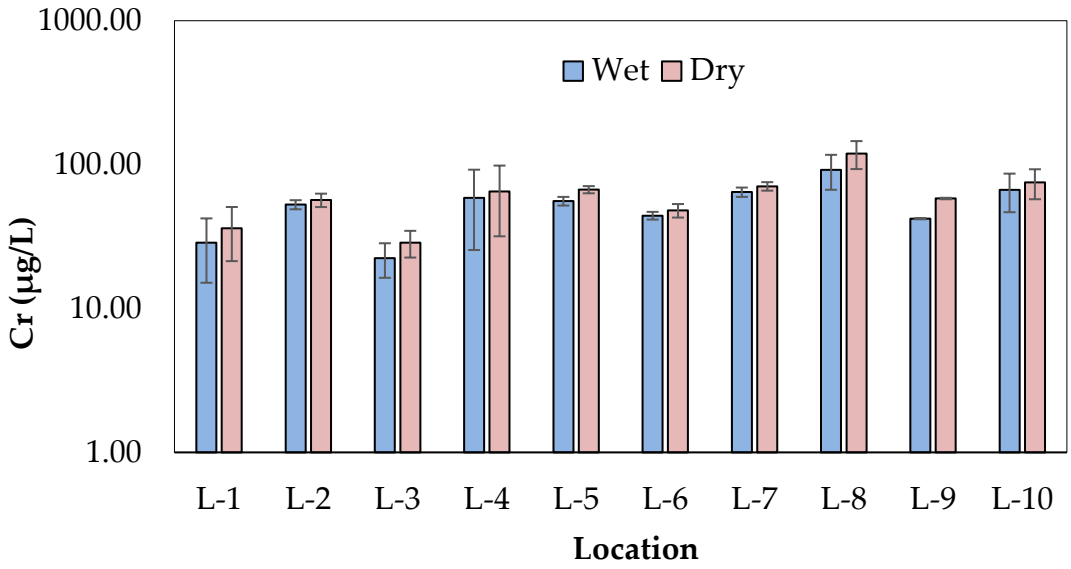


Fig 4.12: Concentration of Cr in the surface water samples during the wet and dry seasons

The elevated Cr concentrations in the surface water at the estuary of location 8 (FMC Dockyard khal) and other sampling areas during the wet season could be linked to tanneries, industrial waste, and shipping-related activities in these regions. This finding is consistent with Kumar et al. (2020), who observed elevated Cr levels in nearly all samples from the Ganga River in India, attributing this to significant tannery effluents, municipal waste, and industries related to laundry, paint, dye, and textiles.

During the dry season, the highest Cr concentration was recorded at 119.4 µg/L in the surface water at location 8 (FMC Dockyard khal), while the lowest was 28.63 µg/L at location 3 (Bolirhat khal). Locations 2, 4, 5, 9, and 10 also exhibited higher Cr concentrations, whereas locations 1 and 6 showed comparatively lower levels. The unexpectedly high Cr concentration in the surface water at location 8 (FMC Dockyard khal) could be attributed to the absence of rainfall, increased

discharge of industrial waste containing high levels of Cr, and shipbuilding activities in the area. This observation aligns with findings by Nguyen et al. (2023), who also reported elevated Cr levels during the dry season, attributing this to the lack of precipitation and increased human activities.

Cadmium (Cd):

Table 4.4 highlights the concerning levels of Cd concentration in the surface waters of estuaries connected to the Karnaphuli river. The study revealed that the mean Cd concentration was recorded at 14.95 ± 3.34 μg/L during the wet season and 22.20 ± 5.12 μg/L in the dry season. These values significantly exceed the surface water quality standards established by WHO (2017, 1996), USEPA (2017-2018), and DoE (2002, 2016), indicating substantial Cd pollution throughout the year. Similarly, Rakib et al. (2022) reported mean Cd concentrations of 0.032 μg/L during the wet season and 0.04 μg/L in the dry season in the Halda River, both of which surpass the maximum contaminant level (MCL) for drinking water set by USEPA (2020).

The data clearly demonstrate a higher mean Cd concentration in the surface water of these estuaries during the dry season compared to the wet season as shown in Fig. 4.13. This seasonal increase can be attributed to the reduced water flow and volume during the dry season, which results in less dilution and consequently higher concentrations of dissolved metals. Supporting this, Eliku and Leta (2018) observed a similar pattern, with a higher mean Cd concentration of 0.13 μg/L during the dry season compared to 0.06 μg/L during the wet season, linking this rise to diminished river flow and volume.

Further analysis of Table 4.4 reveals that among the estuaries of the 10 studied khals feeding into the Karnaphuli river, the highest Cd concentration during the wet season was recorded at 29.15 μg/L at location 8 (FMC Dockyard khal), while the lowest was 2.48 μg/L at location 1 (West Kalurghat khal). Locations 6, 7, 9,

and 10 also showed elevated Cd levels, whereas the remaining sites displayed concentrations below 10 μg/L. The significant Cd levels at location 8 during the wet season are likely due to the disposal of industrial waste, runoff from upstream agricultural activities involving cadmium-containing phosphate fertilizers, and untreated sewage disposal.

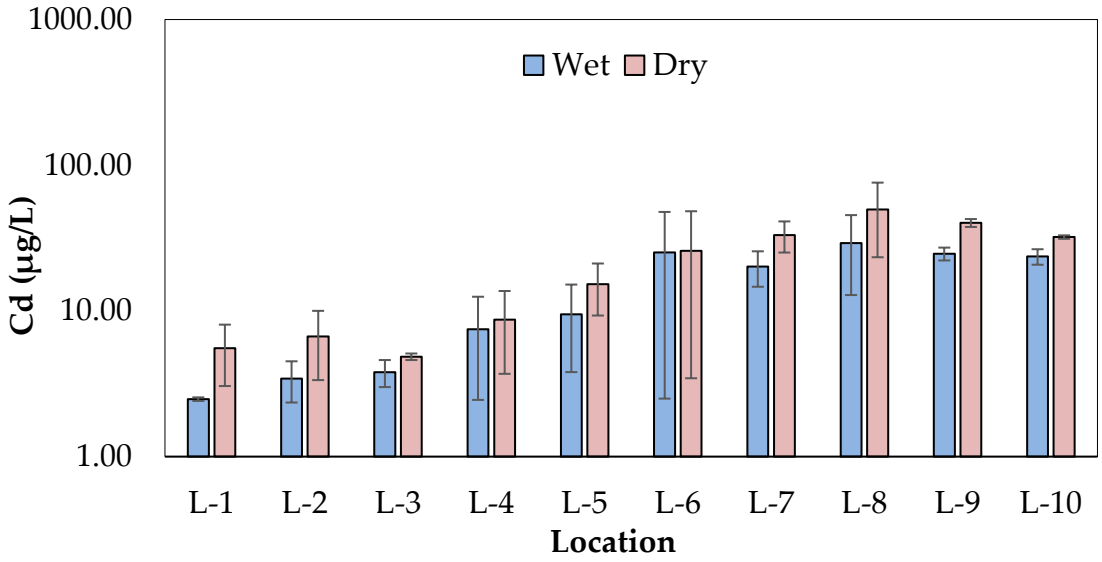


Fig 4.13: Concentration of Cd in the surface water samples during wet and dry seasons

In the dry season, the highest Cd concentration was observed at 49.65 μg/L in the sediment at location 8 (FMC Dockyard khal), with the lowest at 4.85 μg/L at location 3 (Bolirhat khal). Locations 5, 6, 7, 9, and 10 also exhibited elevated Cd concentrations, while the other sites maintained levels below 9 μg/L. This seasonal increase in Cd levels can be attributed to runoff from agricultural activities using Cd-containing fertilizers and pesticides, industrial waste, and shipbuilding activities, including painting, coating, and metal electroplating. Sanusi et al. (2024) echoed these findings, reporting elevated Cd levels during the dry season and attributing them to runoff from phosphate fertilizers, which contain Cd as a contaminant, and emissions from combustion processes.

Lead (Pb):

Table 4.4 provides crucial insights into the Pb concentrations in the surface water of estuaries from the 10 studied khals feeding into the Karnaphuli river. The mean Pb levels were recorded at 52.15 ±6.93 μg/L during the wet season and increased to 72.25 ±11.68 μg/L in the dry season, both of which exceed the standards set by the WHO (1996, 2017), USEPA (2017-2018), and DoE (2002, 2016) for Pb in surface water. In a related study, Mohanta et al. (2019) reported average Pb concentrations of 0.3782 ±0.01 μg/L during the wet season and 0.1649 ±0.01 μg/L during the dry season, similarly surpassing WHO guidelines for Pb levels in water.

As shown in Fig. 4.14, the data reveal a clear seasonal variation, with Pb concentrations being higher in the dry season compared to the wet season. This seasonal increase in Pb concentration during the dry season can be attributed to the reduced dilution effect, as heavy rainfall during the wet season typically dilutes the concentration of pollutants in river water. This observation is consistent with the findings of Islam et al. (2023), who also reported elevated Pb levels during the dry season and attributed the increase to reduced water flow and dilution capacity in the river.

Further examination of Table 4.4 shows that among the 10 studied khals, the highest Pb concentration during the wet season was observed at 89.88 μg/L in the surface water of the estuary at location 6 (Mohesh khal), while the lowest concentration was 24.68 μg/L at location 2 (Ispahani khal). Locations 5, 7, and 8 also recorded higher Pb concentrations, whereas the remaining locations exhibited lower Pb levels, generally below 37 μg/L. The elevated Pb concentration at location 6 (Mohesh khal) and other high-Pb locations is likely due to industrial discharges, particularly from marine workshops and municipal waste in the area. This notion is supported by the findings of Okon et al. (2019), who linked higher Pb levels in urban rivers to runoff carrying significant amounts of Pb from traffic emissions and industrial waste.

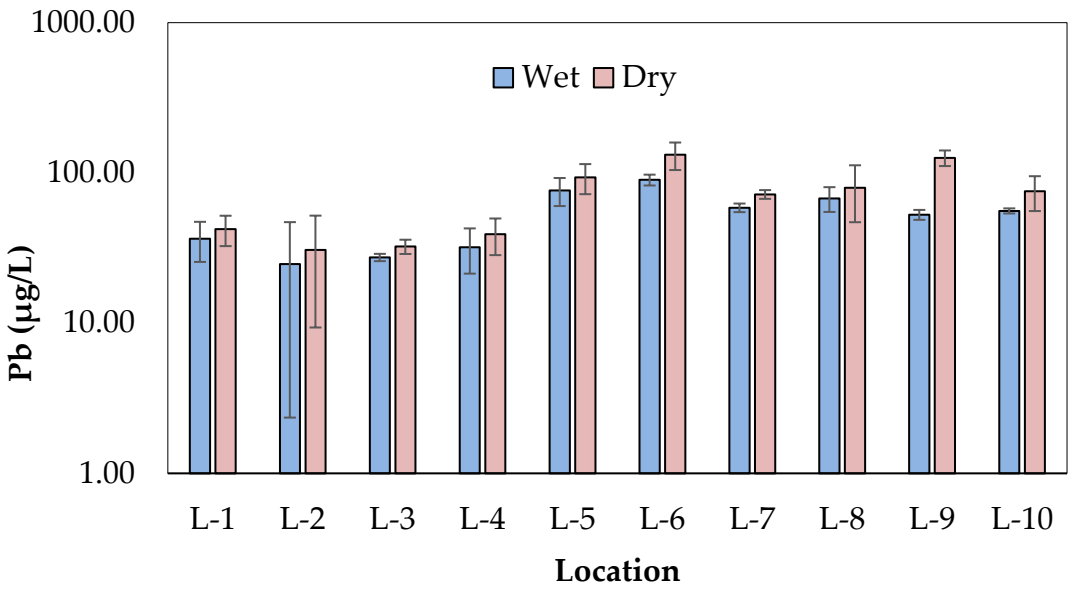


Fig 4.14: Concentration of Pb in the surface water samples during wet and dry seasons

During the dry season, Pb concentrations peaked at 131.88 µg/L in the surface water of the estuary at location 6 (Mohesh khal), with the lowest concentration of 30.65 µg/L again recorded at location 2 (Ispahani khal). Notably, location 9 (Shikolbaha khal) exhibited an exceptionally high Pb concentration of 126 µg/L, along with elevated levels at locations 5, 7, 8, and 10, while other locations showed much lower concentrations, generally below 43 µg/L. The highest Pb concentration at location 6 and the exceptionally high levels at location 9 (Shikolbaha khal) can be attributed to industrial waste discharges, particularly from marine workshops, dyeing facilities, and cement factories in these areas. These findings are in line with the study by Lipy et al. (2021), which reported elevated Pb levels in the surface water of the Dhaleshwari River in Bangladesh, attributing the pollution to industrial discharges from nearby areas.

Nickel (Ni):

The analysis in Table 4.4 shows that the mean concentration of Ni in the surface water of estuaries from ten studied khals feeding into the Karnaphuli river was recorded at 34.34 ± 3.81 µg/L during the wet season and 38.28 ± 5.31 µg/L in the

dry season. Notably, Ni levels in both seasons exceed WHO standards from 1996 and 2017 but remain within the limits established by USEPA (2017-2018) and DoE (2002, 2016). Kormokar et al. (2023) similarly found elevated Ni concentrations, with 189 µg/L during the dry season and 154 µg/L in the wet season, levels significantly higher than various drinking water reference standards, including DWSB, EuC, and WHO.

The discussion above, along with Fig. 4.15, indicates that mean Ni concentration in the estuaries of the ten khals feeding into the Karnaphuli river is higher during the dry season compared to the wet season. This increase is likely due to reduced water flow and volume in the river during the dry season, leading to higher pollutant concentrations. Similar findings were reported by Eliku and Leta (2018) in their study on the Awash River in Ethiopia, where heavy metal concentrations, including Ni, were significantly higher during the dry season due to decreased water flow and dilution.

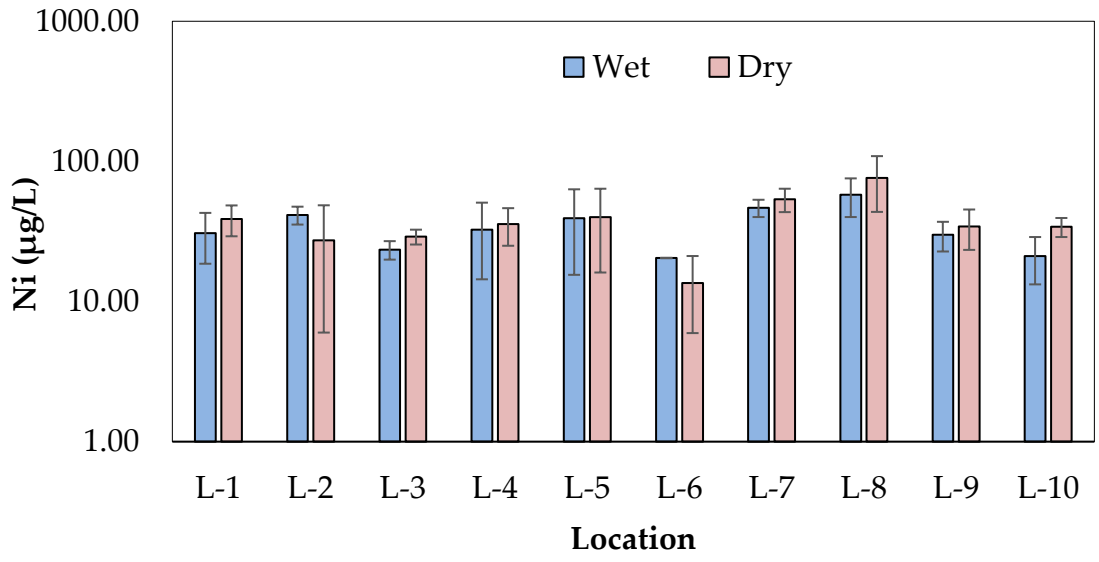


Fig 4.15: Concentration of Ni in the surface water samples during wet and dry seasons

Table 4.4 also shows that during the wet season, the highest Ni concentration was recorded at 57.85 µg/L in the surface water of the estuary at location 8 (FMC

Dockyard khal), while the lowest was 20.43 μg/L at location 6 (Mohesh khal). Most other khals, except locations 3, 9, and 10, exhibited comparatively higher Ni concentrations. This elevated Ni level in certain areas is likely due to industrial activities such as stainless steel production, shipbreaking, and the dumping of rechargeable batteries. This observation aligns with the findings of Raknuzzaman (2018), who also linked elevated Ni levels in surface water to industrial discharges from activities like steel manufacturing, shipbreaking, and metal ceramics production in the area.

