ASSESSMENT OF HEAVY METAL POLLUTION IN GANGA RIVER FROM KANPUR TO PRAYAGRAJ STRETCH, INDIA

Thesis Submitted
in Partial Fulfillment of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY

in

DEPARTMENT OF CIVIL ENGINEERING

by

MOHIT AGGARWAL

(Roll No. 2K17/PhD/CE/33)

Under the Supervision of

Prof. S ANBUKUMAR	Prof. T VIJAYA KUMAR
Delhi Technological University	**Delhi Technological University**

To the
Department of Civil Engineering
DELHI TECHNOLOGICAL UNIVERSITY
Formerly Delhi College of Engineering)
Shahbad Daulatpur, Main Bawana Road, Delhi-110042, India
December, 2024

CANDIDATE'S DECLARATION

I declare that the research work reported in the thesis entitled **"Assessment of Heavy Metal Pollution in Ganga River from Kanpur to Prayagraj Stretch, India"** for the award of the degree *of Doctor of Philosophy* in the *Department of Civil Engineering* has been carried out by me under the supervision of *Dr. S Anbukumar & Dr. T Vijaya Kumar*, Professor in Department of Civil Engineering, Delhi Technological University, Delhi, India.

The research work embodied in this thesis, except where otherwise indicated, is my original research. This thesis has not been submitted earlier in part or full to any other University or Institute for the award of any degree or diploma. This thesis does not contain other person's data, graphs, or other information unless specifically acknowledged.

Date:05/12/2024   **Mohit Aggarwal**

                                                                                                              2K17/PhD/CE/33

CERTIFICATE

This is to certify that the work contained in the thesis entitled **"Assessment of Heavy Metal Pollution in Ganga River from Kanpur to Prayagraj Stretch, India"** submitted by Mr. Mohit Aggarwal (Reg. No.: 2K17/PhD/CE/33) for the award of degree of Doctor of Philosophy to the Delhi Technological University is based on the original research work carried out by him. He has worked under my supervision and has fulfilled the requirements as per the requisite standard for the submission of the thesis. It is further certified that the work embodied in this thesis has neither partially nor fully submitted to any other university or institution for the award of any degree or diploma.

Prof. S Anbukumar
Supervisor
Department of Civil Engineering
Delhi Technological University, Delhi

Prof. T Vijaya Kumar
Supervisor
Department of Civil Engineering
Delhi Technological University, Delhi

ACKNOWLEDGMENT

ABSTRACT

The growing population, the discharge of untreated industrial effluents, and the improper use of pesticides in agriculture pose significant risks of heavy metal contamination in rivers. Heavy metals not only remain in river water but also bind to suspended sediments, which eventually settle as riverbed sediment. These contaminated sediments can persist in the riverbed for extended periods and may be re-suspended during periods of high-water flow, leading to recurrent contamination of the river and downstream areas. The Ganga River holds immense cultural, spiritual, and historical significance in India.

The primary objective of this study is to investigate the presence of eight heavy metals-Cadmium (Cd), Chromium (Cr), Copper (Cu), Iron (Fe), Manganese (Mn), Nickel (Ni), Lead (Pb) and Zinc (Zn) in the riverbed and suspended sediments of the Ganga River over a 225 km stretch. This stretch lies between the urban centers of Kanpur and Prayagraj in Uttar Pradesh, India. Riverbed sediment samples were collected in 2019 and 2021, while suspended sediment samples were gathered in 2021 and 2022 using standard sampling methods. The concentrations of these metals were determined using Atomic Absorption Spectroscopy (AAS) (Shimadzu AA-6300).

The analysis of riverbed sediment from both sampling years showed a consistent decreasing order of metal presence: Fe > Mn > Cr > Zn > Ni > Pb > Cu > Cd. For suspended sediments, the metal occurrence varied between the two sampling years, following the order Fe > Mn > Zn > Cr > Pb > Ni > Cu > Cd in 2021, and Fe > Mn > Cr > Zn > Pb > Ni > Cu > Cd in 2022. Iron (Fe) was the most abundant metal, while Cadmium (Cd) was found in the lowest concentrations. The pH of collected riverbed sediment was recorded above 7 which showed mild alkaline condition. The OM (%) in 2019 in the riverbed sediment varies from 7.31 to 9.82, with a mean of 8.35 ± 0.91 whereas in 2021 OM in the riverbed sediment varies from 4.73 to 6.57, with a mean of 5.79 ± 0.60.

Risk analysis was conducted using several sediment quality indices, including the geoaccumulation index (Igeo), enrichment factor (EF), contamination factor (CF), and pollution load index (PLI). Igeo values indicated moderate contamination (0 < Igeo < 1) of Cd in riverbed sediments, while suspended sediments were moderately

contaminated by Cr. The average EF values pointed to moderate enrichment (2 < EF < 5) of Cd in riverbed sediments, but the suspended sediments showed only mineral-level enrichment with no contamination. CF values revealed moderate contamination (1 < CF < 3) of Pb and Cd in riverbed sediments, and moderate contamination of Cr in suspended sediments. The PLI indicated that all sites studied were overall unpolluted (PLI < 1), reflecting baseline pollution levels.

Based on these indices, it can be concluded that riverbed sediments are moderately contaminated by Pb and Cd, while suspended sediments are moderately contaminated by Cr.

The analysis of anthropogenic (Ac) and lithogenic content (Lc) in the sediments suggested that Cd and Pb in riverbed sediments originated from human activities, while suspended sediments contained anthropogenic contributions of Pb, Cr, Zn, Fe, and Mn. Correlation study among metals, pH and organic matter showed a strong correlation between Fe and most other metals, whereas Cd had the weakest correlations with other metals. Most metals showed positive correlation with pH and organic matter.

When compared to the global average of other rivers, the concentrations of Cd, Pb, and Cr in the Ganga River sediments are concerning and could lead to further degradation of sediment quality if unchecked. Given the increasing anthropogenic pressures in the river basin, appropriate management strategies are crucial to limit the direct discharge of domestic and industrial wastewater into the river. Additionally, agencies like the Central Pollution Control Board (CPCB) and State Pollution Control Boards (SPCBs) must enforce strict compliance with environmental regulations for both municipal and industrial effluents to protect the Ganga River from further degradation.

Keywords: Ganga River; Riverbed Sediment; Suspended Sediment; Heavy Metal Contamination; Enrichment Factor; Contamination Factor; Pollution Load Index; Geoaccumulation Index; Correlation Analysis

List of Figures

List of Tables

List of Abbreviations and Symbols

µg/g	Microgram per Gram
µm	Micrometer
AAS	atomic absorption spectroscopy
Al	Aluminium
APHA	American Public Health Association
As	Arsenic
C	Celsius
Cd	Cadmium
CF	Contamination Factor
Co	Cobalt
CPCB	Central Pollution Control Board
Cr	Chromium
Cu	Copper
EF	Enrichment Factor
Fe	Iron
Hg	Mercury
HNO_3	Nitric Acid
Igeo	Geoaccumulation Index
ISO	International Organization for Standardization
km	Kilometre
Mn	Manganese
Ni	Nickel
Pb	Lead
PC	Principal Component
PCA	Principal Component Analysis
PEC	Probable Effect Concentration
PLI	Pollution Load Index
PPM	Parts Per Million
Sn	Tin
SPCB	State Pollution Control Board
SQG	Sediment Quality Guidelines
SS	Suspended Sediment
TEC	Threshold Effect Concentration
U.P.	Uttar Pradesh
WHO	World Health Organisation
Zn	Zinc

Table of Contents

x

Chapter 1
INTRODUCTION

1.1 General Background

To fulfil the needs of a fast-rising population, India saw tremendous urban-industrial expansion and increased food production in the last decade of the twentieth century. As a result, large amounts of contaminants, especially heavy metals, enter surface water bodies. Because of the hazardous nature of heavy metals, their presence in surface waterways is of special concern. Metals accumulate in water, sediment and biota after entering water resources. Sediment are thought to be the ultimate sink and indication of changes in the water column, as well as the impact of anthropogenic activities on air and watersheds (Ramesh et al. 1990). Anthropogenic heavy metals enter rivers as inorganic complexes or hydrated ions, which are readily adsorbed on the surface of suspended sediment and comprise the labile fraction (Vukovic et al. 2014). Turbulence, water pH, redox potential, seasonal floods and storms all promote remobilization of polluted surface sediment, making bottom sediment a possible source of heavy metal contamination (Osakwe et al. 2014). According to previous research, 30-98% of heavy metals in rivers are conveyed in sediment-associated forms (Wang *et al*. 2011).

The baseline level of metals in the river is formed by natural processes such as weathering, erosion and the dissolution of water-soluble salts, but those added by anthropogenic activities significantly increase the amounts in sediment (Rzetala 2015). Because metals are non-biodegradable, they accumulate in sediment and biota along the food chain, causing long-term environmental effects. Benthic creatures in direct contact with sediment are more vulnerable to such exposures. Some metals, such as Pb and Cd, are non-essential and toxic even at low quantities (Pehlivan et al. 2009). Secondary pollution of the water column impacts plankton (Copaja et al. 2014) and a food chain-related transfer may potentially harm human health. Heavy metals infiltrate river channels near metropolitan areas from both natural and artificial sources, such as industrial waste, home trash and municipal sewage. Furthermore, metals in airborne particles enter the environment both directly and indirectly through atmospheric deposition (Pandey et al. 2013). According to some studies (Singh et al. 2002;

Dhanakumar et al. 2011; Kumar, D et al. 2020), heavy metal levels in river sediment is increasing in India.

1.2 Ganga River and its Importance

The Ganga River, also known as the Ganges, is one of the most iconic and revered rivers in the world, particularly in India. It holds a special place in the hearts and minds of millions of people due to its cultural, spiritual and historical significance. This sacred river has shaped the landscape, culture and way of life in the Indian subcontinent for millennia.

1.2.1 Geography

The Ganga River is one of the major rivers in the Indian subcontinent, flowing through northern India and parts of Bangladesh (Figure 1.1). It originates from the Gangotri Glacier of Himalayas in the Uttarakhand State and then flows in southeastern direction, across Uttar Pradesh, Bihar and West Bengal, covering about 2,525 kilometres and finally enter the Bay of Bengal in the Sundarbans Delta. The rivers Brahmaputra and Meghna converge with it in central Bangladesh. The confluence of their respective streams, known as the Padma River, culminates in the Bay of Bengal, creating a vast 354 kilometres broad delta that is jointly shared between Bangladesh and India. The plain is renowned for being amongst the most productive and heavily inhabited places globally (Ansari et al. 2000). The Bhagirathi River originates from a cave near Gaumukh in the Uttarakhand Himalayas, where glacial water flows. Gaumukh is characterized as a barren location situated at an elevation of around 4,000 meters. Gangotri, the initial settlement along the river's course, is located 23 kilometers away from Gaumukh. Gangotri attracts a multitude of tourists annually, hailing from all corners of the globe (Jain 2002). The river that converges with river Alaknanda in Devaprayag in Uttarakhand, to form the Ganga. The Ganges flows through the valleys of the Himalayas and enters the northern plains of India near the Haridwar town (Beg and Ali 2008).

The Ganga flows through several densely populated towns in India, such as Kanpur, Prayagraj, Kolkata, Varanasi and Patna (Jain 2002). River Yamuna, that begins less than a hundred kilometres to the east of river Bhagirathi, runs alongside the river

Ganga to the south for the most of its path before joining the river Ganga in Prayagraj, often referred to as Triveni Sangam. New Delhi, the India's capital and Agra, the location of the Taj Mahal, are prominent urban centers situated along the river Yamuna (Khwaja et al. 2001).