During the dry season, the highest Ni concentration was recorded at 76.30 μg/L in the surface water of the estuary at location 8 (FMC Dockyard Khal), while the lowest was 13.53 μg/L at location 6 (Mohesh Khal). Most other khals recorded Ni concentrations below 40 μg/L, except for a notably higher concentration of 53.63 μg/L at location 7 (MAF Newsprint Khal). The elevated Ni levels during the dry season at these locations could be associated with reduced water volume, coupled with increased discharge from metal plating, shipbuilding activities, industrial wastewater, and domestic waste upstream. These findings are consistent with the study by Ahamad et al. (2020), which also attributed the rise in heavy metals, including Ni, in surface water to heightened anthropogenic activities such as brick production, excavation, and power generation.

Manganese (Mn):

Table 4.4 shows that the mean concentration of Mn in the surface water of estuaries from ten studied khals feeding into the Karnaphuli river was recorded at 64.90 ± 12.44 μg/L during the wet season and 69.90 ± 12.97 μg/L in the dry season. The Mn levels in both seasons remain within the permissible limits set by WHO (2017, 1996), USEPA (2017-2018), and DoE (2002, 2016). Akter et al. (2019) reported similar findings, with Mn concentrations in river water ranging from

0.003 µg/L to 0.016 µg/L in the wet season and 0.014 µg/L to 0.062 µg/L in the dry season, all within the standards set by ECR (1997).

The discussion above and Fig. 4.16 reveal that that Mn concentrations in the estuaries of the ten khals feeding into the Karnaphuli river are higher during the dry season compared to the wet season.

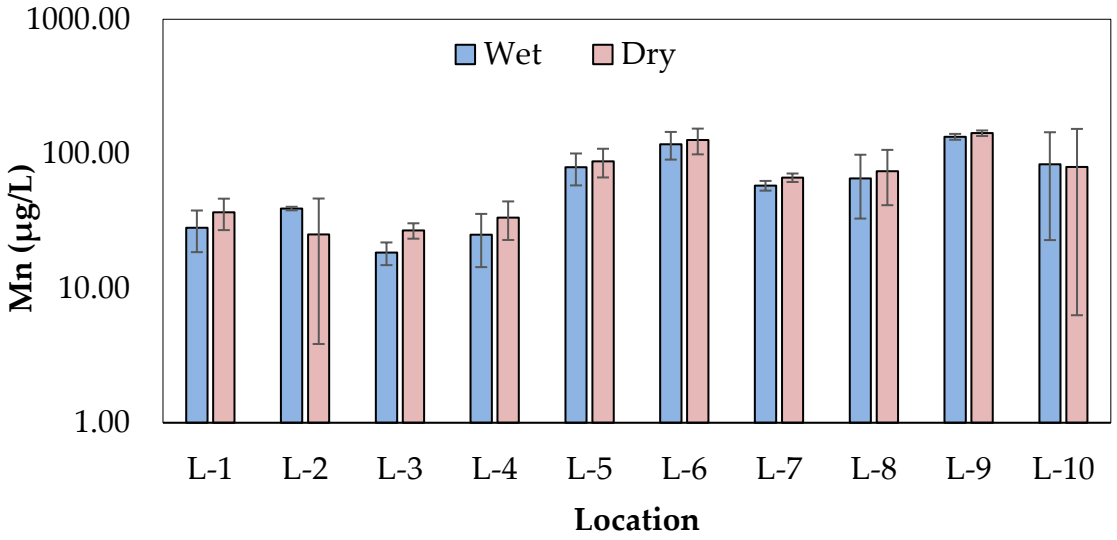


Fig 4.16: Concentration of Mn in the surface water samples during wet and dry seasons

This increase is likely due to reduced water volume and lack of rainfall during the dry season, leading to a concentration of Mn. Similar findings were observed by Edokpayi et al. (2017), who also noted elevated Mn levels during the dry season, attributing this to reduced water flow and increased evaporation from water bodies.

Table 4.4 further indicates that during the wet season, the highest Mn concentration was recorded at 133.75 µg/L in the sediment of the estuary at location 9 (Shikolbaha Khal), while the lowest was 18.38 µg/L at location 3 (Bolirhat Khal). Locations 5, 7, 8, and 10 also showed relatively higher Mn concentrations, with a notably high level of 117.88 µg/L at location 6 (Mohesh Khal). The elevated Mn levels at location 9 can be attributed to increased

industrial waste, agricultural runoff, and untreated dye wastewater in the area. This observation aligns with the findings of Haidar et al. (2022), who linked higher Mn concentrations to industrial activities, intensive agriculture, urbanization, and tourism.

During dry season, the highest Mn concentration was recorded at 142.25 μg/L in the surface water of the estuary at location 9 (Shikolbaha Khal), while the lowest was 25.15 μg/L at location 2 (Ispahani Khal). Most other locations showed higher Mn concentrations, with an exceptionally high level of 126.38 μg/L at location 6 (Mohesh Khal), while the remaining khals displayed much lower Mn levels. The elevated Mn concentrations in these estuaries, particularly at location 9, can be attributed to untreated industrial effluent from dye factories and agricultural waste containing Mn-based fertilizers and pesticides. This observation is supported by the findings of Edokpayi et al. (2017), who linked elevated Mn levels in the surface water of the Spekboom River to industrial activities, fossil fuel use, and the application of Mn-containing fertilizers, pesticides, varnishes, fungicides, and livestock feed supplements in the area.

Arsenic (As):

Table 4.4 illustrates the mean concentration of As in the surface water of estuaries from 10 studied khals feeding into the Karnaphuli river, recorded at 9.41 ±1.52 μg/L during the wet season and 15.03 ± 3.15 μg/L in the dry season. While the As levels during both seasons fall within the permissible limits set by the USEPA (2017-2018) and DoE (2002, 2016), the dry season's mean concentration exceeds the WHO (2017; 1996) guidelines. Similarly, Pari-Huaquisto (2020) observed As concentrations with maximum values of 0.331 mg/L in the rainy season and 0.765 mg/L in the dry season, both of which exceeded water quality standards (WQS) for human consumption, irrigation, and livestock.

The discussion above and Fig. 4.17 illustrate that the mean As concentration in the estuaries feeding into the Karnaphuli river is lower during the wet season compared to the dry season. This can be attributed to the dilution effect of heavy rainfall during the wet season, which reduces As concentrations. Lipy et al. (2021) support this observation, noting an elevated As level of 0.75 μg/L during the dry season, compared to 0.41 μg/L in the wet season, attributing the lower wet season concentration to the dilution effect from monsoon rains in Bangladesh.

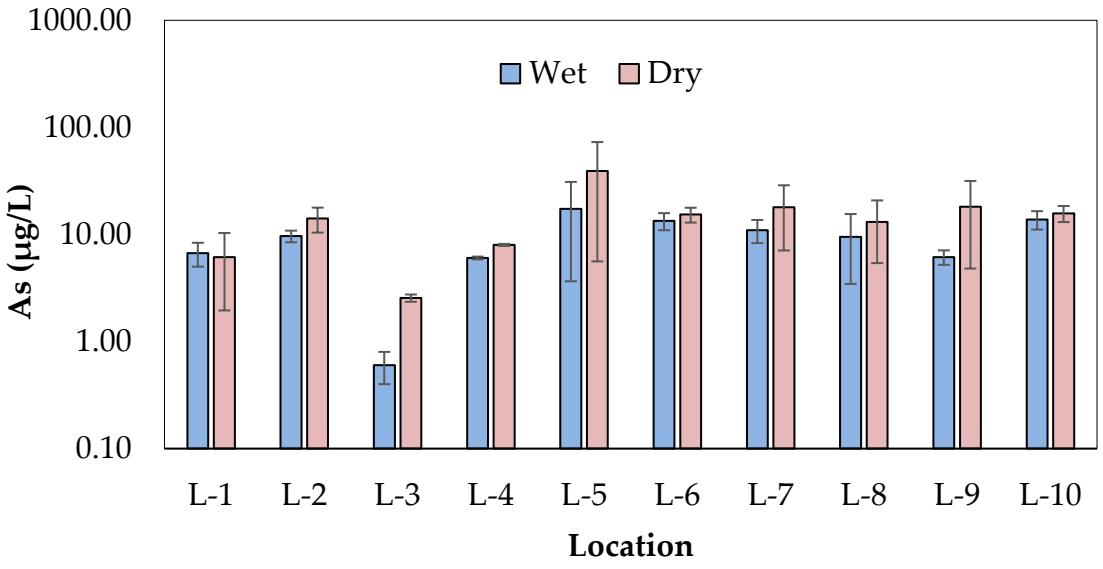


Fig 4.17: Concentration of As in the surface water samples during wet and dry seasons.

Further analysis of Table 4.4 shows that during the wet season, the highest As concentration was 17.30 μg/L, recorded at the estuary of location 5 (Custom Khal), while the lowest was 0.60 μg/L at location 3 (Bolirhat khal). Most estuaries showed relatively higher As concentrations below 14.0 μg/L. The elevated As concentration at location 5 could be linked to increased runoff from upstream areas, which carries As-based pesticides and fertilizers used in agriculture, as well as industrial effluents related to metal welding and painting, particularly from the ship-breaking industry in the area. Gunes et al. (2022) corroborate this by linking elevated As levels in the surface water of the Bartin River to leakages

from irregular solid waste landfills, as well as fertilizers and pesticides used in nearby agricultural fields.

During the dry season, the highest As concentration was recorded at 39.25 μg/L at the estuary of location 5 (Custom khal), while the lowest was 2.55 μg/L at location 3 (Bolirhat khal). The increased As concentration in the dry season can be attributed to reduced water volume, coupled with industrial discharges related to metal plating and agricultural runoff. This is supported by Fu et al. (2014), who linked elevated As levels in surface water to anthropogenic activities, such as the use of arsenical pesticides and fertilizers in agricultural practices.

Zinc (Zn):

Table 4.4 reports that the mean concentration of Zn in the surface water of estuaries from ten studied khals feeding into the Karnaphuli river was 60.37 ± 7.39 μg/L during the wet season and 75.03 ± 12.68 μg/L in the dry season. These Zn levels in both seasons fall within the permissible limits established by WHO (2017, 1996), USEPA (2017-2018), and DoE (2002, 2016) for surface water quality. In contrast, Kormokar et al. (2023) observed significantly higher Zn concentrations in the Buriganga River, Bangladesh, with levels reaching 320 μg/L during the dry season and 293 μg/L in the wet season, both exceeding the standards recommended by DWSB and WHO.

The data depicted in Fig. 4.18 indicate that Zn concentrations in the estuaries of the ten khals feeding into the Karnaphuli river are higher during the dry season than in the wet season. This increase can be attributed to reduced water levels and flow during the dry season, leading to a decrease in water volume and a corresponding rise in Zn concentration. Haque (2019) made a similar observation, noting that low water levels and insufficient flow during the dry season hindered the dilution of sewage sludge and industrial effluents from septic tanks and metal industries, resulting in an accumulation of metal concentrations in river water under low-flow conditions.

Further analysis of Table 4.4 reveals that, among all the estuaries of the studied khals, the highest Zn concentration during the wet season was recorded at 95.83 µg/L in the surface water of the estuary at location 10 (Ichanogor khal), while the lowest was 28.63 µg/L at location 3 (Bolirhat khal). Most of the other estuaries also showed relatively higher Zn concentrations, except for locations 1 and 4.

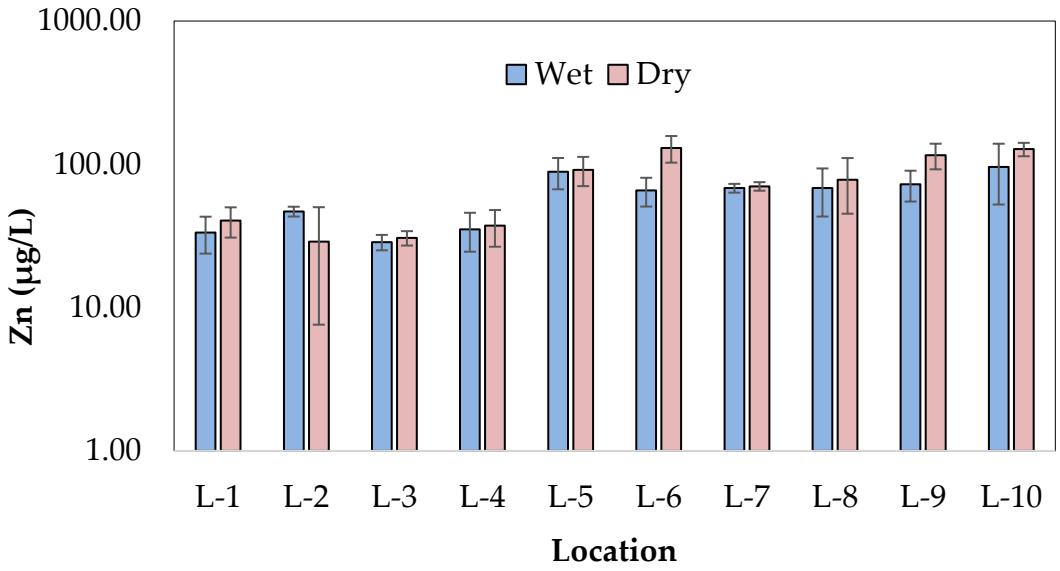


Fig 4.18: Concentration of Zn in the surface water samples during wet and dry seasons.

The elevated Zn levels at location 10 can be attributed to the presence of industrial settlements, drainage networks, and waste from agricultural runoff, along with activities such as brick manufacturing, dredging, power production, transporting industrial emissions, galvanizing, refining, sludge disposal, and energy production in the area. These findings are supported by Akter et al. (2019), who also observed elevated Zn levels in the surface water of the Meghna River in Bangladesh and linked them to effluent discharge from textile industries, pollution from brick kilns, waste dumping, and agricultural runoff.