Figure 1.1 Map of Ganga River and its tributaries with major cities

The river currently travels in an easterly direction and converges with the Tamsa River, also known as Tons. The Tamsa River originates at the Kaimur Range and adds an approximate volume of around 190 cubic metres per second to the combined flow. The Gomti River, originating from the Himalayas, merges with the Tamsa River in a southward direction. The Gomti river has an average annual flow rate of around 234 cubic metres per second. Subsequently, the Ghaghara River (also known as the Karnali River), originating from the southern slopes of the Himalayas in Nepal, converges with the Ganga River. The Ghaghara River, also known as the Karnali River, has an average annual flow rate of around 2,990 cubic metres per second, making it the greatest tributary of river Ganga. Son river join river Ganga from the south after the confluence of the Ghaghara (Karnali), adding approximately 1,000 cubic metres per second to its flow. River Gandaki and river Kosi, originating from Nepal, converge from the north and provide around 1,654 cubic metres per second and 2,166 cubic metres per second

of water flow, respectively. River Kosi is the Ganges' third most significant tributary, ranking after the Ghaghara (Karnali) and Yamuna.

Table 1.1 displays the details about the Ganga River, which flows through both Bangladesh and India. Additionally, the table provides details on the subsidiary rivers of the Ganga.

Table 1.1 Details of Ganga River

Countries	India, Bangladesh
States of India	Uttarakhand, Uttar Pradesh, Bihar, Jharkhand, West Bengal
Tributaries	Left- Gandak, Gomti, Koshi, Ghaghara, Mahananda, Gandaki, Ramganga, Burhi Right- Punpun, Yamuna, Son, Tamsa
Towns	Rishikesh, Haridwar, Kanpur, Jajmau, Ghazipur Prayagraj, Mirzapur, Varanasi, Patna, Munger, Bhagalpur, Baharampur, Kolkata
Source	Gangotri Glacier, Khatling Glacier, Satopanth Glacier and waters from melted snow from such peaks as, Trisul, Nanda Kot, Kedarnath, Nanda Devi and Kamet.
Location	Uttarakhand, India
Elevation	3,892 metres
Coordinates	30°59′N 78°55E
Mouth	Ganges Delta
Location	Bay of Bengal, Bangladesh & India
Elevation	0 meter
Coordinates	22°05'N 90°50E
Length	2525 kilometres
Basin	10.8 Lacs square kilometres

The Ganges flows through several towns including Mirzapur, Chunar, Varanasi, Ara, Ghazipur, Patna, Bhagalpur, Ballia, Buxar, Simaria, Sultanganj and Saidpur, while traveling from Prayagraj to Malda, West Bengal. In Bhagalpur, the river changes its direction and starts flowing towards the south of southeast. From Pakur, it starts to divide, with its first branch, the Bhāgirathi-Hooghly, separating and eventually becoming the Hooghly River. The Farakka Barrage, located near the border with Bangladesh, regulates the water flow of the Ganges River. It redirects a portion of water in a feeder canal that connects with the river Hooghly. This is done to maintain

the Hooghly river's cleanliness by reducing the amount of sediment present in the water (Singh et al. 2003). River Hooghly is created from the merging of river Bhagirathi River and river Jalangi in Nabadwip. Additionally, the Hooghly River has its several own tributaries. River Damodar holds the distinction of being the biggest, measuring 541 kilometres in length and encompassing a drainage basin of 25,820 square kilometres. The Hooghly River discharges into the Bay of Bengal near Sagar Island. River Hooghly flows through the cities and towns of Kolkata, Murshidabad, Howrah and Nabadwip, as it stretches from Malda to the Bay of Bengal.

The collective discharge of the Ganga, Brahmaputra and Surma-Meghna River system is ranked as the third largest in terms of average flow, following only the Amazon and Congo rivers.

The Indian subcontinent is situated atop the Indian tectonic plate, which is a smaller plate within the larger Indo-Australian Plate. Approximately seventy-five million years ago, the subcontinent initiated geological processes while being part of the southern supercontinent Gondwana. During this time, it embarked on a north-eastward drift across the then-unformed Indian Ocean, a journey that spanned fifty million years. The subsequent collision of the Indian subcontinent with the Eurasian Plate, along with its subduction beneath it, gave rise to the formation of the Himalayas, the tallest mountain range on Earth. As a result of this collision, a vast trough was created in the former seabed just south of the emerging Himalayas. Over time, plate movements led to the gradual filling of this trough with sediment, carried by rivers such as the Indus and its tributaries, as well as the Ganges and its tributaries. This process has contributed to the formation of the Indo-Gangetic Plain.

1.2.2 Historical significance
The Ganga has had a significant impact on the history and development of the Indian subcontinent. It has been the lifeline for many ancient and medieval civilizations, including the Indus Valley Civilization, the Vedic period and the Maurya and Gupta Empires. It was also a crucial trade route and contributed to the flourishing of trade and commerce in the region.

During the Late Harappan period, which occurred approximately between 1900 and 1300 BCE, the Harappan civilization expanded its settlements towards the east, moving from the Indus River basin to the Ganges-Yamuna doab. However, they did not establish any settlements on the eastern bank of the Ganges River. The dissolution of the Harappan civilization, occurring in the early 2nd century BC, signifies the moment when the focal point of Indian civilization transitioned from the Indus basin to the Ganges basin. Possible connections exist between the Late Harappan settlement in the Ganges basin, the archaeological civilization referred to as "Cemetery H," the Indo-Aryan population and the Vedic era.

The Ganges River holds the distinction of being the longest river in India. In the early Vedic Age of the Rigveda, the Indus and Sarasvati rivers held more religious significance compared to the Ganges. However, the subsequent three Vedas place even greater significance on the Ganges. The Gangetic Plain emerged as the focal point of multiple dominant states, spanning from the Maurya Empire to the Mughal Empire.

In 1951, a water allocation conflict emerged between India and Bangladesh (then known as East Pakistan) following India's announcement of its plan to construct the Farakka Barrage. The primary objective of the barrage, finalized in 1975, was to redirect a maximum of 1,100 cubic metres per second of water from the Ganges River to the Bhagirathi-Hooghly distributary. This was done with the aim of improving the navigability of the Port of Kolkata. It was hypothesized that during the most severe dry season, the Ganges River would have a flow rate of around 1,400 to 1,600 cubic metres per second, so leaving 280 to 420 cubic metres per second for East Pakistan. East Pakistan expressed opposition, leading to a prolonged dispute. A contract with a duration of 30 years was concluded in 1996. The agreement stipulates that if the flow of the Ganges at Farakka falls below 2,000 cubic meters per second, India and Bangladesh will each get an equal share of 50% of the water. During alternating ten-day intervals, each country would receive at least 990 cubic metres per second. However, within a year, the water flow at Farakka significantly decreased, dropping much below the usual average. As a result, it became impracticable to carry out the promised water sharing. In March 1997, the volume of water flowing in the Ganges River in Bangladesh reached its lowest level ever recorded, at 180 cubic metres per

second. Subsequent years witnessed a restoration of dry season flows to their usual levels, accompanied by proactive measures to tackle the issue. There is a proposal to construct an additional barrage in Bangladesh, namely at Pangsha, which is located to the west of Dhaka. This barrage will enhance Bangladesh's capacity to optimize the allocation of the Ganga's water resources.

1.2.3 Irrigation by River Ganga

The Ganges River alone encompasses a region exceeding one million square kilometres, sustaining a population of more than 407 million. The livelihoods of millions are intertwined with the sacred river, relying on its waters for various purposes such as drinking, bathing, agriculture, industrial activities and household tasks (Pandey et al. 2010).

Having traversed 250 kilometres through its confined Himalayan valley, the Ganges River emerges from the mountains at Rishikesh and then enters the Gangetic Plain at the sacred town of Haridwar. At Haridwar, a dam redirects a portion of its waters into the Ganges Canal, facilitating irrigation in the Doab region of Uttar Pradesh. Up to this juncture, the river has generally followed a southwest course, but from here onwards, it takes a southeast direction through the plains of northern India.

The Ganges Basin, characterized by its fertile soil, plays a pivotal role in the agricultural economies of both India and Bangladesh. The Ganges, along with its tributaries, serves as a continuous source of irrigation for a vast expanse. Primary crops cultivated in this region encompass rice, sugarcane, lentils, oilseeds, potatoes and wheat. The riverbanks feature swamps and lakes, creating favourable conditions for the growth of crops such as legumes, chillies, mustard, sesame, sugarcane and jute. Despite the abundant opportunities for fishing along the river, its waters are heavily polluted. Notably, Kanpur, the world's largest leather-producing city, is situated on the banks of the Ganges (Beg and Ali 2008).

1.2.4 Dependency of living creatures on Ganga River

The Ganga River is the longest in India and ranks as the second largest in the world in terms of water output. The Ganges basin is the most densely inhabited river basin

globally, accommodating more than 400 million individuals and exhibiting a population density of over 390 residents per square kilometres (Beg and Ali 2008).

The basin spans regions in four countries: China, India, Nepal and Bangladesh and covers eleven Indian states: Rajasthan, Himachal Pradesh, Jharkhand, Uttarakhand, Punjab, Uttar Pradesh, Madhya Pradesh, Bihar, Haryana, West Bengal, Chhattisgarh and the Union Territory of Delhi (Ansari et al. 2000). The Ganges basin, excluding the Brahmaputra or Meghna basins, has an approximate area of 1,080,000 square kilometres. India contributes the most substantial portion, covering 861,000 square kilometres, or around 80% of the total area. Nepal accounts for 140,000 square kilometres, constituting about 13% of the basin. Bangladesh occupies 46,000 square kilometres, making up 4% of the basin, while China covers 33,000 square kilometres, representing 3% of the basin's total area. The Ganges and Brahmaputra-Meghna drainage basins are sometimes combined, resulting in a merged area of approximately 1,600,000 square kilometres or 1,621,000 square kilometres. The GBM drainage basin, encompassing China, Bangladesh, India, Nepal and Bhutan, is formed by the convergence of the Ganges, Brahmaputra and Meghna rivers. The Ganges basin spans from the Himalaya and the Trans-Himalaya in the north to the northern slopes of the Vindhya range in the south and from the Aravalli in the west to the Chota Nagpur plateau and the Sunderbans delta in the east. The Ganges flow is significantly influenced by the Himalayan Mountain system. Extending over 1,200 kilometres within the Himalaya, the Ganges basin stretches from the Yamuna-Satluj split along the Simla ridge, which forms the western boundary with the Indus basin, to the Singalila Ridge along the Nepal-Sikkim border, marking the eastern boundary with the Brahmaputra basin. This Himalayan region boasts nine of the world's fourteen tallest peaks, each exceeding 8,000 metres in elevation, including Mount Everest, the highest point in the Ganges basin.

The discharge of the Ganges varies depending on its source. Discharge measurements often focus on the mouth of the Meghna River, where the Ganges, Brahmaputra and Meghna converge (Pandey et al. 2010). This results in a combined annual discharge of about 38,000 cubic meters per second or 42,470 cubic meters per second. Alternatively, individual annual discharge figures are sometimes provided for the Ganges,

Brahmaputra and Meghna. In such cases, the Ganges is reported to have an average discharge of approximately 16,650 cubic metres per second, the Brahmaputra at around 19,820 cubic metres per second and the Meghna at approximately 5,100 cubic metres per second.

The original forest in the upper Gangetic Plain has been extensively depleted, making it challenging to precisely identify a natural vegetation type. Only small remnants of forest persist, indicating that the upper plains likely originally featured a tropical wet deciduous forest dominated by sal (Shorea robusta) as the climax species (Ansari et al. 2000).

The gharial (Gavialis gangeticus) and the mugger crocodile (Crocodylus palustris) live in the Ganges River. The Ganges River dolphin, scientifically known as Platanista gangetica, has been officially recognized as India's national aquatic mammal.

1.2.5 Economic importance

The Ganga River basin is residence to a significant part of the Indian population and it supports a wide range of economic activities, including agriculture, fishing and tourism. The river is also crucial for supply of water and irrigation in the area, contributing to the livelihoods of millions of people.

The Southwest Monsoon governs the hydrologic cycle in the Ganges basin. From June to September, the monsoon season accounts for around 84% of total rainfall. As a result, Ganges stream flow is largely seasonal. As measured at Hardinge Bridge, the discharge in monsoon season is 6 times more than in the dry season. This substantial seasonal variance underpins many of the region's water resource development and land issues. The flow's seasonality is so severe that it can produce both drought and flooding (Beg et al. 2008). Bangladesh, in instance, usually faces drought during the dry season and significant flooding during the monsoon season.

In the Ganges Delta, numerous major rivers converge, creating an intricate network of channels through merging and bifurcating. The Ganges and Brahmaputra rivers both divide into distributary channels, with the largest ones combining with other significant rivers before converging. The current channel arrangement is not static, as rivers in the Ganges Delta have undergone course changes over time, influencing the

intricate network of channels. Additionally, tourism is another related activity in the region.

The Ganges-Brahmaputra-Meghna basin holds immense hydropower potential, estimated between 200,000 to 250,000 megawatts, with about half of it considered readily exploitable. However, as of 1999, India has tapped only around 12% of the hydroelectric potential of the Ganges and a mere 1% of the vast potential of the Brahmaputra. The Ganges faces severe pollution, negatively impacting the lives of approximately 400 million people residing near the river. Due to its course through densely populated areas, the Ganges receives pollutants from various sources, including sewage from multiple cities along its path, industrial waste and nondegradable plastics used in religious offerings. Compounding the issue is the regular use of the river by many poorer individuals for activities such as bathing, cooking and washing. This exacerbates the pollution problem, posing significant challenges to the environmental health of the Ganges.

1.2.6 Spiritual and Cultural Significance
The Ganga River is considered holy and is central to the religious beliefs of Hindus. It is personified as the goddess and taking a dip in its holy waters is believed to cleanse one of sins and provide spiritual purification. The banks of the river are dotted with various pilgrimage sites, temples and ashrams, making it a spiritual hub for millions of people. Many past imperial or provincial capitals (including Prayagraj, Kara, Patliputra, Murshidabad, Kannauj, Kashi, Munger, Kolkata, Kampilya and Baharampur) were located at its banks (Pandey et al. 2010).

The Ganges River originates from the merging of the Bhagirathi and Alaknanda rivers. Although the Alaknanda is longer, Hindu culture and mythology consider the Bhagirathi as the true source. The Alaknanda's headwaters are fed by snowmelt from peaks such as Nanda Devi, Trisul and Kamet. The Bhagirathi starts at Gaumukh, located at the base of the Gangotri Glacier, situated at an elevation of 3,892 metres. Spanning an 800-kilometre course through Kanpur, Kannauj and Farukhabad, the Ganges is joined by the Ramganga, contributing an average annual flow of approximately 500 cubic metres per second. The Ganges and Yamuna rivers converge

at Prayagraj's Triveni Sangam, a sacred Hindu confluence. Despite the Ganges being smaller at this point, the Yamuna contributes around 2,950 cubic metres per second, accounting for approximately 58.5% of the total flow (Khwaja et al. 2001).

Thousands of Hindu pilgrims go to the waters of three Hindu holy towns: Haridwar, Prayagraj (Allahabad) and Varanasi. Thousands of Hindu pilgrims visit these three locations to bathe in the Ganges, which is believed to wash sins and aid in salvation. The Ganges rapids are also famous for river rafting, drawing hundreds of thrill seekers throughout the summer months. Street sellers sell handcrafted floral bowls with diyas to the pilgrims to place in the river during the sunset.

1.2.7 Ecology and Environmental Challenges

In recent years, the Ganga has faced severe environmental challenges due to pollution, industrial discharges and the dumping of untreated sewage. Efforts have been made to clean and rejuvenate the river, including the "Namami Gange" program launched by the Indian government. These initiatives aim to restore the river's ecological balance and preserve its cultural and environmental significance.

Human activities, primarily related to agriculture, have displaced nearly all the original natural vegetation in the Ganges basin. Over 95% of the upper Gangetic Plain has undergone degradation or conversion to agriculture and urban development. A significant portion of relatively intact habitat remains along the Himalayan foothills, including Rajaji National Park, Jim Corbett National Park and Dudhwa National Park. In the past, the upper Gangetic Plain was inhabited by various wildlife, such as Wild Asian elephants, tigers, Indian rhinoceros, gaurs, barasinghas, sloth bears and Indian lions. However, in the 16th and 17th centuries, these large creatures were present. Presently, the region mostly hosts smaller wild animals like deer, boars, wildcats, as well as a few wolves, jackals and foxes. Bengal tigers are now primarily found in the Sundarbans region of the Ganges Delta, which is also home to crocodiles and barasingha. Unfortunately, the Sundarbans freshwater swamp ecoregion is on the brink of extinction. The upper Gangetic Plain is a habitat for endangered species like tigers, elephants, sloth bears and chousingha. Fish are abundant in the major rivers of the Ganges basin and play a crucial role in the sustenance of many people. Various fish

species, including featherbacks, barbs, walking catfish, gouramis and milkfish, are prevalent in the Bengal area. The Ganges and its surroundings are also home to the critically endangered Ganges shark. The basin supports a diverse bird population, including crows, fowls, kites, mynas, parrots and partridges. During the winter, migratory ducks and snipes flock to the wetlands, attracted by the region's abundance. The upper Gangetic Plain, however, lacks endemic bird species. Notable globally vulnerable species in the area include the Great Indian Bustard and the Lesser Florican. The lower plains feature extensive open woodlands, primarily characterized by Albizzia procera, Bombax ceiba, Sterculia vilosa and Duabanga grandiflora (Okonkwo et al., 2011). If natural forest succession proceeds, early seral forest communities would eventually be dominated by the climax species sal (Shorea robusta). However, human activities often hinder forests from reaching their peak conditions. Despite several millennia of human habitation, the woodlands in the lower Gangetic Plain remained largely untouched until the early twentieth century. Presently, only about 3% of the ecoregion is covered by natural forests and the largest remaining block is located south of Varanasi. The ecoregion hosts around forty protected areas, but more than half of them are smaller than 100 square kilometres. Fauna in the lower Gangetic Plain resembles that of the higher plains, with the addition of some new species such as the Smooth-coated Otter (Lutrogale perspicillata) and the Large Indian Civet (Viverra zibetha).

1.3 Pollution in Ganga River

Water pollution is defined as any chemical, biological, or physical change in water quality that causes harm to living creatures or renders water unsuitable for use. Metal contamination in rivers is a significant environmental concern, as it can have adverse effects on both aquatic ecosystems and human health. Heavy metals enter rivers through various sources, including industrial discharges, agricultural runoff, urban stormwater and atmospheric deposition. The sources and sinks of heavy metals are shown with the help of Figure 1.2.
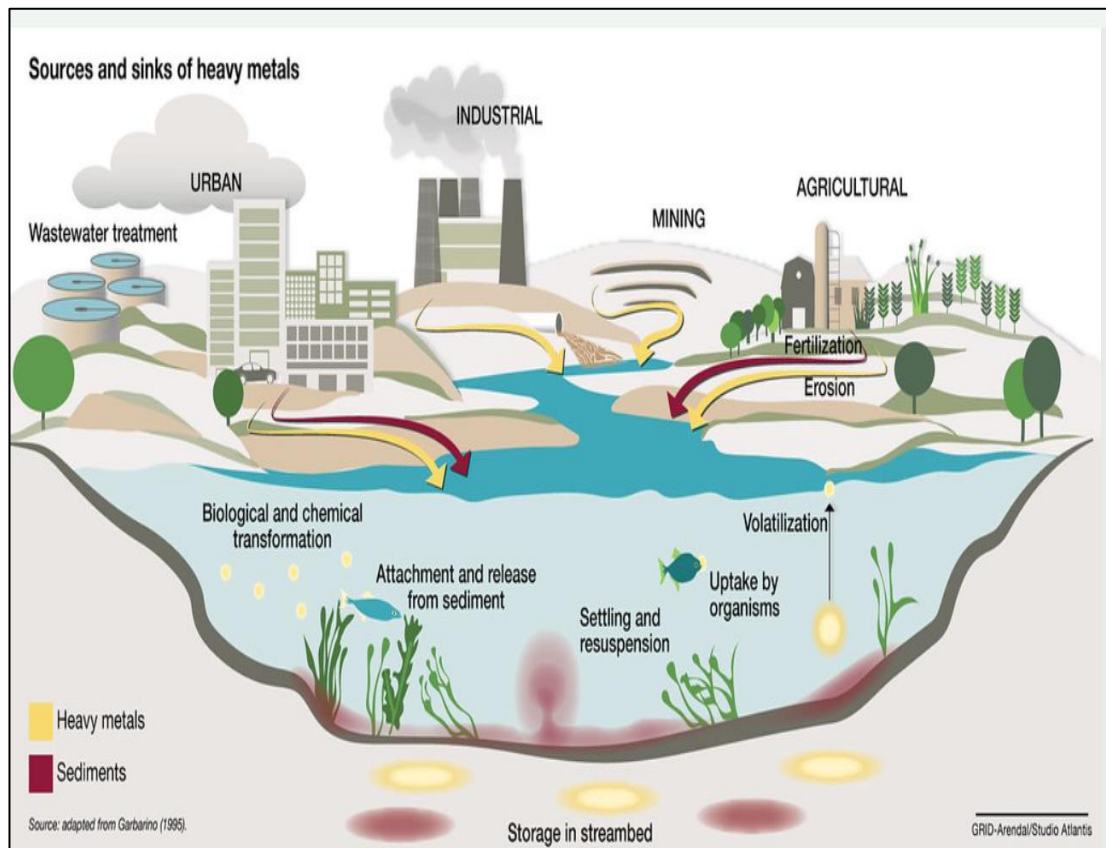
Figure 1.2 Sources and sinks of heavy metals

The Ganges was declared one of the world's five most polluted rivers in 2007, with faecal/coliform levels surpassing official Indian government regulations near Varanasi. Pollution endangers more than 140 fish species, 90 amphibian species and the endangered Ganges River's dolphin (Pandey et al. 2010). The Ganga Action Plan, an environmental effort to clean up the river, has been a colossal failure thus far due to corruption and a lack of technical competence, a lack of sufficient environmental planning and a lack of support from religious authorities (Singh et al. 2003).

Here are some key points to consider regarding heavy metal contamination in rivers:

1.3.1 Sources of contamination

There are two types of pollution sources: point sources, where the source of the pollutant is known and non-point sources, where the source of the pollutant is unknown.