The highest Zn concentration was recorded at 130.13 µg/L in the surface water of the estuary at location 6 (Mohesh khal), while the lowest was 28.9 µg/L at location 2 (Ispahani khal) during the dry season. Most other estuaries also showed

elevated Zn levels, with the exception of locations 1, 3, and 4. The higher Zn concentration at location 6 can be attributed to the increased discharge of industrial effluent, galvanizing activities, marine workshops, and domestic wastewater. This observation aligns with the findings of Kormokar et al. (2023), who attributed elevated Zn levels in river surface water to increased anthropogenic activities, including brick manufacturing, dredging, power production, industrial emissions, galvanizing, refining, sludge disposal, and energy production in the area.

Fig. 4.19 shows a comparison between mean concentrations of Cu, Cr, Cd, Pb, Ni, Mn, As and Zn in the surface water samples at the estuaries of different khals feeding to Karnaphuli river during wet and dry seasons. This figure also reveals that the water flows through the studied khals contains more heavy metals in dry season than in wet season.

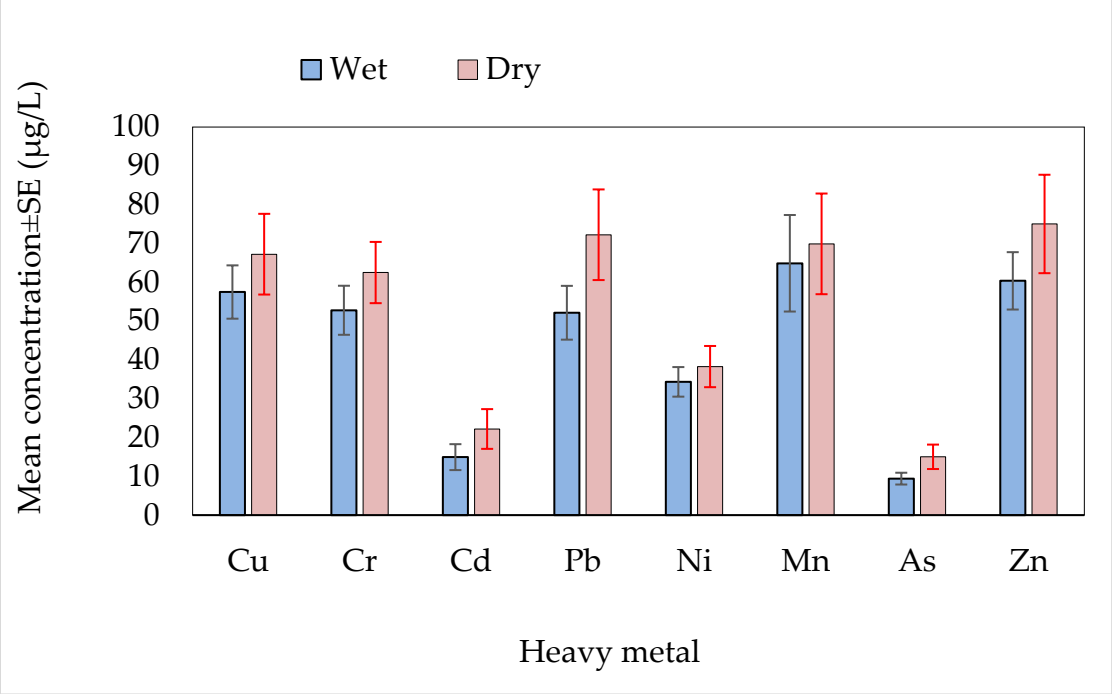


Fig. 4.19: Mean concentrations of Cu, Cr, Cd, Pb, Ni, Mn, As and Zn in the surface water samples during wet and dry seasons

4.2.2 Comparison of Heavy Metals Concentration in Surface Water of the Present Study with Some Other Studies

A comparison of the mean heavy metal concentration in the surface water at the estuaries of ten studied khals feeding into the Karnaphuli river during wet and dry season with some other selected national and international rivers is shown in Table 4.5.

Table 4.5: Heavy metal content in surface water in the present study and results of similar work reported in literature

Water	Heavy metals (mg/L)								References
	Cu	Cr	Cd	Pb	Ni	Mn	As	Zn	
Karnaphuli River (dry)	0.0652	0.0625	0.0222	0.0722	0.0382	0.0699	0.0150	0.0750	Present study
Karnaphuli River Bangladesh (wet)	0.0574	0.0527	0.0149	0.0521	0.0343	0.0649	0.0094	0.0603	Present study
Korotoa River (wet)	NS	0.078	0.007	0.067	NS	NS	0.069	NS	Hasan et al., 2024
Korotoa River (dry)	NS	0.102	0.013	0.078	NS	NS	0.082	NS	Hasan et al., 2024
Turag River Bangladesh	0.007	NS	0.002	0.01	NS	5.8	NS	3.35	Bhuyan et al., 2022
Balu River Bangladesh	0.03	NS	0.002	0.007	NS	12.01	NS	3.26	Bhuyan et al., 2022
Halda River Bangladesh (wet)	NS	0.004	0.032	0.030	NS	NS	1.34	NS	Rakib et al. (2022)
Halda River Bangladesh (dry)	NS	0.060	0.04	0.104	NS	NS	1.07	NS	Rakib et al. (2022)
Old Brahmaputra River, Bangladesh	0.12	0.01	0.001	0.11	0.44	1.44	NS	0.01	Bhuyan et al. (2019)
Shitalakhya River, Bangladesh	NS	0.08	0.003	0.05	NS	NS	NS	NS	Islam et al. (2014)
Turag River, Bangladesh	NS	NS	0.01	0.002	NS	NS	NS	NS	Mokaddes et al. (2013)
Buriganga River, Bangladesh	NS	0.114	0.059	0.112	NS	NS	NS	NS	Mokaddes et al. (2013)
Nile River Egypt	0.07	0.03	NS	0.07	0.03	0.22	NS	0.13	Al-Afify & Abdel-Satar (2022)
Danjiangkou Reservoir, China	NS	0.0063	0.0117	0.0106	NS	NS	0.0111	NS	Li et al. (2008)

4.2.3 Environmental pollution assessment of heavy metals in the surface water

The environmental pollution impact of heavy metals in the surface water surface water at the estuaries of different khals feeding to Karnaphuli river during wet and dry seasons was assessed by applying the metal pollution index (MPI).

Metal pollution index (MPI)

The MPI for a particular location during wet and dry seasons was calculated by the sum of the ratios between the concentration of selected metals and their respective maximum allowable concentration (MAC). The contamination level was checked for understanding the pollution status of different stations using MPI. Table 4.6 shows the calculated metal pollution index (MPI) of different heavy metals in surface water at the estuaries of ten selected khals feeding to Karnaphuli river during wet and dry seasons.

Table 4.6. Metal pollution index (MPI) of surface water at ten different locations during wet and dry seasons

Q1	MPI in wet season	MPI in dry season
L-1	6.24	8.08
L-2	6.35	8.31
L-3	4.92	6.19
L-4	8.04	9.53
L-5	14.47	20.54
L-6	20.24	24.93
L-7	15.83	22.45
L-8	20.32	29.55
L-9	15.77	29.91
L-10	16.77	22.09
MPI = $\sum Ci/(MAC)i$	12.90	18.16

Water quality is categorised by Caerio et al. (2005) into six different classes on the basis of metal pollution index (MPI). According to their report, an MPI of < 0.3 represents very pure (Class I), 0.3–1.0 represents pure (Class II), 1.0–2.0 represents slightly affected (Class III), 2.0–4.0 represents moderately affected (Class IV), 4.0–6.0 represents strongly affected (Class V), and > 6.0 represents seriously affected (Class VI).

Table 4.6 indicates that metal pollution at the estuaries of different khals of Karnaphuli river is higher than maximum allowable limit, 6.0. On the basis of MPI values of heavy metals present in surface water at all the studied locations it can be considered that the water at all the points is strongly or seriously affected in both wet and dry seasons. The accumulation of heavy metals from agricultural runoff, municipal, industrial and sewage wastes are responsible for heavy metal pollution of water at the locations. Table 4.6 also showed that overall MPI values for wet and dry seasons were found as 12.90 and 18.16 respectively.

Fig. 4.20 shows that MPI values of water samples at all locations, except L-3 were above the maximum allowable concentration in the both seasons.

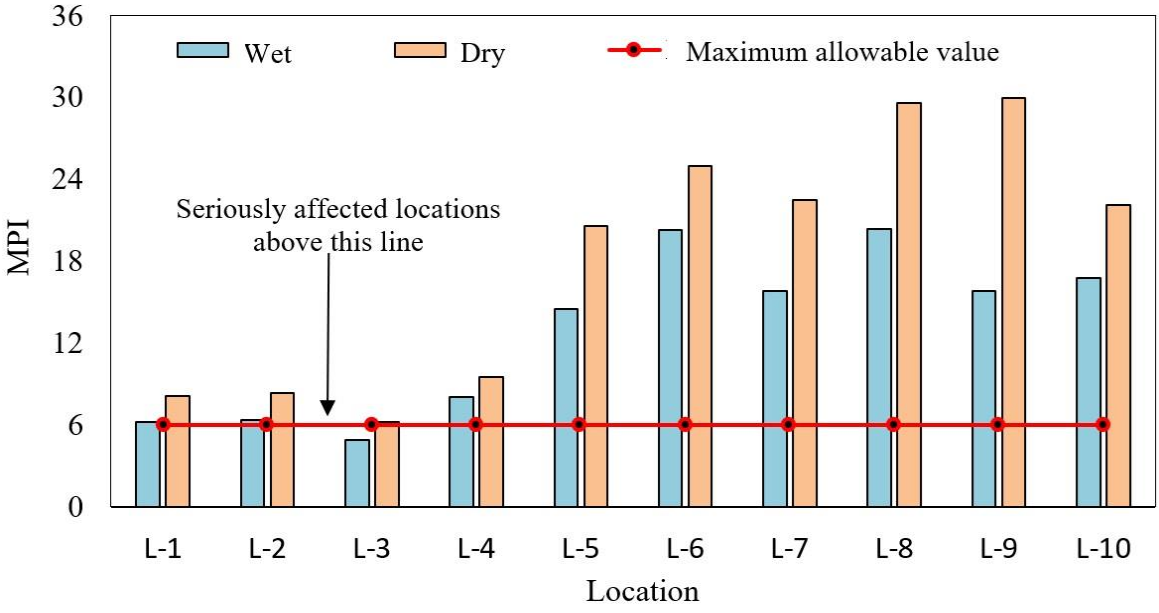


Fig. 4.20. Metal pollution index (MPI) of heavy metals for different locations during wet and dry seasons along with the maximum allowable limit

MPI results revealed that only L-3 (Bolirhat khal) during wet season stood in class V, which indicates a strongly affected area where all other locations during both wet and dry seasons were in class VI which means a seriously affected areas (Caerio et al., 2005). MPI results also indicates that the pollution level is very high at the L-5 to L-10 during both season. Fig. 4.20 also shows that the MPI values in dry season is remarkably higher than the corresponding MPI values in wet seasons at all locations.

4.2.4. Health Risk Assessment

4.2.4.1 Non-carcinogenic

The calculated mean exposure value of a non-carcinogenic health risk associated with dermal contact of heavy metals in surface water at the estuaries of different khals feeding to Karnaphuli river during wet and dry is presented in Table 4.7.

Table 4.7 Non-carcinogenic health risk assessment of heavy metals in surface water at the estuaries of different khals feeding to Karnaphuli river.

Heavy metals	RfDo (mg/Kg)	Exposure assessment	Non-carcinogenic risk
		CDI_{derm}	HQ_{derm}
Cu	4×10^{-2}	1.22×10^{-07}	1.95×10^{-06}
Cr	3×10^{-3}	1.1×10^{-07}	3.04×10^{-06}
Cd	1×10^{-3}	3.6×10^{-08}	3.63×10^{-08}
Pb	3.5×10^{-3}	1.2×10^{-07}	5.21×10^{-06}
Ni	1.1×10^{-2}	7.1×10^{-08}	8.59×10^{-08}
Mn	2.4×10^{-2}	1.3×10^{-07}	7.59×10^{-06}
As	3×10^{-4}	7.16×10^{-07}	5.80×10^{-05}
Zn	3×10^{-1}	1.3×10^{-07}	3.97×10^{-07}
HI_{derm}			6.95×10^{-05}

Note: CDI_{derm}= Chronic daily intake via dermal contact, HQ_{derm}=Hazard quotient via dermal contact, HI_{derm}= Hazard Index via dermal contact.

The HQ value showed the following order: Zn > Mn > Pb > Cr > Cu > As > Ni > Cd. The calculated HI_{derm} for each metal was found lower than 1 and the mean value (6.95×10^{-05}) of the investigated metals is also lower than 1 (USEPA, 2002). This indicates that there is no probability for potential non-carcinogenic health effects in the investigated surface water of khals feeding to Karnaphuli river through dermal contact.

4.2 Carcinogenic Health Risk Assessment

Table 4.8 illustrates the carcinogenic health risk calculated for some heavy metals in surface water collected from the estuaries of selected khals feeding to Karnaphuli river.

Table 4.8 Carcinogenic health risk of heavy metals in surface water of khals feeding to Karnaphuli river.

Heavy metals	CDI_{derm}	SF	Carcinogenic risk ($CDI_i \times SF_i$)
Cr	1.21×10^{-07}	0.5	2.25×10^{-07}
Cd	3.63×10^{-08}	15	2.42×10^{-09}
Pb	1.22×10^{-07}	0.0085	1.43×10^{-05}
As	7.16×10^{-07}	1.5	4.78×10^{-07}
LCR			1.50×10^{-05}

Table 4.8 shows that the carcinogenic risk for Cr, Cd, Pb, and As through adult dermal exposure falls within the acceptable range of 1×10^{-6} to 1×10^{-4}, indicating that lifetime cancer risk from these heavy metals in the study area remains within safe limits.

4.2.5 Pearson's Correlation Coefficient

Pearson's correlation coefficient matrix among the Cu, Cr, Cd, Pb, Ni, Mn, As and Zn in surface water at the estuaries of different khals feeding to Karnaphuli river during wet and dry seasons is shown in Table 4.9.

Table 4.9 Pearson's correlation coefficient matrix among the water quality parameters of surface water of khals feeding to Karnaphuli river.

Heavy metals	Cu	Cr	Cd	Pb	Ni	Mn	As	Zn
Cu	1							
Cr	0.40	1						
Cd	**0.71***	**0.68***	1					
Pb	**0.93****	0.27	**0.71***	1				
Ni	-0.01	**0.76***	0.41	-0.04	1			
Mn	**0.81****	0.18	**0.72***	**0.93****	-0.15	1		
As	**0.67***	0.36	0.28	0.61	0.14	0.51	1	
Zn	**0.92****	0.38	**0.74***	**0.86****	-0.07	**0.87****	**0.67***	1

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

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

The relationship between the heavy metals indicates the sources and pathway of heavy metals in the investigated surface water samples. Pb shows significant positive correlation with Cu and Cd (r = 0.93 at $p < 0.01$ level; r = 0.71 at $p < 0.05$ level) whereas Cd is significantly correlated with Cu and Cr (r = 0.71, r = 0.68) at $p < 0.05$ level. Ni is also significantly correlated with Cr (r = 0.76) at $p < 0.05$ level. Significant positive correlation was observed between Mn with Cu, Pb and Cd (r = 0.81; r = 0.93 at $p < 0.01$ level; r = 0.72 at $p < 0.05$ level); As also showed significant correlation with Cu (r= 0.67 at p $p<0.05$ level). Zn showed significant positive correlation between with Cu, Pb, Mn, Cd and As (r = 0.92; r = 0.86, r = 0.87 at $p < 0.01$ level; r = 0.74 and r = 0.67 at $p < 0.05$ level). The high significant correlations

between heavy metals may reflect the fact that these heavy metals had similar pollution levels and similar pollution sources (Armah et al., 2010). On the other hand, the rest elemental pairs show no significant correlation with each other, suggesting that these metals are not associated with each other and lack of their identical behavior transport in the water samples of the aquatic environment.