Kanpur is the largest route in India for leather industry, with much of it exported to consumers in the United States, Europe and the rest of the world. These tanneries release hazardous effluents containing sulphides and chromates, as well as heavy metals such as Cd, Cr, Pb and Zn. Kanpur has over 400 tanneries that dump untreated sewage effluent into the Ganga. Many communities spread from the Ganga River and immediately discharged their waste into the Ganga. Cremation and dumping of animal carcasses in Ganga are also important sources of germs and other pollutants. Some religious holiday customs contribute to Ganga pollution. Many different types of statues made of plaster of Paris were dumped into water for religious purposes, resulting in a poisonous river.

Industrial Pollution: Industries that produce or use heavy metals, such as mining, manufacturing and metal processing, may release these contaminants into nearby rivers. There are two major sources of heavy metal contamination in rivers: human activities and economic setup. Human Beings engage in a variety of economic activities such as industrial development, thermal power plant setup, nuclear power plant installation, poultry farm and so on. Some events take place on the riverbank, while others take place elsewhere.

Industries on the river's bank discharge their garbage straight into the water. However, the government and legislation determined the quality parameters of waste water released into rivers, but industries do not follow the rules effectively, causing the quality of river water to deteriorate. Apart from the bank, the concentration of faecal coliforms in the river's waters climbs from 60,000 to 1.5 million after flowing through Varanasi and absorbing 32 streams of raw sewage from the city, with recorded peak values of 100 million per 100 ml. As a result, drinking and swimming in its waters involves a considerable risk of illness.

Rather than industries, there are several sources of heavy metals in water. While industries are the primary source of heavy metals in water, several other sources are also to blame and these are as follows:

- Input from anthropogenic sources
- Lead from domestic waste

- Paint and Dyes
- Fertilizers utilized for Agriculture
- Battery waste.
- Transportation
- Natural Input like rocks weathering

Mining: Mining operations often involve the extracting and then processing of ores of heavy metals, which can result in input of these metals into rivers, especially if proper containment measures are not in place.

Waste from temples: Hindus believe in worshiping God using flowers, Roli, Chandan and many colours. After devotion, all of these items are discarded into the river. It is moreover a practice for worshipping the Ganga River, in which case people drop a variety of items into the river, deteriorating the water quality. In the time of Ganesh Puja and Durga Puja, sculptures constructed entirely of plaster of Paris are flowed into the river, which is less soluble in water and generates a variety of pollutants. The colors used in sculptures can also be a source of heavy metals pollution.

Taking Holy Bath: Millions of people who come for taking "holy dip" into the Ganga each day, are dumping over two hundred million gallons of untreated waste of humans in the river, which resulted in high quantities of faecal coliform bacteria. As per the statutory guidelines, water used for bathing must not have greater than five hundred faecal coliforms per 100ml, however the river water upstream of Kanpur's ghaats currently has 120 times that amount, sixty thousand faecal coliforms per 100 ml.

Runoff from Agriculture: The application of heavy metal-containing herbicides, pesticides and fertilizers for agricultural purpose may lead to runoff that carries these contaminants into rivers.

Urban Stormwater: Urban areas with high traffic and industrial activity can contribute to heavy metal contamination. Rainwater can wash heavy metals from roads, rooftops and other urban surfaces into stormwater systems and eventually into rivers.

1.3.2 Effect of heavy metal contamination in rivers

Ecological Impact: Heavy metals may be toxic for aquatic life, causing harm to fish, invertebrates and more organisms. This may cause disruption in the food chain and ecosystem balance, leading to reduced biodiversity.

Water Quality: Heavy metal contamination affects the characteristics of water both physical and chemical, leading it unsafe for utilization and other uses. High concentrations of heavy metals can render water unfit for drinking, irrigation and industrial processes.

Human Health Risk: If heavy metal-contaminated river water is used for irrigation, drinking or cooking, it may pose a serious risk to health of human. Prolonged exposure to substantial amounts of heavy metals like lead, mercury and cadmium may result in various health problems like organ damage, neurological issues and even cancer.

1.3.3 Monitoring and Remediation

Monitoring: Governments and environmental agencies monitor water quality in rivers to assess heavy metal contamination levels. Regular testing and data analysis help identify polluted areas and guide mitigation efforts.

Remediation: Remediation efforts aim to reduce heavy metal contamination in rivers. Common techniques include the treatment of wastewater from industries, implementing best agricultural practices to reduce runoff and implementing stormwater management measures in urban areas.

Sediment Remediation: In many cases, heavy metals can accumulate in river sediment. Remediation efforts may involve removing or capping contaminated sediment to prevent further contamination of the water column.

Restoration: Efforts to restore damaged ecosystems may include planting native vegetation along riverbanks, which can help filter pollutants and stabilize the riverbanks.

Addressing heavy metal contamination in rivers requires a multidisciplinary approach involving government regulations, industrial practices and public awareness. It is

crucial to prevent further contamination and to undertake restoration efforts in affected areas to protect both the human health and environment.

1.4 Heavy Metals

Heavy metals are a group of metallic elements characterized by their high density and often toxic properties. These metals have a higher atomic weight than most common elements and they include elements such as lead (Pb), mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), Manganese (Mn), Nickle (Ni) and others. While some heavy metals are essential trace elements that the human body needs in small amounts such as iron (Fe), zinc (Zn) and copper (Cu), many others can be harmful to living creatures if present in excess quantity.

Here are some key characteristics and information about heavy metals:

1.4.1 Toxicity

Many heavy metals are highly toxic to living creatures like human beings, when they accumulate in the body beyond safe levels. They can cause a wide range of health problems that includes development issues in children, neurological disorders, damage of organs and cancer.

1.4.2 Bioaccumulation

Heavy metals tend to accumulate in living organisms, especially in the food chain. This means that smaller organisms absorb these metals from their environment and when larger organisms consume them, the heavy metals accumulate at higher concentrations. This is a major concern for ecosystems and human health.

1.4.3 Common heavy metals with their associated risk to humans

Lead (Pb): Lead is a toxic and unessential heavy metal. It is generated from both natural and anthropogenic sources. The main sources of lead concentrations are airborne particles, effluents of leather factories, forest fires, emissions from vehicles, volcanoes, waste incineration, paints, and pesticides. Earth's crust contains 15 to 20 µg/g of Pb concentration (Abadin et al., 2007). Lead exposure can lead to neurological and developmental problems, especially in children. Lead poisoning, also known as colica, pictonum, plumbism and saturnism, is a medical condition resulting from

elevated levels of the lead metal in the body (Padmapriya and Murugesan 2012). Lead alters various physiological processes and poses a threat to numerous organs and tissues, including the bones, heart, intestines, kidneys, neurological system and reproductive system. Its impact on nervous system development makes it particularly harmful to children, potentially causing irreversible cognitive and behavioural impairments (Voijant et al. 2011). Symptoms of lead poisoning encompass anemia, disorientation, headaches, irritability stomach discomfort and in severe cases, convulsions, coma and death (Sauve et al. 1999)

Copper (Cu): Copper, a trace element present in all tissues, plays a crucial role in respiration of cells, neurotransmitter biosynthesis, pigment formation, peptide amidation and the strength of connective tissues. Copper is an essential nutrient in freshwater and river sediment for the growth of aquatic life, but its higher concentration is toxic. It is induced in the environment from natural sources such as decaying vegetation, volcanic eruptions, sea spray, forest fires, and from anthropogenic activities like wastewater from industries and municipal corporations (Dorsey & Ingerman 2004). After several natural processes, the dissolved Cu finally gets adsorbed in the sediment. It serves as a cofactor for numerous enzymes and is vital for the development of the central nervous system; insufficient copper levels may lead to incomplete development (Kayser et al. 2000), while excess copper can be harmful. Copper has been linked to the generation of free radicals through the Haber-Weiss reaction, causing damage to mitochondria, DNA breakage and impairment of neurons. The presence of faulty copper transport and improper interactions between copper and proteins in various human neurological disorders underscores the essential role of this trace metal in healthy neurodevelopment and neurological function (Padmapriya and Murugesan 2012). Biochemical features of human diseases related to copper homeostasis suggest potential copper status biomarkers applicable to broader populations (Sauve et al., 1999). In some Alzheimer's disease patients, elevated copper levels in cerebral fluid have been observed despite normal plasma copper concentrations. Neuronal damage results in the loss of muscular strength and respiratory issues, ultimately leading to a fatal outcome (Cavet et al. 2003).

Manganese (Mn): Mn concentration in the earth's crust ranges between 40 and 900 µg/g (Williams et al. 2013). Sewage sludge, municipal wastewater, mining waste, waste from various metal processing units, alloy production unit emissions, and fossil fuel combustion is the source of manganese in sediment.

Nickel (Ni): Ni is used in alloys with chromium, iron, copper, and zinc. It is widely used in the industry such as fuel production, household appliances, food production, electroplating, pigments, ceramics, jewellery manufacturing, heat exchangers, magnets, coins, medical prostheses, batteries, etc.

Cadmium (Cd): Cd, a byproduct generated during the production of zinc, poses a significant threat to human health when encountered in occupational settings or the surrounding environment. Once absorbed, Cd is effectively retained in the human body and accumulates over a person's lifetime (Brown et al. 1995). Cadmium is an unessential element and adversely affects the growth of plants. Cd is a by-product of Zn and Pb mining and smelting and is more mobile in aquatic environments than most of the other metals. Cd is released into the environment by metallurgical industries, atmospheric deposits, power plants, fertilizers, natural atmospheric processes, municipal solid waste (MSW) incineration, and discharge of toxic effluents from industries and wastewater treatment units (WHO 2019). It is extremely important to study this contaminant because it is highly toxic and water soluble. Earth's crust contains 0.1 to 0.5 µg/g of Cd (Faroon et al. 2013). The kidney is particularly susceptible to the harmful effects of Cd, especially in the proximal tubular cells, where the metal primarily accumulates. Additionally, Cd can contribute to bone demineralization, either through direct destruction of bone or indirectly through renal failure. Prolonged exposure to airborne Cd in workplaces may impair lung function and elevate the risk of lung cancer (Hammer et al. 2003). While these detrimental effects have been observed in individuals exposed to moderately high Cd levels in industrial or heavily polluted areas, recent studies suggest that even chronic low-level exposure to Cd, common in industrialized nations, may adversely affect the kidneys and bones of the general population (Knight et al. 1997). These studies establish consistent associations between various indicators of renal and bone health and the excretion of Cd in urine, a measure used to assess the body's Cd burden (Kayser, 2000). However, the full implications of these findings for public health remain uncertain.

Further research is essential to confirm whether these correlations are causative or if they arise from concurrent changes in Cd metabolism, bone or kidney function due to factors such as aging or unrelated disorders (Smilde et al. 1992).

Zinc (Zn): While zinc is essential for human health, excessive concentrations of it can lead to problems for most individuals when applied to the skin or taken orally in doses exceeding 40 mg per day (Whiting et al. 2001). The regular supplementation of zinc is not recommended without the guidance of a healthcare professional (Kayser et al. 2000). In certain individuals, zinc may trigger adverse effects such as nausea, vomiting, diarrhea, a metallic taste and damage to the kidneys and stomach (Shen et al. 1997). When applied to injured skin, zinc can cause sensations like burning, stinging, itching and tingling (Delorme et al. 2001). Taking large doses of zinc is potentially hazardous and may lead to symptoms such as fever, coughing, stomach ache, fatigue and various other side effects. The risk of prostate cancer increases when taking more than 100 mg of supplementary zinc daily for ten years or more. Additionally, there is concern that combining a multivitamin with a separate zinc supplement may elevate the risk of death from prostate cancer. Ingesting 450 mg or more of zinc per day may induce iron deficiency and single zinc doses ranging from 10 to 30 grams can be lethal. Sediment may contain up to 100 µg/g of zinc in its natural state. Human activities and natural processes are the sources of Zn. The use of fertilizers for agricultural purposes in the catchment of the rivers leads to increase in Zn concentrations in river sediment (WHO 2000).

Chromium (Cr): Hexavalent chromium (Cr (VI)) is recognized as a carcinogen and has the potential to induce respiratory and skin-related health issues. Chromium has an average concentration of 100 µg/g in the earth's crust. Chromium compounds are used in dyes, paints factories, and leather industries, these compounds get transported in the soil and groundwater of industrial sites (Abadin et al. 2012). Paints base containing chromium is used for automotive refinishing applications that lead to chromium pollution in the rivers.

The source, health impacts and effect of various heavy metals on humans are summarized in Table 1.2 and Figure 1.3.

Figure 1.3 Effects of various heavy metals on health of humans
(Source: Bayuo et al., 2022)

Table 1.2 Heavy metals, their possible sources and health impacts

Heavy Metal	Source	Health Impacts
Arsenic (As)	Fossil fuel, Fungicides, Metal Smelters, Paint, Pesticides, Textiles industries	Bronchitis, Dermatitis (Skin irritation)
Cadmium (Cd)	Cd-Ni batteries, Electroplating, Fertilizers, PVC products, Pesticides, Nuclear fission plant, Welding	Bone marrow cancer, Bronchitis, Gastrointestinal disorder, Kidney damage
Chromium (Cr)	Electroplating, Metallurgical industries, Photography, Rubber, Tannery Industries, Textile	Rapid loss of hair, Respiration problem
Copper (Cu)	Electronics waste, Electroplating, Mining, Pesticides	Failure of Brain and Kidney, Intestinal irritation, Severe anaemia
Lead (Pb)	Automobile emission, Burning of coal, Mining, Paint, Pesticide, Smoking, Wastewater	Gastrointestinal damage, Kidney, Liver, Mental retardation in children
Manganese (Mn)	Fertilizers, Ferromanganese production, Fuel, Welding	Inhaling or coming into contact with it results in harm to the central nervous system.
Mercury (Hg)	Batteries, Chemical industries, Paper industry, Pesticides, Polluted water, Scientific instrument,	Nervous system damage
Nickel (Ni)	Battery industries, Electroplating, Fertilizers, Iron-steel industries, Zinc base casting	Genotoxic, Hepatotoxic Immunotoxic, Lungs, throat and stomach cancers, Neurotoxic, Rapid hair fall
Zinc (Zn)	Brass manufacture, Galvanisation metal Plating, Immersion of painted idols, Refineries	Exposure to zinc fumes can cause corrosive effects on the skin, induce nerve membrane damage

1.4.4 Regulation

Due to their harmful effects, many countries have strict regulations on the permissible range of heavy metals in air, water, soil, consumer products and food.

1.4.5 Remediation

Remediation efforts involve removing or reducing heavy metal contamination in the environment. Techniques include soil and water treatments, phytoremediation (using plants to absorb and accumulate metals) and waste management practices. It is important to monitor and manage heavy metal contamination to protect the environment and human health, as their persistence and toxicity pose significant risks (Chen et al. 2016).

1.5 Heavy Metal Accumulation in River Sediment

The contamination by trace metals poses a severe threat to aquatic systems due to their toxicity, abundance, persistence in the environment and subsequent accumulation in aquatic habitats (Fu et al. 2014; Qadir & Malik 2011). Research indicates that water sources are contaminated by trace elements through processes such as geological erosion and erosion (Kaushik et al. 2009), atmospheric deposition (Demirak et al. 2006), disposal of treated and untreated liquid effluents, fertilizers and pesticides containing metals (Iqbal & Shah 2014), as well as chemicals from diverse urban, industrial and agricultural activities (Park & Presley 1997; Xiao et al. 2013).

Sediment plays a crucial role in the aquatic ecosystem, serving as a source of nutrients for the substrate and supporting micro and macro flora and fauna, forming the foundation for living aquatic resources. Some studies suggest that sediment quality can act as an indicator of pollution levels and sediment can serve as a tool for identifying historical pollution and recent environmental changes. Elevated levels of trace metals in aquatic sediment may pose a potential risk to human health as they transfer to aquatic biota and, ultimately, the food chain (Salati & Moore 2010; Varol & Sen 2012).

During the latter part of the 20th century, rapid urban-industrial growth and increased food production to meet the needs of a growing population led to surface water bodies receiving substantial amounts of contaminants, including heavy metals. Sediment, being the final sink and indicator of changes in the water column, reflect the influence

of anthropogenic activities on air and watersheds. Anthropogenic heavy metals, entering rivers as inorganic complexes or hydrated ions, easily adsorb onto sediment surfaces, constituting the labile fraction. Environmental variables such as turbulence, water pH, redox potential, seasonal flooding and storms can periodically remobilize contaminated surface sediment, making them a potential source.

Metals introduced through natural processes like erosion, weathering and dissolution of water-soluble salts constitute the background level, but those added by anthropogenic activities significantly increase sediment concentrations. As non-biodegradable substances, metals accumulate in sediment and biota along the food chain, exerting a long-term impact on the ecosystem. Benthic organisms, in direct contact with sediment, are particularly susceptible to such exposures. Non-essential metals like Cd and Pb can be harmful even at very low concentrations (Pehlivan et al. 2009).

Plankton is affected by secondary contamination of the water column (Copaja et al. 2014) and transfer through the food chain may eventually lead to adverse effects on human health. River channels near urban areas receive heavy metals from both anthropogenic and natural sources, including household waste, industrial wastes and municipal sewage. Additionally, particulate metals in air suspension arrive directly through atmospheric deposition and indirectly through surface runoff (Pandey et al. 2014).

Heavy metals accumulate in river sediments through natural processes like rock weathering and soil erosion, as well as human activities such as industrial discharge, agricultural runoff, and urban pollution. These metals are transported in dissolved or particulate forms, often attaching to fine-grained particles like clay or organic matter.

Key processes include adsorption (binding to sediment particles), co-precipitation (forming compounds that settle), and deposition in slow-flowing areas. Factors such as pH, redox conditions, sediment grain size, and organic matter content influence accumulation. Over time, sediments act as a long-term sink for heavy metals, though disturbances can remobilize them, posing environmental risks.

The accumulation of heavy metals in river sediment is demonstrated with a conceptual diagram in Figure 1.4.
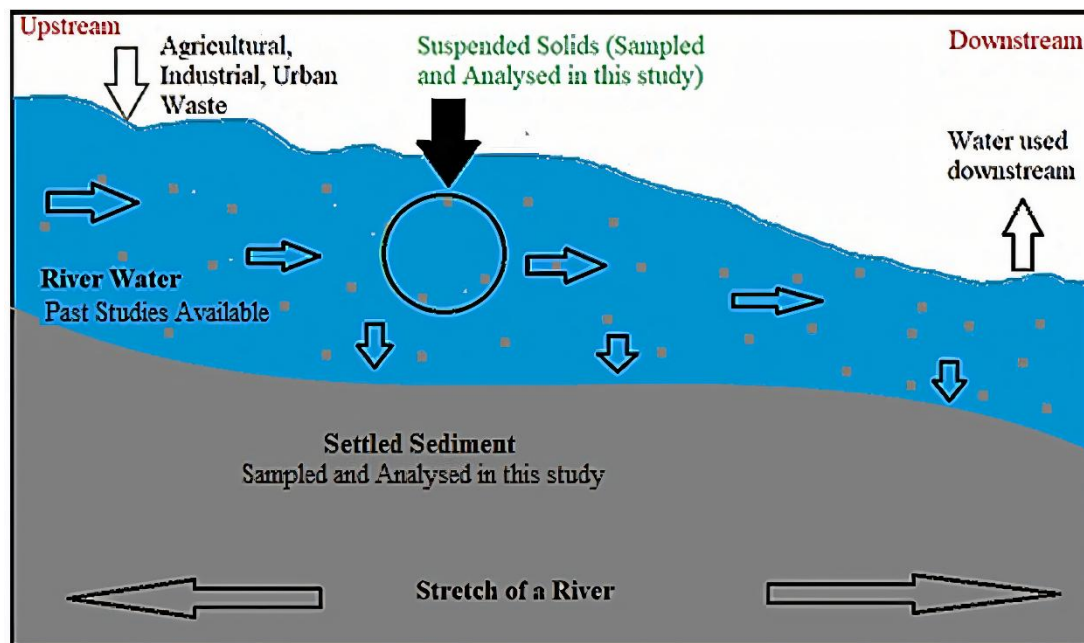
Figure 1.4 Conceptual diagram showing the movement and settling of sediment in the river

1.6 Research Objectives

The primary objective of this research is to examine the heavy metals present in riverbed sediment and suspended sediment of river Ganga within a stretch of 225 km between Kanpur to Prayagraj, U.P., India.

The specific objectives of this study are:

1. To identify the heavy metal (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) concentrations in the riverbed sediment and suspended sediment of Ganga River.
2. To study the variations in the heavy metal concentrations along the stretch of Ganga River.
3. To classify the source of heavy metal contamination as Natural or Anthropogenic.
4. To do the risk assessment of heavy metals contamination with the help of various sediment pollution indices like geoaccumulation index, enrichment factor, contamination factor and pollution load index and comparing them with sediment quality guidelines (SQGs).

1.7 Organization of Thesis

This thesis is structured into five chapters. A concise overview of each is provided as follows:

Chapter 1: This chapter provides a succinct introduction to the Ganga River and its significance, outlines the adverse effects of heavy metals, discusses the contamination of rivers by heavy metals, introduces the risk assessment procedure and highlights the novelty along with the objectives of the current study.

Chapter 2: This chapter presents a review of relevant literature related to heavy metal studies conducted on various rivers including Ganga River.

Chapter 3: This chapter explained the study area and selected sampling locations, sampling procedure and methodology to detect concentrations of heavy metals in riverbed sediment and suspended sediment of Ganga River. Sediment quality indices used to assess heavy metal contamination and procedure for statistical investigation have been discussed.

Chapter 4: This chapter incorporates the results with the concentrations of heavy metals and their risk assessment in riverbed sediment and suspended sediment of Ganga River using various Sediment quality indices. Variations in metal concentrations along sites, correlation matrix and classification of source are also discussed in this chapter.

Chapter 5: This chapter presents the conclusions drawn from the current study. Additionally, it proposes potential future directions for further research in this field.

Chapter 2
REVIEW OF LITERATURE

2.1 General

In Kanpur and Prayagraj, rapid industrialization is causing a continuous release of toxic heavy metals into aquatic environments. The existence of these metals poses a substantial ecological challenge owing to their elevated toxicity and the propensity to accumulate in living organisms. Numerous toxicologists focused to analyze and detect heavy metal levels in various elements such as sediment, water bodies, fish organs, soil and plankton. This chapter aims to offer a comprehensive review of concentrations of heavy metal in water and sediment, providing recommendations to mitigate health risks associated with consumption.