4.3 Heavy Metals in Surface Sediments

4.3.1 Concentration of Heavy Metals in Surface Sediments

The concentrations of eight heavy metals—Cu, Cr, Cd, Pb, Ni, Mn, As, and Zn were systematically measured in surface sediment samples from two distinct points at the estuaries of khals feeding to the Karnaphuli river. Detailed data, including mean concentrations for both the wet and dry seasons, are presented in Appendices 5 and 6.

Table 4.10 provides a summary of the concentration ranges, mean values with standard errors, and the permissible limits as recommended by national and international bodies, including the Average Shale Value (ASV) from Turekian and Wedepohl (1961), and guidelines from the USEPA (2002, 2017, 2019).

During the wet season, the heavy metals were ranked in the following order based on their concentrations: Zn > Mn > Cr > Ni > Pb > Cu > Cd > As. Zinc showed the highest concentration, while arsenic had the lowest. The concentration ranges for Cu, Cr, Cd, Pb, Ni, Mn, As, and Zn in surface sediments during the wet season were 22.07-64.36, 23.26-74.86, 0.18-6.25, 22.67-71.81, 26.69-73.47, 46.95-76.95, 0.15-2.28, and 49.55-144.24 mg/Kg, respectively. The mean concentration along with standard error were found 38.83±2.60, 46.92±2.99, 2.18±0.34, 42.98±3.04, 43.39±2.89, 63.04±2.48, 1.34±0.17, and 91.93±5.94 mg/Kg respectively.

Table 4.10 Concentrations of Cu, Cr, Cd, Pb, Ni, Mn, As and Zn in surface sediments at the estuaries of different khals feeding to Karnaphuli river during wet and dry seasons.

Location	Season	Concentration (mg/Kg)							
		Cu	Cr	Cd	Pb	Ni	Mn	As	Zn
L-1	Wet	39.72	56.49	1.83	55.95	44.76	69.92	1.54	76.22
	Dry	49.07	57.75	2.19	53.88	67.74	44.42	0.59	121.86
L-2	Wet	51.93	27.5	1.03	27.93	49.88	49.69	1.66	56.48
	Dry	60.04	61.21	2.73	68.32	52.75	22.97	0.18	89.89
L-3	Wet	49.25	47.81	2.01	50.3	30.64	59.73	1.69	66.4
	Dry	55.9	55.63	2.33	58.88	68.21	77.93	0.74	83.52
L-4	Wet	28.04	41.36	1.34	49.44	51.57	65.47	1.39	79.69
	Dry	40.61	62.47	2.05	58.45	40.12	99.84	0.55	90.87
L-5	Wet	37.72	35.66	1.7	25.86	34.84	57.15	1.32	101.03
	Dry	37.75	55.8	3.44	53.5	48.52	89.81	0.48	87.88
L-6	Wet	35.68	39.1	3.62	31.38	36.82	62.54	1.73	93.18
	Dry	54.47	57.5	2.41	68.28	37.4	75.86	2.28	111.75
L-7	Wet	30.47	45.28	1.83	35.86	36.94	80.24	0.33	102.99
	Dry	53.97	50.76	2.32	47.5	33.04	45.55	0.99	98.18
L-8	Wet	58.86	70.66	5.40	63.28	69.32	57.85	2.25	139.62
	Dry	66.9	69.55	2.32	87.33	83.27	31.56	4.56	123.86
L-9	Wet	26.61	50.87	2.01	41.21	40.28	70.63	0.45	115.57
	Dry	50.5	57.92	2.23	43.5	36.66	51.14	5.59	119.66
L-10	Wet	30.08	54.48	1.07	48.58	38.83	57.15	1.03	88.11
	Dry	42.04	63.75	3.17	70.82	28.92	46.37	6.18	116.9
Range	Wet	26.61-58.86	27.50-70.66	1.03-5.40	25.86-63.28	30.64-69.32	49.69-80.24	0.33-2.25	56.48-139.62
	Dry	37.75-66.89	50.76-69.55	2.05-3.44	43.49-87.33	28.92-83.27	22.97-99.84	0.18-6.18	83.52-123.86
Mean ± SE	Wet	38.84± 3.50	46.92± 3.84	2.18± 0.42	42.98± 3.97	43.39± 3.55	63.04± 2.77	1.34± 0.19	91.93± 7.72
	Dry	51.13± 2.88	59.23± 1.65	2.52± 0.14	61.05± 4.09	49.66± 5.70	58.55± 8.11	2.21± 0.74	104.44± 5.02
ASV (average shale value) (Turekian and Wedepohl, 1961)		-	90	0.3	20	68	850	13	95
USEPA, 2002	Unpolluted	<25	-	-	<40	<20	-	-	<90
	Moderately	25-75	-	-	40-60	20-50	-	-	90-200
	Heavily polluted	>75	-	-	>60	>50	-	-	>200
USEPA, 2017; 2019		16	26	0.6	31	16	-	6	110

Fig. 4.21-4.28 refers the mean concentration of Cu, Cr, Cd, Pb, Ni, Mn, As and Zn in surface sediments at the estuaries of selected khals feeding to Karnaphuli river during wet and dry seasons.

Copper (Cu):

Table 4.10 reveals that the mean concentration of Cu in the sediment of estuaries connected to the Karnaphuli river from 10 studied khals was recorded at 38.84 ± 3.50 mg/Kg during the wet season and 51.13 ± 2.88 mg/Kg in the dry season. These concentrations fall within the moderately polluted range according to USEPA (2002) guidelines but exceed the acceptable limits set by USEPA in 2017 and 2019. Consequently, the river sediment is considered moderately polluted with Cu in both seasons. Similarly, a study by Mohanta et al. (2019) reported mean Cu concentrations in the sediment of the Dhaleshwari River at 88.63 ± 15.15 mg/Kg during the wet season and 176.904 ± 71.9 mg/Kg in the dry season, significantly surpassing the EPA TEL limits year-round, indicating consistent Cu pollution.

As illustrated in Fig. 4.21, the data clearly demonstrate that the mean Cu concentration in the sediment of the estuaries feeding into the Karnaphuli river is significantly higher during the dry season compared to the wet season. This seasonal increase could be attributed to reduced water levels and flow during the dry season, which accelerates the sedimentation of Cu-rich municipal and domestic wastes. Jewel et al. (2020) also observed elevated Cu concentrations in the sediment of the Ganges River during the dry season, attributing this to lower water flow, which results in the accumulation of higher metal concentrations, including Cu.

Further analysis of Table 4.10 indicates that among the estuaries of the 10 studied khals, the highest Cu concentration in the sediment during the wet season was 58.86 mg/Kgat location 8 (FMC Dockyard Khal), while the lowest was 26.61 mg/Kg at location 9 (Shikolbaha Khal). Locations 2 (Ispahani Khal) and 3 (Bolirhat

Khal) also exhibited higher concentrations, while the remaining locations displayed Cu concentrations ranging from 28.04 mg/Kg to 39.72 mg/Kg. The elevated Cu levels at locations 8, 2, and 3 can be linked to industrial discharges, urban runoff and agricultural practices using Cu-based pesticides and fertilizers, and effluents from wastewater treatment plants. This observation aligns with the findings of Effendi et al. (2021), who reported higher sediment Cu concentrations in the Donan River Estuary due to anthropogenic activities such as port operations, industrial activities, settlements, and agriculture.

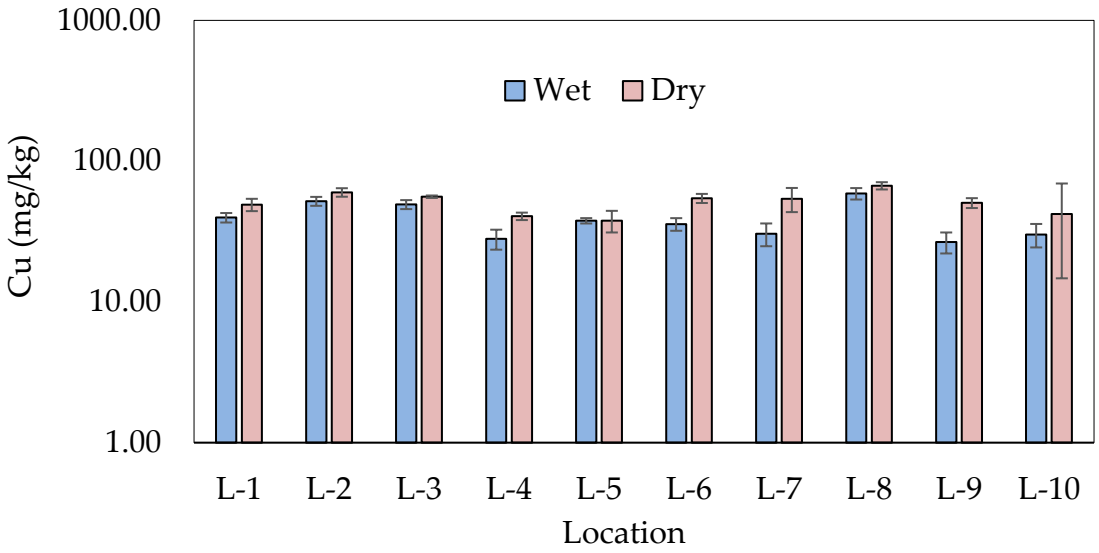


Fig. 4.21: Concentration of Cu in surface sediments during wet and dry seasons

During the dry season, the highest Cu concentration in sediment was recorded at 66.9 mg/Kg at location 8 (FMC Dockyard Khal), with the lowest at 37.75 mg/Kg at location 5 (Custom Khal). Other khals exhibited Cu concentrations ranging from 49.07 mg/Kg to 60.04 mg/Kg, while locations 4 (Muradpur Khal) and 10 (Ichanogor Khal) showed concentrations between 40.61 mg/Kg and 42.04 mg/Kg. The elevated Cu levels in these sediments are likely due to substantial industrial waste, including dyes from shipbuilding companies, and domestic sewage directly discharged into the river via these khals. This conclusion is supported by Masrura (2019), who found higher Cu levels in the sediment of the Turag River,

attributing them to industrial dye discharge and waste from local fish markets and domestic sewage.

Chromium (Cr):

The mean concentrations of Cr in the sediments samples collected from the estuaries of 10 studied khals feeding into the Karnaphuli river can be seen in Table 4.10. The concentrations were 27.50 ± 70.66 mg/kg during the wet season and 50.76 ± 69.55 mg/kg in the dry season, indicating significant Cr enrichment throughout both periods. Although these Cr levels fall within the Average Shale Value (ASV) limits established by Turekian and Wedepohl (1961), they exceed the standards set by the USEPA (2017, 2019). This finding aligns with the study by Lipy et al. (2021), who reported elevated Cr levels in the Dhaleshwari River sediments, with mean concentrations of 96.02 ± 18.13 mg/Kg in the wet season and 118.37 ± 30.08 mg/Kg in the dry season, both surpassing the TRV, TEL, and PEL thresholds.

The data shown in Fig. 4.22 highlight that Cr concentrations in the estuarine sediments of the studied khals feeding into the Karnaphuli river are significantly lower during the wet season than in the dry season. This reduction can likely be attributed to the dilution effect caused by heavy rainfall and increased water volume during the wet season. Supporting this, Jolly et al. (2023) observed a mean Cr concentration of 66.85 ± 0.53 mg/Kg during the wet season, which rose to 69.42 ± 0.56 mg/Kg in the dry season, attributing the lower wet season values to the dilution of pollutants by rainwater.

Further analysis of Table 4.10 reveals that the highest Cr concentration during the wet season was 70.66 mg/Kg in the sediment at the estuary of location 8 (FMC Dockyard Khal), while the lowest was 27.50 mg/Kg at location 2 (Ispahani Khal). Locations 1, 9, and 10 also exhibited elevated Cr levels, whereas the other khals showed comparatively lower concentrations. The significant Cr concentration at location 8 and other high-contributing khals during the wet season is likely due

to increased waste discharge from shipbuilding activities, along with domestic waste and sewage flowing into the estuary. This is corroborated by Nwoke et al. (2022), who reported higher Cr concentrations in river sediments during the wet season, attributing this to illegal petroleum trade and the washing of domestic waste and sewage into the river.

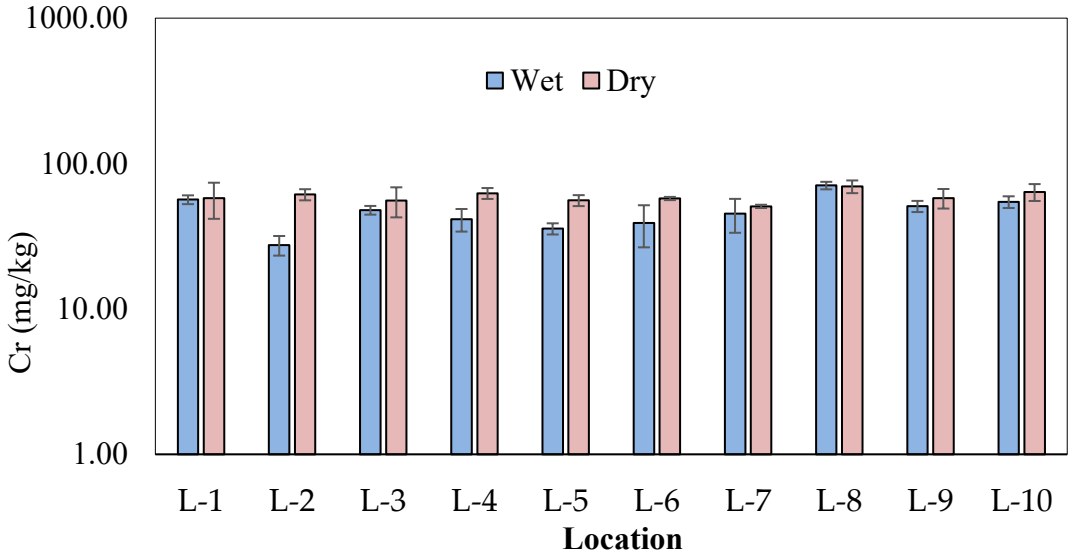


Fig. 4.22: Concentration of Cr in surface sediments during wet and dry seasons

In the dry season, the highest Cr concentration was recorded at 69.55 mg/Kg in the sediment of the estuary at location 8, while the lowest was 50.76 mg/Kg at location 7 (MAF Newsprint Khal). Other estuaries feeding into the Karnaphuli river also showed elevated Cr concentrations during this period. This increase can be linked to the reduced estuary volume due to evaporation and heightened waste discharge from the shipping industry and domestic sources. Nwoke et al. (2022) supports this, attributing the higher Cr concentrations in river sediments during the dry season to decreased river volume from evaporation, along with increased boating and commercial activities.