There are many industries near the banks of the river, emerging as a primary contributor to pollution. This pollution poses health risks for the population that relies on the consumption of contaminated water and associated food items. Numerous publications worldwide address the detection of heavy metals, a topic extensively explored in this chapter. Various heavy metal studies conducted on river Ganga and on other world rivers, sediment quality indices have been discussed in Chapter 2.

2.2 Assessing Heavy Metal Pollution in Rivers

Assessing river pollution caused by heavy metals is crucial for understanding the extent of contamination, its potential environmental and human health impacts and for developing effective remediation and management strategies. Various agencies like the United States Environmental Protection Agency (USEPA), World Health Organization (WHO), the European Union (EU) and various other environmental agencies in different countries, contribute to the development of methodologies and guidelines for assessment of river pollution by heavy metals. Researchers and experts related to the fields of environmental science, chemistry and ecology also play a significant role in shaping these assessment procedures. The assessment typically involves a combination of field investigations, water and sediment sampling, laboratory analysis and data interpretation. Here is a step-by-step guide to assess heavy metal pollution in rivers:

i. ***Define Objectives:***

Objectives are defined depending on the type of study. Whether is it focused on a specific river segment, a particular heavy metal, or its impacts on aquatic life and human health? Knowing the objectives, the assessment will be guided.

ii. ***Study Area Selection:***

Specific river or river segment to be assessed is chosen. This may depend on factors like geographic location, known pollution sources and the availability of resources for sampling and analysis.

iii. ***Literature Review:***

A literature review is carried out to collect prevailing information about the river, including its history of pollution, known pollution sources and any previous assessments or studies related to heavy metals.

iv. ***Field Investigations:***

Field investigations are conducted to collect primary data. This may include the following:

    a. *Water Sampling:* Collect water samples at various points along the river, considering different seasons and flow conditions. Use appropriate sampling equipment to minimize contamination.

    b. Sediment Sampling: Collect sediment samples from the riverbed at the same locations as water samples. Sediment often accumulates heavy metals over time and can provide valuable insights.

    c. Biological Samples: Collect aquatic organisms (e.g., fish or benthic invertebrates) if applicable. The heavy metals concentrations in aquatic organisms can indicate bioaccumulation.

v. ***Laboratory Analysis:***

Collected samples are analysed in a laboratory for heavy metal concentrations. Common analytical techniques include Atomic Absorption Spectroscopy (AAS).

vi. ***Data Interpretation:***

Results of the laboratory analysis are interpreted. Heavy metal concentrations of the study are compared with regulatory standards or established guidelines to determine the extent of pollution.

vii. Graphing:

Graphs are created to illustrate the distribution and variations of heavy metals in the river.

viii. Risk Assessment

The ecological and human health risks related to the observed heavy metal pollution are assessed. Evaluation of potential impacts on aquatic life and communities living near the river is carried out.

ix. Source Identification:

Sources of heavy metal pollution are classified (anthropogenic or natural) and identified. This may require further investigations and collaboration with relevant authorities.

x. Reporting and Recommendations:

Findings of the study are compiled into a comprehensive report. Maps, tables and graphs to are included to present the data clearly.

Recommendations for remediation and management actions are provided. These could include improving wastewater treatment, regulating industrial discharges and promoting sustainable land use practices in the watershed.

xi. Monitoring and Follow-up:

A monitoring plan can be established to trace variations in heavy metal levels over time. Regular assessments can be done to measure the effectiveness of pollution control efforts.

xii. Public Awareness and Engagement:

Engage with local communities and stakeholders to raise awareness about the issue and involve them in the remediation and conservation efforts.

Assessing heavy metal pollution in rivers is a complex and multidisciplinary task that requires collaboration between scientists, environmental agencies and local communities. The results of such assessments are vital for protecting the aquatic ecosystems health as well as the well-being of people who rely on these water bodies for various purposes.

2.3 Heavy Metal Status in River Ganga Water and Sediment

Numerous researchers have conducted comprehensive investigations into the heavy metal contamination of the Ganga River.

Ansari et al. (1999) measured Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sn and Zn contents in Ganga sediment in the Kanpur-Unnao industrial zone. According to them, anthropogenic input accounts for approximately 90% of the levels of Cd, Cr and Sn; 50-75% of organic carbon, Cu and Zn; and 25% of Co, Ni and Pb in sediment.

Ansari et al. (2000) investigated the role of monsoon rain on metal pollutant concentrations and dispersion patterns in Ganga sediment in the Kanpur-Unnao industrial region and discovered that monsoon rain decreases the contents of Co, Cr, Fe and Ni while increasing the contents of Cd, Sn and Zn.

In a study, Sarkar et al. (2007) examined the concentrations of dissolved heavy metals, including Fe, Zn, Mn, Cu, Pb and Hg, in three ecologically distinct zones along the Ganga River in West Bengal: Gangasagar, Diamond Harbour and Babughaat. The authors noted that Hg and Pb had elevated values, which they attributed to the discharge from pulp and paper manufacturing units and automobile emissions runoff.

Purushothaman & Chakrapani (2007) performed an evaluation of the levels of heavy metals (Fe, Mn, Co, Cu, Zn, Pb, Ni and Cr) in different chemical fractions of sediment. The research entailed the utilization of the Sequential Extraction Technique (SM&T protocol) to partition metals in sediment. For various fractions, the Metal Enrichment Factor (MEF) and Geo-accumulation Index (GAI)were computed. The GAI values varied from 4 to 5 and the MEF values surpassed 20 at nearly all downstream locations. The results of this study indicate that metals may be introduced via industrial and urban effluents. On the contrary, uncontaminated river sediment originating from the rivers in the Himalayas displayed diminished levels of metal concentrations, as well as reduced amounts of GAI and MEF.

Beg & Ali (2008) conducted a study of the sediment quality in the Ganga River, which flows through the city of Kanpur and is the discharge point of effluents from tannery industries. In addition to toxicity bioassays, sediment samples were collected from

both upstream and downstream regions for trace metal analysis. The research findings indicated that the concentration of Cr in sediment downstream was thirty times greater than that of sediment upstream, among a range of trace metals. In addition, it was determined that the Cr concentration in the sediment downstream exceeded the probable effect level, suggesting that the river system's ecological health could be negatively impacted.

A study was undertaken by Kar et al. (2008) to assess the water quality of the Ganga River in West Bengal from 2004 to 2005. From April 2004 to March 2005, the authors gathered a cumulative of 96 surface water samples from two locations i.e. from a discharge point and the middle of the river stretch—at four monitoring stations: Berhampore, Palta, Dakshineshwar and Uluberia. A multitude of parameters were assessed on the gathered samples, encompassing pH, electrical conductivity (EC), Fe, Mn, Zn, Cu, Cd, Pb, Cr and Ni. The results of the study indicated that the sequence of heavy metal dominance in the Ganga River's surface water was as follows: Fe > Mn > Ni > Cr > Pb > Zn > Cu > Cd. A notable positive correlation was observed between conductivity and both Cd and Cr concentrations in the water. On the other hand, conductivity was negatively correlated with Mn. The acquired data were subjected to statistical analysis utilizing SPSS software, which comprised analysis of variance (ANOVA) and correlation analysis among all parameters.

Bhattacharya et al. (2008), between 2006 and 2007 investigated the deposition of heavy metals in water, sediment and tissues of various edible fish species in the Rishra-Konnagar region, located on the upper portion of the Gangetic River in West Bengal. The concentrations of Zn, Cr, Cu, Cd and Pb in sediment, water and commercially consumable fish samples at the sampling station exhibited a distinct seasonal oscillation, according to them. The order of heavy metal concentrations is as follows: Zn > Cr > Cu > Cd > Pb.

Gupta et al. (2009) examined the presence and accumulation of heavy metals in the riverine water, detritus and musculature of two catfish species, namely Channa punctatus (C. punctatus) and Aorichthys aor (A. aor), both of which were collected from the Ganges River in Prayagraj. The heavy metals examined in the study included

Cu, Cr, Cd, Pb and Zn. During the period of 2005-2006, water, detritus and two species of fish were sampled bimonthly by the researchers from different locations along the Ganges River in Prayagraj. The findings of the research indicated that the heavy metal concentrations in the water samples were as follows: Zn > Pb > Cu > Cr > Cd. Zn accumulated the most in sediment analysis, followed by Pb, Cr, Cu and Cd. In a similar fashion, the accumulation of heavy metals in fish musculature followed the following sequence: Zn > Pb > Cu > Cr > Cd. In comparison to other metals, Zn accumulated the most in the musculature and detritus of both fish species, according to the findings.

Kumar et al. (2009) investigated the effects of effluents discharged into the Ganga from diverse sources on Kanpur and Varanasi in terms of chemical composition, energy transformation rate and heavy metal concentration. As per their report, the effluents contained elevated concentrations of heavy metals (Cu, Cr, Cd, Pb and Zn) at the discharge site, while a significant decline in concentration was observed below the discharge zone.

Pandey et al. (2009) examined the issue of heavy metal contamination in the Ganga River as it pertained to atmospheric deposition. The researchers found that while Cr and Cu concentrations remained below the maximum allowable levels, mid-stream waters at five of the six sampling stations contained levels of Cd and Pb that exceeded their respective maximum allowable concentrations.

Pandey et al. (2010) conducted an investigation at Varanasi, India for the water quality of the midstream Ganga River, focusing on the influence of aerially-driven heavy metals. Water samples were collected from twelve sampling stations at fortnightly intervals between March 2006 and February 2008. The analysis included the examination of Cu, Cd, Ni, Cr, Zn and Pb concentrations. The findings indicated that the midstream water of the Ganga River at Varanasi consistently showed contamination by heavy metals. The highest concentrations of Cu, Cr, Cd, Pb and Ni were observed during the winter, while Zn exhibited its highest concentration during the summer season. The overall concentration trend of heavy metals in the water was Zn > Ni > Cr > Pb > Cu > Cd. While the levels of these heavy metals in the water remained below the permissible limits set by Indian standards for potable water, three

locations surpassed the globally prescribed maximum allowable concentrations (MAC) for Cd, Ni, and Pb.

Wasim Aktar et al. (2010) performed the evaluation of the surface water quality of the Ganga River in the vicinity of Kolkata between November 2005 and October 2006. A multitude of physico-chemical parameters were assessed in the water samples they gathered and analyzed. These parameters comprised total carbon, chemical oxygen demand (COD), biological oxygen demand (BOD), total dissolved solid (TDS), total suspended solid (TSS), total solid (TS), total phenol, total cation exchange capacity (CEC), and total volatile solid (TVS), total fixed solid (TFS). Furthermore, the researchers ascertained the levels of heavy metal concentrations, encompassing Fe, Mn, Cu, Zn, Pb, Cd, Cr, and Ni, at four distinct sites situated along the Ganga River in the vicinity of Kolkata. For each site, they utilized sampling points situated in the stream's midpoint and a discharge point. All of the heavy metals under investigation were found to be present in the water samples, with the exception of Cr, which was not detected in any of the samples analyzed. There was no substantial variation observed in the concentrations of the metals with respect to the sampling locations and discharge points. Conversely, the investigators noted seasonal fluctuations, wherein heavy metal concentrations were highest during the wet season and lowest during the winter.

Kumar et al. (2010) conducted a study on the concentration of arsenic (As) in groundwater within the middle Gangetic Plain of Ghazipur district. The research revealed that there was an enrichment of arsenic in the sampling sites situated in close proximity to the Ganges River. The study also observed greater spatial and temporal variations in arsenic concentrations in the pre-monsoon period as compared to that in the post-monsoon period. To discern the factors contributing to the gradual arsenic enrichment in the middle Gangetic plain, Kumar and colleagues utilized correlation matrices and factor analysis.