Cadmium (Cd):

Table 4.10 reveals significant findings regarding Cd concentrations in the sediments of estuaries from the 10 khals feeding into the Karnaphuli river. The

study measured mean Cd levels at 2.18 ± 0.42 mg/Kg during the wet season and 2.52 ±0.14 mg/Kg during the dry season, indicating substantial Cd enrichment across both seasons. Notably, these concentrations exceeded the Average Shale Value (ASV) limits established by Turekian and Wedepohl (1961) as well as the standards set by the USEPA (2017 and 2019). Similarly, Nyantakyi et al. (2019) observed a higher Cd concentration of 2.44 mg/Kg in sediments during the dry season, compared to a lower 0.182 mg/Kg during the wet season, with dry-season levels exceeding the maximum permissible Cd concentration in sediments as prescribed by the USEPA (2002), while wet-season levels remained within the guidelines.

The data presented in Fig. 4.23 reveal a clear seasonal variation, with mean Cd concentrations in the sediments of the estuaries being higher during the dry season compared to the wet season.

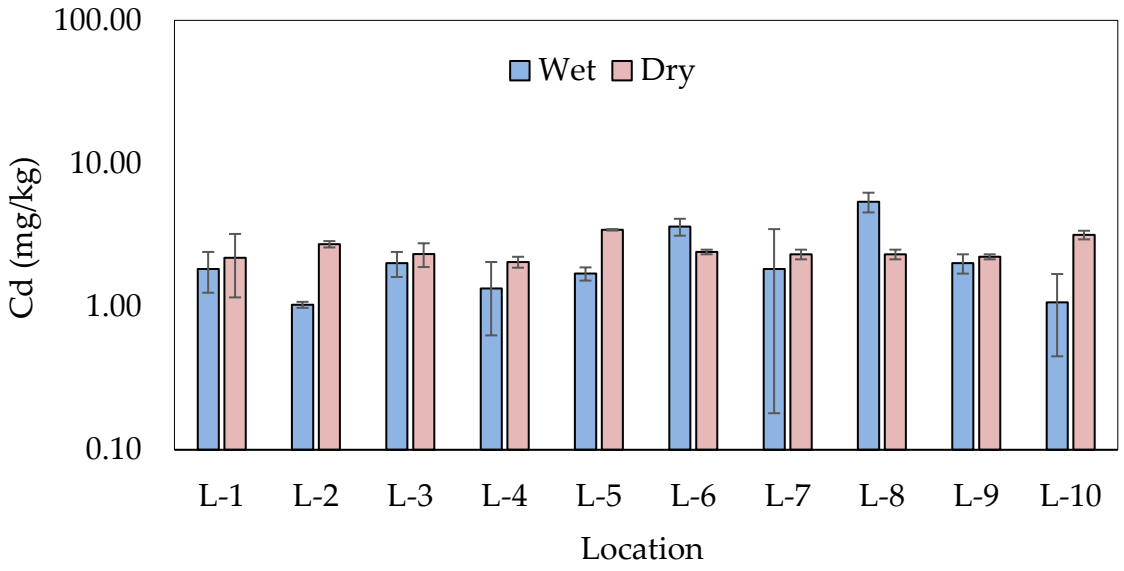


Fig. 4.23: Concentration of Cd in surface sediments during wet and dry seasons

This variation can be attributed to increased rainfall and subsequent river flow during the wet season, which effectively dilutes the Cd concentration in the sediment. This observation is corroborated by Yuan et al. (2022), who also reported lower Cd levels in sediment during the wet season compared to the dry

season, attributing this to the dilution effect of rainwater, which impacts both the concentration and mobility of heavy metals.

Further analysis of Table 4.10 shows that among the 10 studied khals, the highest Cd concentration during the wet season was recorded at 5.40 mg/Kg in the sediment of the estuary at location 8 (FMC Dockyard khal), while the lowest was 1.03 mg/Kg at location 2 (Ispahani khal). Other locations exhibited similar Cd concentrations, except for location 6 (Mohesh khal), where a concentration of 3.62 mg/kg was observed. The relatively higher Cd concentration in the sediment at location 8 during the wet season can be attributed to the increased flow of agricultural waste containing Cd from fertilizers and pesticides, as well as industrial waste discharge from shipping industry activities in the area. This finding aligns with the study by Proshad et al. (2019), which reported elevated Cd concentrations in the sediments of the Rupsa River in Bangladesh, attributing it to industrial activity, atmospheric emissions, and the use of Cd-plated items.

During the dry season, the highest Cd concentration was recorded at 3.44 mg/Kg in the sediment at location 5 (Custom khal), while the lowest was 2.05 mg/Kg at location 4 (Chaktai khal). Other locations exhibited similar Cd concentrations in the sediment of the estuaries feeding into the Karnaphuli river. The higher Cd concentration at location 5 can be linked to waste disposal from agricultural activities and mechanical workshops in the area. This observation is consistent with the findings of Lan et al. (2019), who reported increased Cd concentrations in river sediments, attributing them to sulfide weathering and agricultural activities in upstream areas.

Lead (Pb):

Table 4.10 reveals significant findings regarding the concentration of Pb in the sediments of estuaries from 10 studied khals feeding into the Karnaphuli river. The mean Pb concentrations were recorded at 42.98 ± 3.97 mg/kg during the wet season and increased to 61.05±4.09 mg/kg in the dry season. These concentrations

exceed the Average Shale Value (ASV) as defined by Turekian and Wedepohl (1961) and also surpass the standards set by the USEPA (2017, 2019). The sediment is categorized as moderately polluted during the wet season and heavily polluted during the dry season according to USEPA (2002) guidelines. A similar study by Madzlan et al. (2023) reported Pb concentrations peaking at 39.5 μg/g dry weight in the wet season and 92.9 μg/g dry weight in the dry season, both of which exceed the average background level of 17.0 μg/g dry weight.

The data shown in Fig. 4.24 clearly indicate that Pb concentrations in the sediment are significantly higher during the dry season than in the wet season.

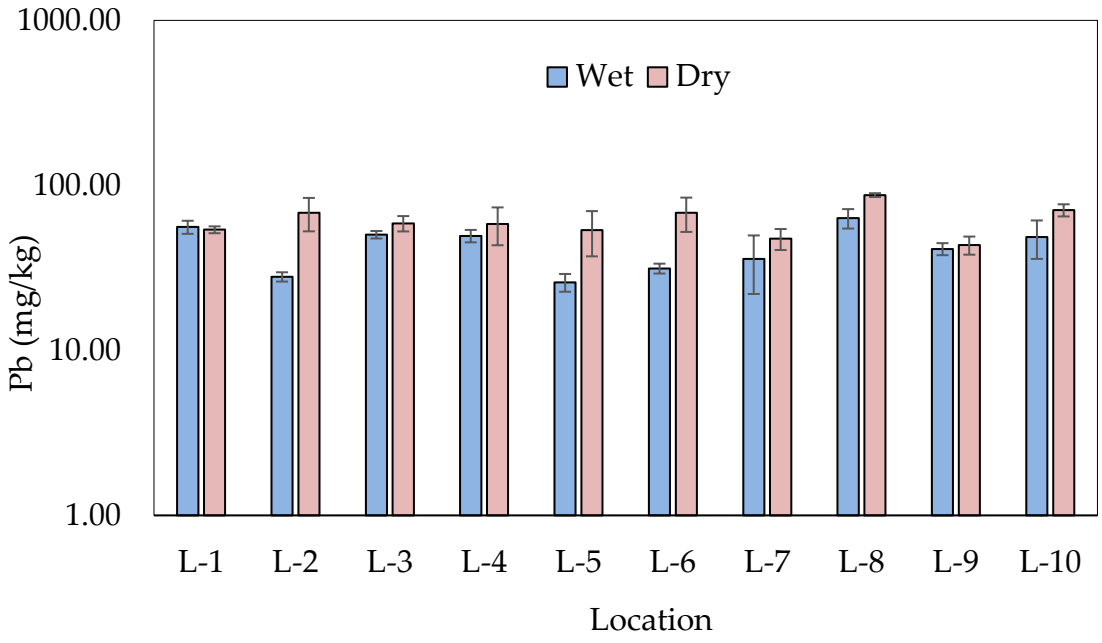


Fig. 4.24: Concentration of Pb in surface sediments during wet and dry seasons

This increase can likely be attributed to the reduction in river volume due to evaporation during the dry season, leading to less dilution of pollutants. This observation is supported by Nwoke et al. (2022), who found that the average Pb concentration in sediment was higher during the dry season (3.39 ± 0.05 mg/kg) compared to the wet season (3.21 ± 0.07 mg/kg), attributing this to decreased river volume caused by evaporation.

Further analysis of Table 4.10 shows that during the wet season, the highest Pb concentration was recorded at 63.28 mg/Kg in the sediment of location 8 (FMC Dockyard Khal), while the lowest was 25.86 mg/Kg at location 5 (Custom Khal). Most of the khals exhibited relatively higher Pb concentrations, with locations 2, 6, 7, and 9 showing lower levels. The elevated Pb concentration at location 8 (FMC Dockyard Khal) is likely due to waste discharges containing Pb from shipbuilding activities in the area. This is consistent with the findings of Mir et al. (2021), who linked elevated Pb levels in sediments to sources such as municipal runoff, atmospheric deposition, leaded gasoline, chemical production, and steelworks.

Nickel (Ni):

Table 4.10 highlights that the mean concentration of Ni in the sediment of estuaries from ten studied khals feeding into the Karnaphuli river was recorded at 43.39 ± 3.55 mg/kg during the wet season and 49.66 ± 5.70 mg/kg in the dry season. Although these Ni levels are within the ASV values, they exceed the permissible limits set by USEPA (2017, 2019) and fall into the "moderately polluted" range according to USEPA's 2002 standards. In contrast, Daniel et al. (2022) found significantly lower mean Ni concentrations of 0.175 ± 0.0715 mg/kg in the dry season and 0.1503 ± 0.0497 mg/kg in the wet season, both within the permissible limits outlined by USEPA.

The discussion above, along with the data presented in Fig. 4.25, reveals that Ni concentration in the sediment of estuaries feeding into the Karnaphuli river is higher during the dry season compared to the wet season. This seasonal difference is likely due to the dilution effect caused by heavy rainfall during the wet season, which reduces the concentration of Ni in the sediment. Jolly et al. (2023) observed a similar pattern, recording higher Ni concentrations of 39.45 ± 0.32 mg/kg during the dry season compared to 35.09 ± 0.28 mg/kg in the wet

season, attributing the decrease in the wet season to the dilution of pollutants by rainwater.

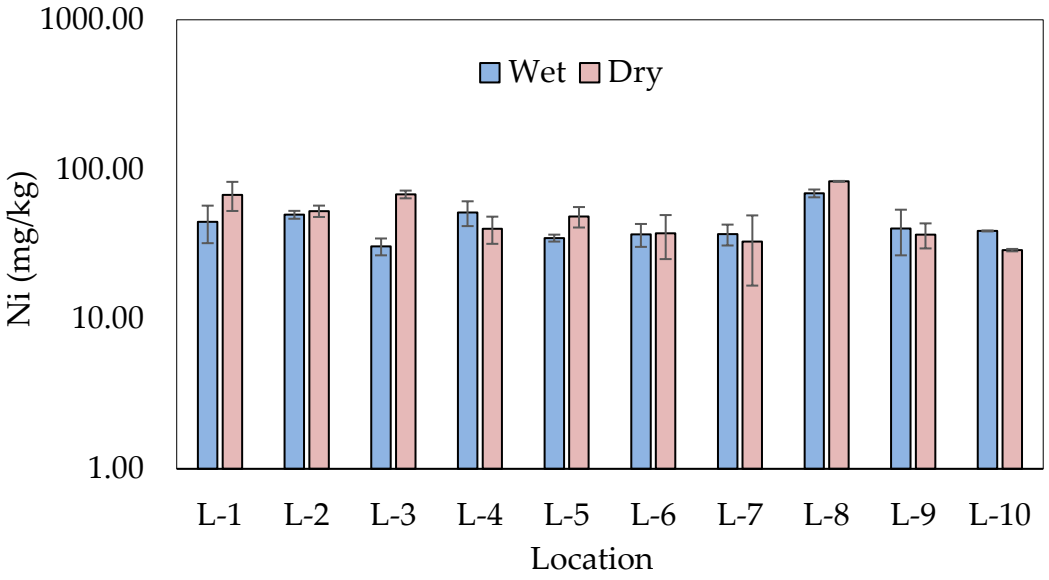


Fig. 4.25: Concentration of Ni in surface sediments during wet and dry seasons

Table 4.10 further indicates that during the wet season, the highest Ni concentration was recorded at 69.32 mg/kg in the sediment of the estuary at location 8 (FMC Dockyard Khal), while the lowest was 30.64 mg/Kg at location 3 (Bolirhat Khal). Locations 1, 2, and 4 also showed elevated Ni concentrations, whereas the remaining locations displayed comparatively lower levels. The high Ni concentration at location 8 can likely be attributed to untreated industrial effluents from shipbuilding and textile industries, as well as increased sewage discharge from the surrounding area. This observation aligns with the findings of Kutlu et al. (2024), who linked elevated Ni concentrations to increased sewage discharge and a burgeoning industrial sector.

During the dry season, the highest Ni concentration was found at 83.27 mg/kg in the sediment of the estuary at location 8 (FMC Dockyard Khal), while the lowest was 28.92 mg/Kg at location 10 (Ichanogor Khal). Most other khals showed relatively higher Ni concentrations, except for locations 6, 7, and 9. The elevated Ni levels in the sediment at location 8 during the dry season can be attributed to

increased industrial waste discharge, particularly from metal plating activities associated with shipbuilding, as well as agricultural waste runoff. This observation is supported by the findings of Addo-Bediako (2022), who also linked elevated Ni levels in sediment to agricultural waste, domestic discharges, and urban activities.

Manganese (Mn):

Table 4.10 details the mean concentration of Mn in the sediment of estuaries from 10 studied khals feeding into the Karnaphuli river, showing values of 63.04 ± 2.77 mg/kg during the wet season and 58.55 ± 8.11 mg/kg in the dry season. Both of these values are within the average shale value (ASV) established by Turekian and Wedepohl (1961). In contrast, Pandit et al. (2024) reported higher Mn concentrations of 126.96 ± 22.01 mg/kg during the dry season compared to 46.76 ± 18.43 mg/kg in the wet season, though these values also fall within the ASV range.

The analysis depicted in Fig. 4.26 shows that Mn concentrations in the sediment of the estuaries feeding into the Karnaphuli river are higher during the wet season than in the dry season. This elevated Mn level during the wet season can be attributed to the increased inflow of Mn-containing pollutants into the river, which subsequently settle in the sediment. This observation aligns with the findings of Yuan et al. (2020), who also noted elevated Mn levels, attributing them to the substantial rainfall during the wet season that causes more pollutants to flow into the river and settle in the sediment.

Furthermore, Table 4.10 indicates that among the estuaries of the 10 studied khals, the highest Mn concentration during the wet season was recorded at 80.24 mg/kg in the sediment at location 7 (MAF Newsprint Khal), while the lowest was 49.69 mg/kg at location 2 (Ispahani Khal). The remaining estuaries also exhibited elevated Mn levels, ranging from 57.15 mg/kg to 70.63 mg/kg. The higher Mn

concentration at location 7 could be linked to increased industrial effluent discharge, along with domestic and agricultural runoff from the area. This observation is supported by (Pandey and Singh, 2017), who attributed elevated Mn concentrations to wastewater, domestic and agricultural runoff, and effluent from local sewage treatment plants (STP) in the studied area.