Rai et al. (2010) did the analysis of water samples collected from three sewage treatment facilities that consistently release effluent into the River Ganga. From March 2005 to February 2006, samples of sewage were gathered from the discharge points of

the treatment facilities into the Ganga during the initial week of every month. The research entailed the examination of a multitude of physio-chemical parameters in water samples, comprising dissolved oxygen (DO), biological oxygen demand (BOD), chemical oxygen demand (COD), nitrate, phosphate, and heavy metals (Zn, Cu, Cd, Pb, and Cr). The findings of the study revealed that the disposed effluents exhibited concentrations of heavy metals, biological oxygen demand, and dissolved oxygen that surpassed allowable thresholds at all three locations. Moreover, coliform counts and the most likely number index of E. coli in water samples were detected in irrigated water samples and vegetables, indicating that severe microbial and faecal pollution poses a grave health risk. The authors analysed the acquired data at each sampling site using statistical tools such as ANOVA, Duncan's multiple range tests, and Pearson's coefficient of correlation, all at three levels.

Kansal et al. (2011) investigated the water quality characteristics concerning heavy metals, namely Cu, Fe, Pb and Zn and their associations with physiological parameters in water bodies flowing through the Garhwal and Kumaon zones of the Uttarakhand state of India during the year 2010. According to their results, every recorded concentration of Pb, Cu, and Fe surpassed the thresholds set by the World Health Organization (WHO) for potable water, while no observations of Zn surpassed the standard limit. Cu exhibited the highest concentration among all the samples, with a particularly elevated concentration in the water bodies of the Kumaon region. Additionally, all the metals showed a negative correlation with dissolved oxygen and pH. The researchers concluded that the water bodies in the Kumaon region are significantly polluted, primarily due to heavy industrial discharge and untreated sewage disposal.

Katiyar (2011) examined the impact of tannery effluent on the physicochemical properties and heavy metal concentrations of river Ganga water in the vicinity of Jajmau, Kanpur, in relation to seasonal variations. With seasonal variation, chromium concentrations were high at almost all sampling locations; consequently, the effluent from tanneries had a severe negative impact on the Ganga River.

Leena et al. (2012) conducted an analysis of the heavy metals' concentrations, specifically Zn, Cr, Cd, Ni and Cu, in both water and sediment at three different sites along the river channel: Champanala, Mond Ghaat and Burning Ghaat. The study spanned a two-year period from January 2007 to December 2008. Furthermore, an assessment was conducted on a range of physico-chemical parameters, such as phosphate-phosphorus, total hardness, pH, dissolved oxygen, and nitrate-nitrogen, in order to determine whether they had a direct or indirect impact on the occurrence, movement, or speciation of heavy metals. According to the authors, the sediment of the Ganga River from Champanala to Barai were deemed devoid of Ni, Cd and Cu contamination. On the other hand, the contamination status of the river segment was indicated by the Cr and Zn concentrations, which could be detrimental to its abundant biodiversity.

Sharma et al. (2012) investigated the distribution of nonradioactive heavy metals (Zn, Cd, Cu, and Pb) in the water of the Ganga River from Rishikesh to Prayagraj. The investigation findings indicated that certain sites exhibited heavy metal concentrations that surpassed the established limits, suggesting a greater degree of anthropogenic activity.

Paul & Sinha (2013) conducted a study to investigate seasonal changes in quality of river water, particularly regarding contamination by heavy metal. The researchers collected water samples from four polluted locations along the Ganga River in West Bengal throughout the year 2011. The samples were examined for heavy metals, including Cr, Pb, Cd and Zn. The results revealed that, during the study year, the maximum concentrations of Cr, Zn, Cd and Pb occurred in the summer, whilst the lowest concentrations were observed in the monsoon season. The average concentrations of the studied metals followed the sequence: Zn > Pb > Cr > Cd. Importantly, the study found that during the monitoring period, the concentrations of the majority of these heavy metals consistently surpassed the maximum allowable limits.

Bhatnagar et al. (2013) examined the impact of the waste from tanneries on the sediment of the Ganga River at Jajmau, Kanpur, with a particular focus on heavy

metals. The researchers identified substantially elevated concentrations of heavy metals including Cr, As, Co, Fe, Cu, Mn, Zn, Pb, Cd, and Ni. The sediment concentrations of heavy metals were found to be greater in the downstream Jajmau area compared to the upstream area.

Singh et al. (2013) conducted a study on the geogenic distribution and baseline concentration of heavy metals, including Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, in the sediment of the river Ganga. They applied Muller's geo-accumulation index to classify the sediment of the Ganges River as essentially unpolluted concerning these heavy metals. The study revealed that the concentrations of Cr, Cu and Ni were found to be above the lowest effect level (LEL), indicating the possibility of detrimental effects on the biogeochemistry of the river's ecosystem. The intense weathering of the Himalayas and the monsoon-influenced fluvial processes, according to the researchers, resulted in a significant uniformity of heavy metal distribution in river sediment.

Avantika et al. (2013) quantified the levels of various heavy metals (including Cr, Cu, Fe, Ni, Pb, and Zn) in the Ganga water at Prayagraj. The researchers concluded that all heavy metal concentrations at all sampling locations exceeded the allowable limits. As indicated by the elevated concentrations of heavy metals in the study area, the river is extremely polluted.

Naushad et al., (2014) depicted the distribution and concentration of heavy metals in the water of the Ganga and Yamuna River within Prayagraj city. Samples of water were gathered from four distinct locations, namely Saraswati Ghaat, Sangam, Arail Ghaat and Old Bridge. The researchers analysed several heavy metals, including Ni, Cr, Fe, Cd, Mn and Pb, using an Atomic Absorption Spectrophotometer apparatus. The findings indicated that the heavy metals concentrations in the collected water samples followed a decreasing sequence: Fe > Ni > Cd > Cr > Pb > Mn.

Goswami & Sanjay (2014) investigated the concentrations of lead, cadmium, zinc and copper ions in both water and sediment of the Ganges River at various locations from Rishikesh to Prayagraj using Differential Pulse Anodic Stripping Voltametry (DPASV). The author found that the water samples of Narora barrage exhibited the highest contamination levels with cadmium (Cd) and copper (Cu). Conversely, at

Jajmau in Kanpur, zinc (Zn) and lead (Pb) were observed at their maximum levels compared to other sites. Additionally, Pb, Cd and Cu concentrations in bed sediment were maximum along the riverbank of Narora Ghaat and in Jajmau, Kanpur. Zinc (Zn) was detected in the highest concentrations in the Jajmau river bank sediment and the Narora bed and bank sediment, respectively. The research findings indicate that the water and sediment contamination at Narora Barrage and Jajmau, Kanpur is concerning. These areas have accrued contaminants as a result of point source discharges from tannery industries.

Kumar et al. (2014) examined the potential impact of heavy metal concentrations (Cr, Mn, Fe, Cu, Zn, and Pb) on fish fauna at five locations along the Ganga River in Prayagraj during the different seasons. Their research has revealed that there are greater fluctuations in all parameters between seasons, but fewer fluctuations between sites.

Pandey et al. (2014) utilized sequential extraction process (SEP) and total acid digestion (TAD) to analyse the geochemical fractions of nine heavy metals (Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb) that were found in the sediment of the Ganga River spanning from Samne Ghaat to the Varuna-Ganga confluence in Varanasi. The Geo-accumulation Index (Igeo) and Risk Assessment Code (RAC) demonstrated greater apprehension regarding Cd and Pb, while the accumulation indices for Mn, Fe, and Ni were negative at all sampling stations. The available fraction contained significant amounts of Pb, Cd, Cu, and Ni; nevertheless, the Igeo of Ni was consistently negative at all sampling stations.

2.4 Heavy metal studies on other rivers of India

To assess the eco-toxicological potential of metal ions, Jain (2004) examined their fractionation in bed sediment of the Yamuna River. Copper is typically found in carbonate, residual and reducible fractions, according to the findings. In accordance with the Risk Assessment Code, the exchangeable fraction at the majority of sites contains 30-50% lead, which poses a significant risk of lead contamination the food chain. A low to moderate risk to the aquatic environment was indicated by the zinc fractionation pattern.

Suthar et al. (2009) conducted an evaluation of heavy metal concentrations in the water and sediment of the Hindon River in Ghaziabad, an industrialized city in India. The heavy metals assessed included Cu, Cr, Cd, Fe, Zn, Mn and Pb. A total of six sampling stations were selected to encompass both upstream and downstream locations along the Hindon. The examination of heavy metal enrichment factors in sediment collected from point and non-point polluted stations unveiled variations. The pollution levels in the Hindon River, located in the city of Ghaziabad, were classified as "very strong pollution" for Cd (Igeo > 5) and "unpolluted to moderate pollution" for Mn, Pb, and Zn (Igeo < 1), "moderate pollution" for Cu, Cr, and Fe (Igeo < 2), and "moderate pollution" for Zinc (Igeo < 5).

Reza & Singh (2010) conducted a study to examine the impact of heavy metal contamination on river water quality during different seasons. The research entailed the gathering of water samples from twelve distinct locations along the river and its tributaries over the course of the summer and winter, which occurred between May 2007 and January 2008. An atomic absorption spectrophotometer was employed to determine the concentrations of trace metals, such as Hg, Cd, Cu, Cr, Co, Fe, Ni, Mn, Pb and Zn. The majority of samples, as determined by the researchers, were found to be within the permissible range specified by the Indian drinking water standard (IS: 10500). Furthermore, the researchers computed the Heavy Pollution Index (HPI) for the river water and observed that the values fell below the critical index threshold of 100. This suggests that the adequate flow through the river system played a role in preserving the water quality at levels that were deemed acceptable.

Venkatesha et al. (2012) examined the heavy metal content in the sediment of the river Cauvery, including Cu, Fe, Co, Zn, Cd, Ni, Mn, Cr and Pb. A three-year sampling process was conducted from 2007 to 2009 at twenty-five distinct locations along the river. Utilizing a flame furnace atomic absorption spectrophotometer, the analysis was conducted. The following heavy metal concentrations were measured and reported for the sediment: Cu (11.2 μg/g), Fe (11144 μg/g), Co (1.9 μg/g), Zn (93.1 μg/g), Cd (1.3 μg/g), Ni (27.7 μg/g), Mn (1763.3 μg/g), Cr (389 μg/g) and Pb (4.3 μg/g). These concentrations complied with the guidelines for sediment quality. The researchers utilized multivariate statistical methods, including cluster analysis (CA) and principal

component analysis (PCA), in order to gain a more comprehensive understanding of the variables that influence sediment quality and spatial homogeneity across the sampling stations. The researchers discovered the sediment geo-accumulation index (Igeo) to be as follows: Cd > Zn > Pb > Cr > Cu > Co > Ni > Fe > Mn, with Cd having the highest value (2.69), and Mn having the lowest value (-1.44).

Ambedkar and Muniyan (2012) investigated concentrations of heavy metals such as Cd, Cr, Cu, Pb, Fe, Zn and Mn, in water, sediment and selected organs of five freshwater fish species from the river Gadilam at Visoor, Cuddalore, during January 2010 to December 2010. Fish organs (Intestine, Liver, Kidney, Gill and Muscle) were dissected for heavy metal determination. The analysis revealed the order of magnitude in heavy metal distribution in sediment and water as Cd > Cr > Cu > Pb > Fe > Zn > Mn. In selected fish organs, the order of magnitude was found to be liver > Kidney > Gill > Intestine > Muscle. Elevated levels of heavy metals in the fish species were attributed to increased agricultural runoff, domestic wastes and various anthropogenic activities.