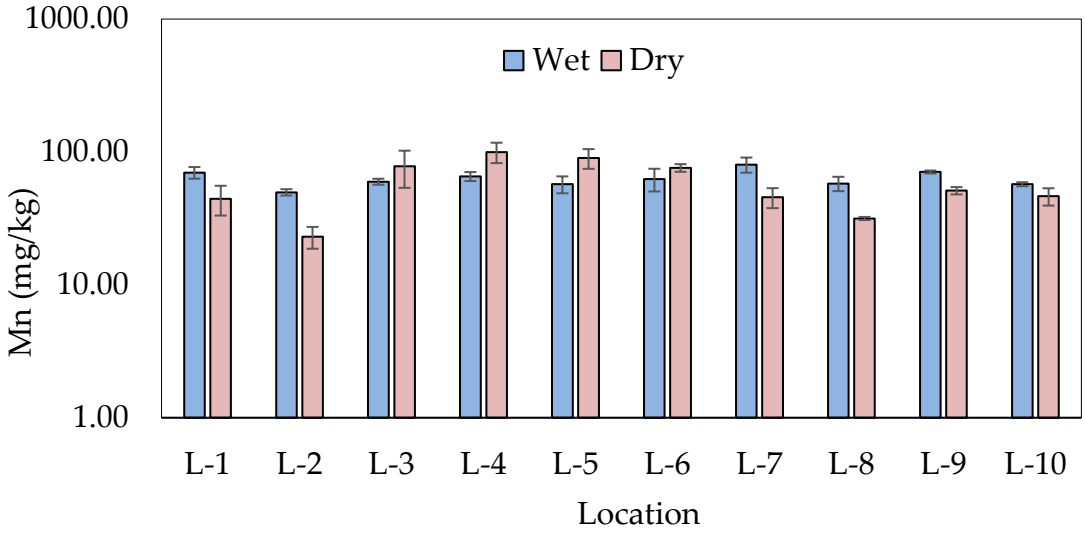


Fig. 4.26: Concentration of Mn in surface sediments during wet and dry season

During dry season, the highest Mn concentration was recorded at 99.84 mg/kg in the sediment at location 4 (Chaktai Khal), while the lowest was 22.97 mg/kg at location 3 (Ispahani Khal). Locations 3, 5, 6, and 9 also showed elevated Mn levels in the sediment, while the remaining estuaries had comparatively lower concentrations. This pattern could be due to the reduced water volume during the dry season, which, coupled with increased agricultural and industrial discharges, leads to higher Mn accumulation. (Shen et al.,2019) similarly observed elevated Mn levels in their study, attributing them to agricultural and industrial activities, including combustion and coal mining, in the area.

Arsenic (As):

Table 4.10 presents the mean concentration of As in the sediment of estuaries from 10 studied khals feeding into the Karnaphuli river, with values recorded at 1.34 ± 0.19 mg/kg during the wet season and 2.21 ± 0.74 mg/kg in the dry season.

These concentrations fall within the ASV (average shale value) as defined by Turekian and Wedepohl (1961) and are within the permissible limits set by the USEPA (2017; 2019). Similarly, Lipy et al. (2021) reported elevated As levels of 6.59 ± 1.42 mg/kg during the wet season and 5.15 ± 0.97 mg/kg during the dry season, noting that while the wet season values were within the limits, the dry season concentrations exceeded the TRV (Toxicity Reference Value) established by the USEPA.

The analysis visualized in Fig. 4.27 clearly shows that As concentrations in the sediment of the estuaries are higher during the dry season compared to the wet season. This increase in As during the dry season can be attributed to reduced water flow, which is caused by lower rainfall, leading to an accumulation of As in the sediment. Hasan et al. (2024) support this observation, finding a similar pattern where higher As concentrations were recorded during the dry season, attributing this to the diminished water flow, which facilitated the accumulation of As in the sediment.

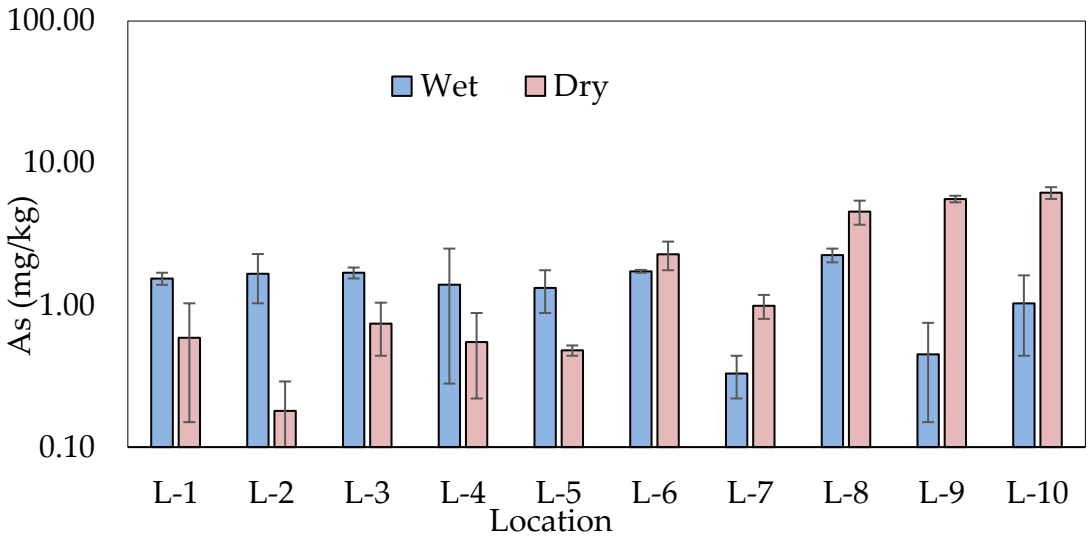


Fig. 4.27: Concentration of As in surface sediments during wet and dry seasons

Further, Table 4.10 shows that during the wet season, the highest As concentration was observed at 2.25 mg/kg in the sediment of the estuary at location 8 (FMC Dockyard Khal), while the lowest was 0.33 mg/kg at location 7

(MAF Newsprint Khal). Most other estuaries exhibited similar As concentrations to the highest value, with the exception of location 9 (Shikolbaha Khal). The elevated As concentration at location 8 could be attributed to runoff from agricultural activities, including the use of arsenic-based fungicides, herbicides, and pesticides, as well as industrial activities such as metal plating and welding in the area.

During the dry season, the highest As concentration was recorded at 6.18 mg/kg in the sediment of the estuary at location 10 (Ichanogor Khal), while the lowest was 0.18 mg/kg at location 2 (Ispahani Khal). Most other estuaries showed comparatively lower As concentrations, with the exceptions of locations 6, 8, and 9. The elevated As levels at location 10 can be attributed to reduced water flow during the dry season, combined with increased industrial discharge from metal-related industries and agricultural runoff containing As-based fertilizers and pesticides.

Zinc (Zn):

Table 4.10 presents data on the mean concentration of Zn in the sediment of estuaries from 10 khals feeding into the Karnaphuli river, showing values of 91.93 ± 7.72 mg/kg in the wet season and 104.44 ± 5.02 mg/kg in the dry season. These concentrations indicate moderate pollution according to USEPA (2002) guidelines and are within the standards prescribed by USEPA (2017, 2019) for sediment. During the wet season, Zn levels were within the average shale value (ASV) as defined by Turekian and Wedepohl (1961), but they exceeded this benchmark in the dry season. Akter et al. (2019) similarly found elevated Zn levels in their study, reporting mean concentrations of 87.87 mg/kg in the wet season and 96.02 mg/kg in the dry season. According to EPA (1977) guidelines, the sediment was moderately polluted during the dry season, although Zn concentrations during the wet season remained within the standard range of 90 to 200 mg/kg.

Fig. 4.28 clearly indicates that Zn concentrations in the sediment of the estuaries feeding into the Karnaphuli river are higher in the dry season compared to the wet season. This reduction in Zn concentration during the wet season is likely due to the dilution effect caused by heavy rainfall. This conclusion aligns with findings by Edokpayi et al. (2017), who also observed higher Zn levels in river sediment during the dry season, attributing this to the dilution of pollutants in the sediment during periods of heavy rain.

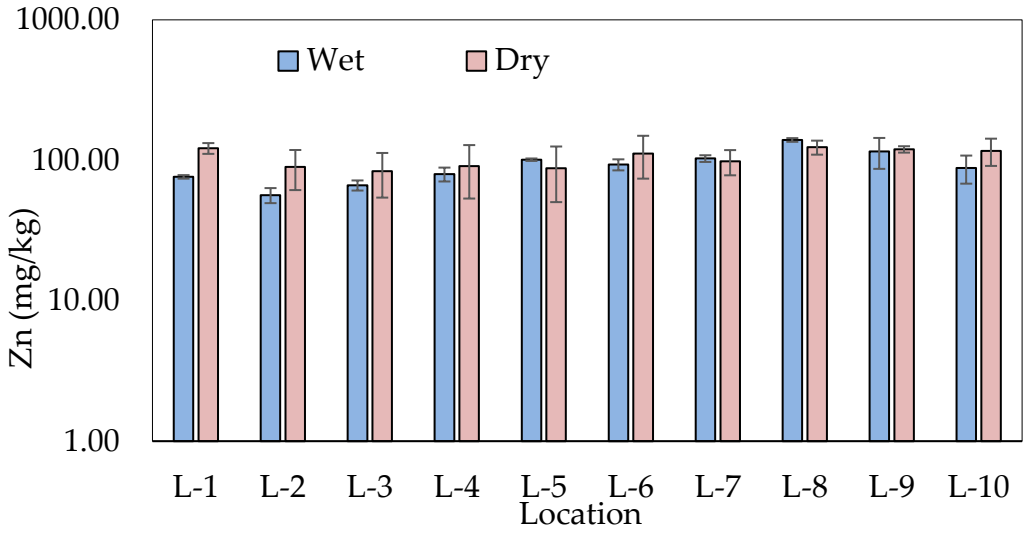


Fig. 4.28: Concentration of Zn in surface sediments during wet and dry seasons

Furthermore, Table 4.10 reveals that during the wet season, the highest Zn concentration in sediment was recorded at 139.62 mg/kg at location 8 (FMC Dockyard Khal), while the lowest was 56.48 mg/kg at location 2 (Ispahani Khal). Other estuaries also showed elevated Zn levels. The significant Zn concentration at location 8 can be linked to runoff from domestic construction, motor vehicle-related sources, and untreated wastewater from upstream areas. This finding is consistent with the study by Gunes (2022), who observed elevated Zn levels in the sediment of the Bartin River and attributed them to riverbank runoff, surface runoff from agricultural and urban areas, domestic construction waste, and untreated wastewater discharge. During the dry season, the highest Zn concentration was recorded at 123.86 mg/kg in the sediment of location 8 (FMC Dockyard Khal), while the lowest was 83.52 mg/kg at location 3 (Bolirhat Khal).

Other estuaries also showed elevated Zn levels. The higher Zn concentration at location 8 during the dry season could be attributed to increased discharge of industrial waste from metal plating industries, particularly from shipbuilding activities, as well as the discharge of domestic and agricultural waste. This observation is supported by Banerjee et al. (2016), who attributed elevated Zn concentrations in river sediment to significant industrial waste discharge from metal plating industries and runoff containing fertilizer residues in the studied area.

Fig. 4.29 offers a comparative analysis of the mean concentrations of Cu, Cr, Cd, Pb, Ni, Mn, As and Zn in surface sediment samples collected from the estuaries of various khals feeding to Karnaphuli river across both wet and seasons.

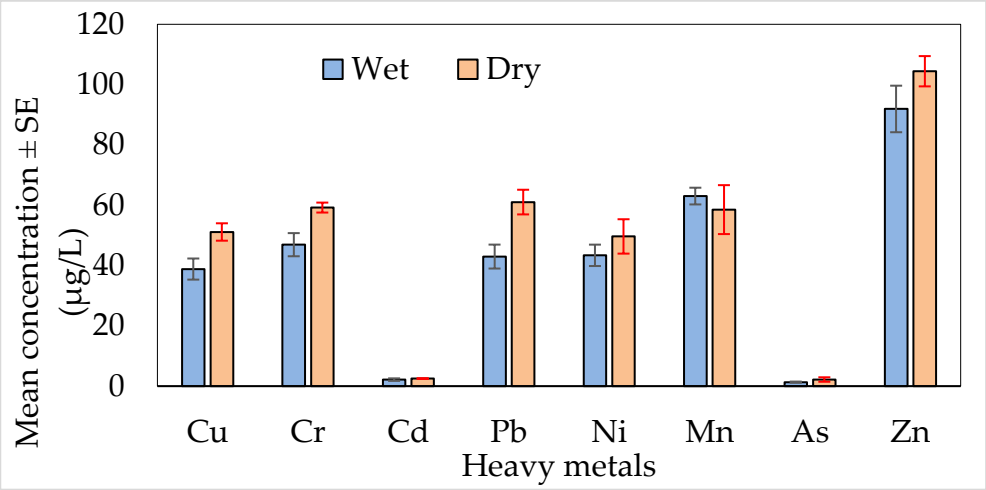


Fig. 4.29: Mean concentrations of heavy metals in surface sediments during wet and dry seasons

4.3.2 Comparison of heavy metals concentration in the surface sediments with some other studies

A comparison of the mean heavy metal concentration in the surface sediment at the estuaries of ten studied khals feeding into the Karnaphuli river during wet and dry season with the sediment of some other selected national and international rivers available in the recent literature is shown in Table 4.11

Table 4.11: Heavy metal content in surface sediments in the present study in comparison with some other recent studies

Locations	Heavy metals (mg/kg)								References
Sediments	Cu	Cr	Cd	Pb	Ni	Mn	As	Zn	
Karnaphuli river, (Dry season)	51.12	59.23	2.52	61.04	49.66	58.54	2.21	104.44	Present study
Karnaphuli river, (Wet season)	38.83	46.92	2.18	42.98	43.39	63.04	1.34	91.93	Present study
Korotoa River (Dry season)	NS	16.016	0.039	9.81	NS	NS	8.502	NS	Hasan et al., 2024
Korotoa River (Wet season)	NS	12.370	0.033	7.204	NS	NS	5.233	NS	Hasan et al., 2024
Bhairab River, Bangladesh	NS	34.17	1.668	25.455	NS	NS	3.998	NS	Ali et al. 2022
Turag River, Bangladesh	3.41	NS	0.32	11.84	NS	12.88	NS	4.24	Bhuyan et al., 2022
Balu River, Bangladesh	10.85	NS	0.14	0.96	NS	19.86	NS	3.25	Bhuyan et al., 2022
Old Brahmaputra	6.20	6.6	NS	7.6	12.8	126.2	NS	52.7	Bhuyan et al. 2019
Rupsa River, Bangladesh	NS	25.26	3.78	32.57	NS	NS	9.31	NS	Proshad et al. 2019
Louhajang River, Bangladesh	NS	9.205	0.083	4.597	NS	NS	8.999	NS	Kormoker et al. 2019
Paira River, Bangladesh	NS	45	0.72	25	NS	NS	12	NS	Islam et al. 2015
Bangshi River, Bangladesh	NS	98	0.61	60	NS	NS	1.93	NS	Rahman et al. 2012
Buriganga River, Bangladesh	NS	178	3.3	70	NS	NS	NS	NS	Ahmad et al. 2010
Okumeshi River, Nigeria	NS	0.87	1.32	0.45	NS	NS	NS	NS	Ekeanyanwu et al. 2011
Munzur Stream	NS	143.0	1.59	31.97	NS	NS	2.2	NS	Kutlu, 2023
Nile River, Egypt	49.52	53.68	NS	58.45	62.74	764.8	NS	166.56	Al-Afify et al. 2022
Yellow River, China	NS	41–128	NS	26–78	NS	NS	14–48	NS	Liu et al. 2009
Gediz River, Turkey	NS	170–220	NS	105–140	NS	NS	NS	NS	Akcay, 2003

4.3.3 Environmental impact assessment of heavy metals in surface sediments

The contamination levels of heavy metals in surface sediments from the estuarine zones of selected khals draining into the Karnaphuli River was evaluated using several indices—RV, CV, EF, CF, Cd, PLI, PERI, PN, and Igeo—as summarized in Table 4.12.

The mean concentrations corresponded to minor enrichment based on Enrichment Factor (EF), indicating minimal anthropogenic input. The modified contamination degree (mCd) revealed low contamination for Cr, Cd, Mn, and As, whereas Cu, Pb, Ni, and Zn reflected moderate levels. Based on pollution categories, Cd, Mn, and As were unpolluted; Cr was moderately polluted; Cu, Ni, and Zn were highly polluted; and Pb showed severe contamination.

Pollution Load Index (PLI) suggested elevated pollution from Cr, Cd, Mn, and As, while Cu, Pb, Ni, and Zn exhibited signs of progressive contamination. Geo-accumulation Index (Igeo) categorized Cu, Cr, Pb, Ni, and Zn as uncontaminated to moderately contaminated; Cd and As as heavily contaminated; and Mn as heavily to extremely contaminated.

According to the Nemerow Pollution Index (PINemerow), all heavy metals were within unpolluted thresholds. The Potential Ecological Risk Index (PERI) indicated low ecological risk for Cr, Cd, Mn, As, and Zn; moderate risk for Cu and Ni; and notable ecological threat from Pb.

Table 4.12 Level of RV, CV, EF, CF, Cd, PLI, PERI, P_N and I_{geo} of surface sediments during wet and dry seasons.

Concentration (mg/Kg)									
Location	Cu	Cr	Cd	Pb	Ni	Mn	As	Zn	Contamination level
L-1	44.39	57.12	2.01	54.9	56.25	57.17	1.07	99.04	
L-2	55.98	44.36	1.88	48.13	51.31	36.33	0.92	73.18	
L-3	52.57	51.72	2.17	54.59	49.43	68.83	1.21	74.96	
L-4	34.32	51.91	1.69	53.94	45.84	82.66	0.97	85.28	
L-5	37.74	45.73	2.57	39.68	41.68	73.48	0.89	94.46	
L-6	45.07	48.3	3.02	49.83	37.11	69.19	2	102.46	
L-7	42.22	48.02	2.08	41.68	34.99	62.89	0.66	100.59	
L-8	62.88	70.11	3.86	75.31	76.29	44.71	3.41	131.74	
L-9	38.56	54.39	2.12	42.35	38.47	60.88	3.02	117.62	
L-10	36.06	59.12	2.12	59.7	33.87	51.75	3.60	102.50	
MV	44.98	53.08	2.35	52.01	46.52	60.79	1.78	98.182	
SD	9.39	7.65	0.65	10.50	12.84	13.87	1.14	17.93	
Max Value	62.88	70.11	3.86	75.31	76.29	82.66	3.60	131.74	
Min Value	34.32	44.36	1.69	39.68	33.87	36.33	0.66	73.18	
RV	33.0[a]	72.2[a]	20[g]	19.0[c]	35.0[e]	850[f]	13.0[d]	95.0[b]	RV-Reference Value
CV[h]	25	35	98	20	20	600	1.5	71	CV- Crust V
EF	1.79	1.52	0.02	2.60	2.33	0.10	1.18	1.38	Minor enrichment
CF	1.36	0.74	0.12	2.74	1.33	0.07	0.14	1.03	Moderate Polluted
mCd	13.63	7.35	1.18	27.37	13.29	0.72	1.37	10.33	High Contaminated
E_f^i	6.81	1.47	3.53	13.69	6.65	0.072	1.37	1.03	Low ecological risk
PLI	1.03	0.97	0.81	1.11	1.03	0.77	0.82	1.00	Progressive deterioration
PERI	68.15	14.70	35.26	136.87	66.46	0.72	13.66	10.33	Low ecological risk
P_N	0.72	0.76	0.61	0.69	0.61	0.74	0.49	0.75	Unpolluted
I_{geo}	-0.14	-1.03	-3.67	0.87	-0.17	-4.39	-3.46	-0.54	Uncontaminated to moderately contaminated
ML-Mean Location, T- Total, MV-Mean Value, RV-Reference Value									

[a]IAEA (1990). Guidebook on applications of radiotracers in industry. Technical Report Series No. 316.

[b] GESAMP (1982). The Review of the Health of the Oceans. Reports and Studies No. 15. GESAMP, Geneva, 108.

[c] Salomons & Forstner (1984). Metals in the Hydro-Cycle. Berlin, Springer.

[d]Mason (1966) Principles of Geochemistry, 3rd edn. John Wiley & Sons, New York.

[e] Wedepohl (1969/1978): Average composition of shallow-water sediment.

[f]ASV (average shale value) proposed by Turekian and Wedepohl

[g] Birch

[h]Taylor and McLennan (1995)

4.3.4 Health Risk Assessment

4.3.4.1 Non-carcinogenic Health Risk

Non-carcinogenic health risk assessment of heavy metals in surface sediments at the estuaries of selected khals feeding to Karnaphuli river is illustrated in Table 4.13.

Table 4.13 Non-carcinogenic health risk of heavy metals in surface sediments.

Heavy metals	RfDo (mg/Kg)	Exposure assessment	Non-carcinogenic risk
		CDI_{derm}	HQ_{derm}
Cu	4×10^{-2}	8.79×10^{-08}	1.41×10^{-06}
Cr	3×10^{-3}	1×10^{-07}	2.80×10^{-06}
Cd	1×10^{-3}	4.6×10^{-09}	4.59×10^{-09}
Pb	3.5×10^{-3}	1×10^{-07}	4.36×10^{-06}
Ni	1.1×10^{-2}	9.1×10^{-08}	1.10×10^{-07}
Mn	2.4×10^{-2}	1.2×10^{-07}	6.84×10^{-07}
As	3×10^{-4}	1.04×10^{-07}	8.44×10^{-06}
Zn	3×10^{-1}	1.9×10^{-07}	5.76×10^{-07}
HI_{derm}			1.84×10^{-05}

Note: CDI_{derm}= Chronic daily intake via dermal contact, HQ_{derm}=Hazard quotient via dermal contact, HI_{derm}= Hazard Index via dermal contact.

The calculated mean exposure value of a non-carcinogenic health risk associated with dermal contact is presented in Table 4.13. The HQ value showed the following order: Cu > As > Pb > Cr > Mn > Zn > Ni > Cd. The calculated HI_{derm} for every metal was found lower than 1 and the mean value (1.84×10^{-05}) of the investigated metals is also found lower than 1 (USEPA, 2002). This indicates that there is no probability for potential non-carcinogenic health effects in the investigated surface sediments at the estuaries of selected khals feeding to Karnaphuli river through dermal contact.

4.3.4.2 Carcinogenic Health Risk

Carcinogenic health risk assessment of heavy metals in surface sediments at the estuaries of selected khals feeding to Karnaphuli river is shown in Table 4.14.

Table 4.14 Carcinogenic health risk of heavy metals in surface sediments.

Heavy metals	CDI_{derm}	SF	Carcinogenic risk ($CDI_i \times SF_i$)
Cr	1.04×10^{-07}	0.5	2.07×10^{-07}
Cd	4.6×10^{-09}	15	3.06×10^{-10}
Pb	1.02×10^{-07}	0.0085	1.20×10^{-05}
As	1.04×10^{-07}	1.5	6.94×10^{-08}
LCR			1.22×10^{-05}

As presented in Table 4.14, the estimated carcinogenic risks from dermal exposure to Cr, Cd, Pb, and As in adults remained within the permissible range of 1×10^{-6} to 1×10^{-4}, indicating that lifetime exposure to these metals in the study area poses an acceptable level of cancer risk.

4.3.5 Pearson's Correlation Coefficient

The Pearson correlation coefficient of heavy metals in surface sediments at the estuaries of selected khal feeding to Karnaphuli river is shown in Table 4.15.

Table 4.15 Pearson's correlation coefficient matrix among the heavy metals in surface sediments

Heavy metals	Cu	Cr	Cd	Pb	Ni	Mn	As	Zn
Cu	1							
Cr	0.33	1						
Cd	0.56	0.55	1					
Pb	0.54	**0.86****	0.55	1				
Ni	**0.77****	0.63	0.53	0.73*	1			
Mn	-0.64*	-0.33	-0.22	-0.38	-0.42	1		
As	0.10	0.73*	0.50	0.56	0.14	-0.37	1	
Zn	0.09	0.72*	0.68*	0.39	0.27	-0.20	0.72*	1

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

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

Table 4.15 shows both positive and negative correlations among heavy metal concentrations in surface sediment samples. Pb exhibited a very strong positive correlation with Cr ($r = 0.86$, $p < 0.01$), while Cu was strongly correlated with Ni ($r = 0.77$, $p < 0.01$). Significant positive associations were also noted between Ni and Pb, As with Cr and Zn, and Zn with Cr and Cd at the $p < 0.05$ level. These correlations suggest that the metals may share common sources and exhibit similar environmental behaviors. Moderate correlations indicate a shared origin but some variation in their environmental interactions.

In contrast, Mn showed a strong negative correlation with Cu, implying differences in source or environmental behavior. Weak correlations among some metals indicate that sediment composition may play a limited role in pollution patterns. Overall, the spatial distribution of heavy metals appears influenced by

multiple anthropogenic sources such as industrial effluents, municipal waste, and agricultural runoff.

Chapter 5: CONCLUSION AND RECMMENDATIONS

5.1 Conclusion

The present research was focused on the environmental contamination and seasonal variation of toxic heavy metals content in the surface water and sediments samples collected during the dry and wet seasons from the confluence of some selected khals feeding to Karnaphuli river. In addition, the physicochemical properties of surface water were analyzed. Seasonal hydrological changes influenced the distribution of both water quality parameters and heavy metals, contributing to ecological imbalances and posing potential threats to the river's environmental health.

The observed values for temperature and pH fell within the permissible limits outlined by ECR (2023) and WHO (2015), whereas dissolved oxygen (DO) was lower than recommended. Meanwhile, elevated levels of BOD, COD, TDS, hardness, and electrical conductivity surpassed the thresholds established by DoE (1997) and WHO (2015). Although heavy metal concentrations were largely within the acceptable limits set by USEPA (2002), inputs from upstream industrial discharges, municipal effluents, and agricultural activities likely contributed to localized elevations. Except for a few metals, their concentrations were generally higher during the dry season than in the wet season.

Current findings suggest that the level of pollution does not yet pose a severe ecological or health risk. However, if pollution through these khals continues unchecked, the river's ecological integrity may deteriorate significantly in the near future, particularly during dry seasons.

The non-carcinogenic risk assessment based on dermal exposure to surface water and sediments indicated no immediate health concern for adults. Correlation

analyses also highlighted varying relationships among metal concentrations in water and sediment samples, reflecting diverse pollution sources and environmental behavior. Therefore, it is critical to implement effective management strategies, including proper treatment of industrial and municipal effluents, maintenance of environmental flow, and integrated watershed management. Continuous monitoring of heavy metal levels in water, sediments, and aquatic organisms is recommended to assess potential risks and safeguard the Karnaphuli River's ecological balance.

5.2 Recommendations

Industrial, municipal and agricultural effluents are the major sources of pollutants that added to the Karnaphuli river through different khals contaminate the water. In this study, the water and sediment quality at the estuaries of some of those feeding khals were evaluated. The findings of the present study show the contamination status of surface water and sediments at estuaries of major khals feeding to Karnaphuli river in two different seasons in terms of important water quality properties and heavy metals content. This study shows the contamination level of water and sediments only at the estuaries of feeding khals. To know the actual extent of contribution of the feeding khals to Karnaphuli river water pollution, a detail study is needed. The detail study may include, measuring the contamination level at different points of the khals and quantity of water flows in each khal in different seasons. Furthermore, a careful inventory on industrial and other water plluting activities alongside the khals can be carried out that will help the concerned authority to take necessary measures for reducing pollutants at the sources of effluents.

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APPENDICES

Appendix 1: Physicochemical parameters of surface water at the estuaries of selected khals feeding to Karnaphuli river during wet season.

Location	Sample ID	Physicochemical parameters								
		T (°C)	pH	DO (ppm)	BOD (ppm)	COD (ppm)	TDS (ppm)	EC $mScm^{-1}$	Salinity (ppt)	Hardness (ppm)
L-1	SW-1	30	7.6	4.6	5.8	11.6	84	120	0.01	77
	SW-2	30	7.6	4.5	6	12	86	134	0.01	78
Mean		30	7.6	4.55	5.9	11.8	85	127	0.01	77.5
L-2	SW-3	30	6.4	1.2	47.6	85.68	470	640	0.01	380
	SW-4	30	6.6	1.2	48	86.4	473	665	0.01	396
Mean		30	6.5	1.2	47.8	86.04	471.5	652.5	0.01	388
L-3	SW-5	30	6.7	4.1	14	24	275	412	0.02	210
	SW-6	29.5	6.7	4.0	14	24.2	270	425	0.02	226
Mean		29.75	6.7	4.05	14	24.1	272.5	418.5	0.02	218
L-4	SW-7	29	7.8	1.8	8	15	250	622	0.05	196
	SW-8	29	7.8	1.8	12	22	266	648	0.06	204
Mean		29	7.8	1.8	10	18.5	258	635	0.05	200
L-5	SW-9	29	7.8	4.3	7.2	12.9	228	535	0.08	194
	SW-10	29	7.8	4.6	7	12.6	236	576	0.08	198
Mean		29	7.8	4.45	7.1	12.75	232	555.5	0.08	196
L-6	SW-11	30	7.5	6.1	8.7	17.2	1560	2940	1.4	946
	SW-12	30	7.5	6.1	8.8	17.5	1500	2800	1.4	950
Mean		30	7.5	6.1	8.75	17.35	1530	2870	1.4	948
L-7	SW-13	30	7.9	5.4	6	10.8	160	388	0.06	120
	SW-14	30	8	5.3	6.2	11.16	150	380	0.06	132
Mean		30	7.95	5.35	6.1	10.98	155	384	0.06	126
L-8	SW-15	29.5	7.9	6.2	5.6	11.2	130	382	0.01	82
	SW-16	29.5	7.8	6.5	5	10	120	375	0.01	80
Mean		29.5	7.85	6.35	5.3	10.6	125	378.5	0.01	81
L-9	SW-17	28	7.3	5.9	8.8	19	220	448	0.02	135
	SW-18	28	7.3	6.0	8.7	18	190	456	0.02	142
Mean		28	7.3	5.95	8.75	18.5	205	452	0.02	138.5
L-10	SW-19	29.5	6.9	5.8	5.6	12	970	2280	1.5	764
	SW-20	29.5	7.1	6.0	5.5	9.0	960	2450	1.6	780
Mean		29.5	7	5.9	5.55	10.5	965	2365	1.55	772

Appendix 2: Physicochemical parameters surface water at the estuaries of selected khals feeding to Karnaphuli river during dry season.

Location	Sample ID	Physicochemical parameters								
		T (°C)	pH	DO (ppm)	BOD (ppm)	COD (ppm)	TDS (ppm)	EC ($mScm^{-1}$)	Salinity (ppt)	Hardness (ppm)
L-1	SW-1	28	7.6	2.3	7.2	14	110	288	0.05	93
	SW-2	28	7.5	2.2	7.2	13.9	112	290	0.05	98
Mean		28	7.55	2.25	7.2	13.95	111	289	0.05	95.5
L-2	SW-3	24.8	6.8	0.8	135	280	590	890	0.18	460
	SW-4	24.8	6.8	0.9	134	276	530	885	0.17	455
Mean		24.8	6.8	0.85	134.5	278	560	887.5	0.175	457.5
L-3	SW-5	28.3	7.5	2.4	22	39	290	680	0.04	278
	SW-6	28.3	7.5	2.4	20.2	38	280	675	0.04	270
Mean		28.3	7.5	2.4	21.1	38.5	285	677.5	0.04	274
L-4	SW-7	26	7.6	1.1	32	72	450	1030	0.08	528
	SW-8	26	7.6	1.2	30.1	69	470	1075	0.09	532
Mean		26	7.6	1.15	31.05	70.5	460	1052.5	0.085	530
L-5	SW-9	27.9	7.1	3.2	14	36	490	1738	0.09	430
	SW-10	27.9	7.2	3.1	14	38	498	1745	0.1	446
Mean		27.9	7.15	3.15	14	37	494	1741.5	0.095	438
L-6	SW-11	28	7.2	5.8	9.6	20	1840	3580	1.7	1408
	SW-12	28	7.1	5.9	9.4	22	1790	3595	1.6	1370
Mean		28	7.15	5.85	9.5	21	1815	3587.5	1.65	1389
L-7	SW-13	27.8	8.2	4.3	8.8	17	240	560	0.06	196
	SW-14	27.8	8.4	4.5	9	18	250	576	0.06	200
Mean		27.8	8.3	4.4	8.9	17.5	245	568	0.06	198
L-8	SW-15	27.4	8	4	6.7	16	170	440	0.04	123
	SW-16	27.4	7.9	4.1	6.5	18	185	445	0.03	130
Mean		27.4	7.95	4.05	6.6	17	177.5	442.5	0.035	126.5
L-9	SW-17	27.3	7.8	5.8	10.2	34	480	510	0.05	450
	SW-18	27.3	7.6	5.8	10	33	455	534	0.04	440
Mean		27.3	7.7	5.8	10.1	33.5	467.5	522	0.045	445
L-10	SW-19	26.9	7.3	4	6.2	14	1200	3280	2.8	964
	SW-20	26.9	7.5	4.1	6.2	14.5	1225	3300	2.8	980
Mean		26.9	7.4	4.05	6.2	14.25	1212.5	3290	2.8	972

Appendix 3: Heavy metal concentrations in surface water samples at the estuaries of selected khals feeding to Karnaphuli river during wet season.

Location	Sample ID	Concentration (µg/L)							
		Cu	Cr	Cd	Pb	Ni	Mn	As	Zn
L-1	SW-1	46.80	42.30	2.40	47.24	42.90	37.85	8.35	43.10
	SW-2	14.30	15.10	2.55	25.55	18.60	18.55	5.00	23.80
Mean		30.55	28.70	2.48	36.39	30.75	28.20	6.68	33.45
L-2	SW-3	43.70	48.95	4.50	47	47.50	37.95	8.45	43.20
	SW-4	6.10	56.60	2.35	2.35	35.40	40.35	10.85	50.60
Mean		24.90	52.78	3.43	24.68	41.45	39.15	9.65	46.90
L-3	SW-5	22.65	28.40	4.60	28.90	26.95	21.90	0.40	32.15
	SW-6	60.60	16.35	3.00	25.85	19.90	14.85	0.80	25.10
Mean		41.63	22.38	3.80	27.38	23.43	18.38	0.60	28.63
L-4	SW-7	55.10	25.50	12.50	21.35	14.40	14.35	5.85	24.60
	SW-8	51.45	92.20	2.45	42.70	50.75	35.70	6.20	45.95
Mean		53.28	58.85	7.48	32.03	32.58	25.03	6.03	35.23
L-5	SW-9	63.90	59.65	15.15	60.15	63.20	58.15	3.65	66.90
	SW-10	101.20	51.95	3.80	92.45	15.50	100.45	30.95	110.70
Mean		82.55	55.80	9.48	76.30	39.35	79.30	17.30	88.80
L-6	SW-11	91.05	41.50	47.80	97.30	20.35	145.30	15.80	80.55
	SW-12	46.20	46.95	2.50	82.45	20.50	90.45	10.95	50.70
Mean		68.63	44.23	25.15	89.88	20.43	117.88	13.38	65.63
L-7	SW-13	58.90	59.65	25.65	62.50	53.20	53.15	13.65	63.40
	SW-14	68.55	69.30	14.65	54.80	40.05	62.80	8.30	73.05
Mean		63.73	64.48	20.15	58.65	46.63	57.98	10.98	68.23
L-8	SW-15	99.10	66.85	12.85	80.35	75.65	98.35	15.50	93.60
	SW-16	38.70	116.95	45.45	54.95	40.05	32.95	3.45	43.20
Mean		68.90	91.90	29.15	67.65	57.85	65.65	9.48	68.40
L-9	SW-17	50.45	41.70	27.20	56.70	37.05	127	5.20	54.95
	SW-18	46.80	42.55	22.20	48.70	22.75	140.50	7.10	90.25
Mean		48.63	42.13	24.70	52.70	29.90	133.75	6.15	72.60
L-10	SW-19	42.30	86.60	20.75	53.70	28.85	144.50	11.10	52.40
	SW-20	141.80	46.70	26.50	58.05	13.25	22.80	16.50	139.25
Mean		92.05	66.65	23.63	55.88	21.05	83.65	13.80	95.83

Appendix 4: Heavy metal concentrations in surface water samples at the estuaries of selected khals feeding to Karnaphuli river during dry season.

Location	Sample ID	Concentration (µg/L)							
		Cu	**Cr**	**Cd**	**Pb**	**Ni**	**Mn**	**As**	**Zn**
L-1	SW-1	9.95	50.75	3.05	51.85	48.50	46.35	10.30	50.10
	SW-2	30.65	21.35	8.05	32.55	29.20	27.05	1.95	30.80
Mean		40.30	36.05	5.55	42.20	38.85	36.70	6.13	40.45
L-2	SW-3	50.05	50.70	10	51.95	48.60	46.45	10.40	50.20
	SW-4	7.45	62.85	3.35	9.35	6.00	3.85	17.80	7.60
Mean		28.75	56.78	6.68	30.65	27.30	25.15	14.10	28.90
L-3	SW-5	34	34.65	5.10	35.90	32.55	30.40	2.35	34.15
	SW-6	26.95	22.60	4.60	28.85	25.50	23.35	2.75	27.10
Mean		30.48	28.63	4.85	32.38	29.03	26.88	2.55	30.63
L-4	SW-7	26.45	31.75	13.70	28.35	25.00	22.85	7.80	26.60
	SW-8	47.80	98.45	3.70	49.70	46.35	44.20	8.15	47.95
Mean		37.13	65.10	8.70	39.03	35.68	33.53	7.98	37.28
L-5	SW-9	70.25	70.90	21.15	72.15	68.80	66.65	5.60	70.40
	SW-10	112.55	63.20	9.30	114.45	11.10	108.95	72.90	112.7
Mean		91.40	67.05	15.23	93.30	39.95	87.80	39.25	91.55
L-6	SW-11	157.40	42.85	48.30	159.30	5.95	153.80	17.75	157.55
	SW-12	102.55	53.20	3.45	104.45	21.10	98.95	12.90	102.70
Mean		129.98	48.03	25.88	131.88	13.53	126.38	15.33	130.13
L-7	SW-13	65.25	65.90	41.15	67.15	63.80	61.65	25.60	65.40
	SW-14	74.90	75.55	25.15	76.80	43.45	71.30	10.25	75.05
Mean		70.08	70.73	33.15	71.98	53.63	66.48	17.93	70.23
L-8	SW-15	110.45	93.10	23.35	112.35	109.00	106.85	20.80	110.60
	SW-16	45.05	145.70	75.95	46.95	43.60	41.45	5.40	45.20
Mean		77.75	119.40	49.65	79.65	76.30	74.15	13.10	77.90
L-9	SW-17	139.10	57.45	42.70	141	45.35	135.50	4.80	139.25
	SW-18	43.15	58.80	37.70	111	23.35	149.00	31.60	92.25
Mean		91.13	58.13	40.20	126	34.35	142.25	18.20	115.75
L-10	SW-19	57.60	92.85	31.25	55.70	39.45	153.00	13.05	113.75
	SW-20	93.15	57.45	33.00	95.05	28.85	6.300	18.45	141.25
Mean		75.38	75.15	32.13	75.38	34.15	79.65	15.75	127.50

Appendix 5: Heavy metal concentrations in surface sediments samples collected from the estuaries of selected khals feeding to Karnaphuli river during wet season.

Location	Sample ID	Concentration (mg/Kg)							
		Cu	Cr	Cd	Pb	Ni	Mn	As	Zn
L-1	SS-1	42.79	60.42	2.41	61.03	57.34	62.89	1.39	74.02
	SS-2	36.64	52.57	1.25	50.86	32.18	76.95	1.69	78.41
Mean		39.72	56.49	1.83	55.95	44.76	69.92	1.54	76.22
L-2	SS-3	48.14	31.74	0.98	29.74	52.90	52.42	2.28	63.41
	SS-4	55.71	23.26	1.07	26.12	46.85	46.95	1.03	49.55
Mean		51.93	27.50	1.03	27.93	49.88	49.69	1.66	56.48
L-3	SS-5	52.86	51.11	2.41	52.93	34.59	62.81	1.84	60.91
	SS-6	45.64	44.51	1.61	47.67	26.69-	56.64	1.54	71.89
Mean		49.25	47.81	2.01	50.30	30.64	59.73	1.69	66.4
L-4	SS-7	23.5	34.03	0.63	45.17	61.29	70.55	0.29	88.71
	SS-8	32.57	48.68	2.05	53.71	41.85	60.39	2.50	70.68
Mean		28.04	41.36	1.34	49.44	51.57	65.47	1.39	79.69
L-5	SS-9	36.07	38.82	1.88	22.67	36.69	65.47	0.88	99.02
	SS-10	39.36	32.50	1.52	29.05	32.98	48.83	1.76	103.03
Mean		37.72	35.66	1.70	25.86	34.84	57.15	1.32	101.03
L-6	SS-11	32.00	51.67	4.11	33.53	43.23	74.69	1.76	84.77
	SS-12	39.36	26.53	3.13	29.22	30.40	50.39	1.69	101.59
Mean		35.68	39.10	3.62	31.38	36.82	62.54	1.73	93.18
L-7	SS-13	36.07	57.15	3.48	21.98	31.05	90.70	0.44	97.35
	SS-14	24.86	33.4	0.18	49.74	42.82	69.77	0.22	108.64
Mean		30.47	45.28	1.83	35.86	36.94	80.24	0.33	102.99
L-8	SS-15	53.36	74.86	6.25	71.81	73.47	65.00	1.99	143.86
	SS-16	64.36	66.46	4.55	54.74	65.16	50.70	2.50	135.38
Mean		58.86	70.66	5.40	63.28	69.32	57.85	2.25	139.62
L-9	SS-17	31.14	55.35	1.69	37.76	26.69	72.42	0.15	144.24
	SS-18	22.07	46.39	2.32	44.66	53.87	68.83	0.74	86.89
Mean		26.61	50.87	2.01	41.21	40.28	70.63	0.45	115.57
L-10	SS-19	35.79	49.44	1.69	35.86	39.11	59.14	0.44	68.18
	SS-20	24.36	59.51	0.45	61.29	38.55	55.16	1.62	108.03
Mean		30.08	54.48	1.07	48.58	38.83	57.15	1.03	88.11

Appendix 6: Heavy metal concentrations in surface sediments samples at the estuaries of selected khals feeding to Karnaphuli river during dry season.

Location	Sample ID	Concentration (mg/Kg)							
		Cu	Cr	Cd	Pb	Ni	Mn	As	Zn
L-1	SS-1	44.14	73.82	3.21	56.47	52.82	33.2	0.15	132.58
	SS-2	54.00	41.67	1.16	51.29	82.66	55.63	1.03	111.14
Mean		49.07	57.75	2.19	53.88	67.74	44.42	0.59	121.86
L-2	SS-3	64.21	55.83	2.86	83.97	48.15	27.27	0.07	61.36
	SS-4	55.86	66.59	2.59	52.67	57.34	18.67	0.29	118.41
Mean		60.04	61.21	2.73	68.32	52.75	22.97	0.18	89.89
L-3	SS-5	57.00	68.61	1.88	65.17	72.26	53.67	1.03	112.8
	SS-6	54.79	42.64	2.77	52.59	64.16	102.19	0.44	54.24
Mean		55.89	55.63	2.33	58.88	68.21	77.93	0.74	83.52
L-4	SS-7	43.07	57.08	2.23	73.53	48.38	82.34	0.88	128.33
	SS-8	38.14	67.85	1.88	43.36	31.85	117.34	0.22	53.41
Mean		40.61	62.47	2.05	58.45	40.12	99.84	0.55	90.87
L-5	SS-9	44.36	50.97	3.39	37.16	40.94	105.00	0.44	125.38
	SS-10	31.14	60.63	3.48	69.83	56.09	74.61	0.51	50.38
Mean		37.75	55.8	3.44	53.49	48.52	89.81	0.48	87.88
L-6	SS-11	50.43	56.04	2.50	52.24	49.61	80.86	1.76	149.47
	SS-12	58.50	58.96	2.32	84.31	25.19	70.85	2.79	74.02
Mean		54.47	57.5	2.41	68.28	37.40	75.86	2.28	111.75
L-7	SS-13	64.50	49.44	2.14	54.39	16.75	53.36	1.18	118.18
	SS-14	43.43	52.08	2.50	40.60	49.33	37.73	0.81	78.18
	Mean	53.97	50.76	2.32	47.49	33.04	45.55	0.99	98.18
L-8	SS-15	62.93	62.57	2.50	89.66	83.87	32.42	3.68	138.03
	SS-16	70.86	76.53	2.14	85.00	82.66	30.7	5.44	109.69
Mean		66.89	69.55	2.32	87.33	83.27	31.56	4.56	123.86
L-9	SS-17	46.43	66.81	2.32	48.97	29.68	54.38	5.29	113.41
	SS-18	54.57	49.03	2.14	38.02	43.63	47.89	5.88	125.91
Mean		50.50	57.92	2.23	43.49	36.66	51.14	5.59	119.66
L-10	SS-19	69.36	72.22	2.95	64.83	28.39	53.28	5.59	142.58
	SS-20	14.71	55.28	3.39	76.81	29.44	39.45	6.76	91.21
Mean		42.035	63.75	3.17	70.82	28.92	46.37	6.18	116.89