Kumar et al. (2012) did a study on the levels of heavy metals in both water and sediment of the river Subarnarekha across six project locations. Water and sediment samples were collected along the river channel and analysed for Cu, Cd, Fe, Cr, Pb, Mn, Ni and Zn using atomic absorption spectrophotometry. The researchers employed various indices such as Contamination factor, Pollution load index (PLI), Contamination degree and Geo-accumulation index (Igeo) to assess the accumulation of heavy metal in the sediment. The results indicated that both river water and sediment were unpolluted, maintaining ecological suitability and sustainability. The lack of substantial human impact in the area was recognized as a crucial element that contributed to the water and sediment' pristine condition. This research provides a significant resource for the surveillance of sediment and water quality throughout the duration of the project and in the aftermath.

Sundaray et al. (2012) executed an investigation on assessment of concentrations of heavy metals, including Cd, Co, Fe, Zn, Cr, Mn, Ni, Pb and Cu, in the surficial water of river Mahanadi. Their study spanned from the Hirakud reservoir to estuary points

at Paradip and Naugarh. Over the course of the year 2002-2003, samples of water were collected from thirty-one locations along the river in the pre-monsoon, monsoon and post-monsoon seasons. The authors observed highly variable elemental concentrations, generally exceeding the World River average. Notably, Fe exhibited the highest concentration, while Cd had the lowest. Temporal variations, particularly higher values for metals like Fe, Cu and Pb, were observed in the monsoon season.

Kumar et al. (2013) investigated seasonal fluctuations in water and in quality of sediment in river Sabarmati and its tributary canal "Kharicut". In the monsoon, pre-monsoon and post-monsoon season, water and sediment samples were taken from five locations. Using inductively coupled plasma spectroscopy, the concentrations of trace elements such as Cr, Cu, Pb, Ni, and Zn were determined. Pre-monsoon seasons had greater quantities of heavy metals in water samples than monsoon and post-monsoon seasons. To measure anthropogenic pressures, the pollution load index, contamination factor, and degree of contamination were used to sediment samples.

2.5 Heavy metal studies on other rivers in the world

Ahdy and Khaled (2009) analysed the concentrations of eight heavy metals (Cu, Cd, Fe, Cr, Mn, Pb, Ni and Zn) in surface sediment samples collected along the western portion of the Egyptian Mediterranean Coast from El-Sallum to Sidi-Kreer. The research revealed a lack of substantial correlations among the majority of these metals, indicating a wide range of natural and anthropogenic origins. To evaluate the heavy metal concentrations in sediment, the geo-accumulation index, contamination factor, and Numerical Sediment Quality Guidelines (SQGs) were utilized. The findings revealed that the concentration of Ni in all samples surpassed the Threshold Effect Concentration (TEC). However, Cu concentrations surpassed the TEC at El-Sallum and Sidi-Barrani stations, suggesting the presence of potential hazards at those locations.

Akan et al. (2010) assessed the level of heavy metal contamination in the sediment of the river "Ngada" in Maiduguri Metropolis of Borno State of Nigeria. Heavy metals, including Pb, Cu, Ni, Zn, As, Co, Cd, Mn, Cr, Mg and Fe, were investigated with the help of a Perkin-Elmer Analyst 300 Atomic Absorption Spectrophotometer. The results

indicated an increase in metal concentrations with the increase in depth of sediment, which implies that heavy metals have accumulated over time due to human activities. All metal levels studied were found to exceed the WHO's standard sediment guideline limits.

Sekabira et al. (2010) investigated the pollution of stream sediment and potential pollutant sources in Uganda, Kampala and Nakivubo Channel. Sediment samples were collected and analyzed for heavy metals, including Cu, Cd, Pb, Fe, Zn and Mn, using flame atomic absorption spectrophotometry. Pollution levels were evaluated using enrichment factor, geoaccumulation index and pollution load index. The results suggested pollution with Pb, Cd and Zn, indicating high anthropogenic influences, while the geoaccumulation index indicated background concentrations for Fe, Cu and Mn in Nakivubo stream sediment.

Sharmin et al. (2010) investigated the geochemical partitioning and mobility patterns of Fe, Mn, Cd, Cu, Cr, and Ni in sediment samples collected from river "Nomi" in Tokyo of Japan. The concentrations of particulate trace metals were determined by means of Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS), in accordance with a five-step sequential extraction procedure. Cd > Cu > Cr > Ni > Fe > Mn was the sequence of potential trace metal mobility in the aquatic environment of the Nomi River. The identification of various clay minerals through X-ray diffraction (XRD) analysis suggests that these minerals were the primary reservoirs of trace metals within the deposits.

Saha & Hossain (2011) conducted an analysis of heavy metal concentrations, including Zn, Pb, Cr, Cd and Cu, in sediment of the Buriganga River in Bangladesh. They utilized the Guidelines of the US Environmental Protection Agency (USEPA) to assess metal contamination in sediment. The study also employed the contamination factor (CF), Index of geo-accumulation (Igeo), and the toxicity characteristics leaching procedure test (TCLP test). The findings indicated that concentration of Zn, Pb and Cu in each sample exceeded EPA guidelines for highly polluted sediment, while Cd and Cr fell within the moderately to highly polluted range. The results of the TCLP test

indicated that the sediment of the Buriganga River was unlikely to release harmful quantities into the environment because of improper management.

Issa et al. (2011) sampled sediment from the coast of River Orogodo in Agbor, Delta State in Nigeria, for four months during May to August. Heavy metals, including Fe, Cd, Cu, Mn, Ni, Cr, Zn and Pb, were analyzed using an atomic absorption spectrophotometer. The study also considered physical and chemical characteristics such as pH, conductivity and organic matter. The results showed significant differences in pH, organic matter, Mn, Zn and Cr levels over the four-month period. The heavy metal concentrations in collected samples followed the sequence of Fe > Mn > Zn > Cu > Pb > Ni > Cd > Cr and significant correlations were observed among some of the metals.

Zakir & Shikazono (2011) investigated the geochemical partitioning and environmental mobility of Fe, Mn, Co, Ni, and Mo in sediment collected from the complete length of the old Nakagawa River (NR) in Tokyo, Japan. The aquatic system of NR exhibited the following order of potential mobility: Ni > Co > Mo > Mn > Fe. The geoaccumulation index (Igeo) values for Ni and Mo were greater at the majority of sampling stations in NR. The evaluation of metal environmental risk was conducted utilizing the risk assessment code (RAC), which assigned Mn, Ni, Co and Mo a medium risk.

2.6 Statistical studies to assess the level of pollution in various rivers

Singh et al. (2005) examined potential origins of heavy metal pollution in the riverbed sediment of the Gomti River, including Ni, Cr, Zn, Cu, Pb, Fe and Mn. A principal component analysis was conducted on a dataset spanning five years between January 1994 to December 1998, that was acquired via consecutive monitoring of bed sediment and river water at eight specifically chosen locations. The research unveiled variations in bed sediment and effluent according to the season, designating sites 4 and 5 as particularly polluted with Cd, Cu, Cr, and Pb. This conclusion is corroborated by the geoaccumulation indices calculated for metals. The results indicated that the riverbed sediment of the Gomti River were contaminated with heavy metals, thereby exacerbating the issue of sediment toxicity within the freshwater ecosystem.

Sargaonkar et al. (2008) adopted multivariate statistical techniques to study groundwater quality of three cities – Varanasi, Faridabad and Prayagraj in the Ganga-Yamuna River basin. Water samples were gathered and examined for physico-chemical, bacteriological and heavy metals concentration. The factors extracted indicated contamination due to leaching of pollutants, with high loadings of several parameters like TDS, chloride, conductivity, hardness, SO_4, Na and Mg. Another factor indicated the higher loadings of F and Ca by the geological conditions of the region. The methodology proved useful for hydrogeological analysis in identifying critical issues related to quality of water and potential pollution sources in river basin.

Mishra (2010) used multivariate statistical approaches, such as principal component analysis (PCA) to analyse parameters of water quality influencing variations in the Ganges River in Varanasi. Sixteen physio-chemical and bacteriological variables in water samples collected over two years from six sampling sites were analysed. PCA identified four principal factors explaining 90% of the dataset's total variance, demonstrating the usefulness of PCA techniques in identifying significant surface water quality parameters.

Thareja et al. (2011) conducted a study on the water quality of the Ganga River at Kanpur city during the period of 2008 (April) to 2009 (March). They collected water samples from the Jalsansthan Benajhwar Kanpur sampling station and analysed them for 14 physio-chemical parameters, including pH, temperature, turbidity, total dissolved solids (TDS), total hardness (TH), iron (Fe), chloride, total alkalinity (TA), Ca^{+2}, Mg^{+2}, SO_4^{-2}, suspended sediment, oxygen consumption (OC) and fluoride. Principal component analysis (PCA) was applied to identify the parameters responsible for the main variability in water quality within Kanpur city. The study found that certain parameters, such as total dissolved solids, total hardness and total alkalinity, were crucial in assessing variations in water quality in the post-monsoon season, while turbidity and suspended sediment were important for the monsoon season. Chloride, Ca^{+2}, Mg^{+2}, SO_4^{-2}, oxygen consumption (OC), pH, temperature, Fe and fluoride were identified as non-principal water quality parameters.

Varol (2011) assessed the contamination level in river "Tigris" of Turkey by analysing the heavy metal concentrations in sediment samples. Sediment pollution assessment involved the use of enrichment factor (EF), contamination factor (CF), geoaccumulation index (Igeo) and pollution load index (PLI). The investigation indicated moderately polluted PLI values at all locations, except at the first site, with Pb, Cu, Zn and Co showing the highest values of Igeo. The concentration of Pb, Cr, Ni and Cu were identified as having the potential to cause harmful effects on sediment-dwelling organisms, based on a comparison with sediment quality guidelines. Cluster analysis and principal component analysis (PCA)/factor analysis (FA) indicated that the anthropogenic origins of As, Zn, Cd, Ni, Co, Mn, Cr, and Cu were implicated, specifically metallurgical effluent from a copper mine facility.

Wang et al. (2014) analysed various heavy metals like Hg, Cu, Cr, Ni, Cd, Pb and Zn in surface sediment of the Luan River Basin and its tributaries (China) during 2012. To interpret the monitoring results, the study utilized correlation analysis, cluster analysis (CA), various pollution indices and principal component analysis (PCA). The sites located downstream demonstrated elevated concentrations of heavy metals and more pronounced pollution. For the ten tributaries, three clusters were identified, with the sites further downstream exhibiting the most pronounced levels of heavy metal contamination. Significant correlations were identified between Pb, Zn and Cu, as well as between Cr in the basin, according to PCA. The purpose of the study was to support future policy development for water quality protection in the Luan River Basin by providing an overview of sediment contamination.

2.7 Novelty of the Proposed Work

Based on the previous literature, it was observed that the following studies were not much emphasized which have been considered in the present study:

- Most of the heavy metal studies conducted on Ganga River were limited to just river water and not focused much on riverbed sediment and suspended sediment.
- Very few studies did the classification of source of heavy metal contamination i.e., Anthropogenic or Natural.

- Correlation among concentrations of various metals were not identified in the previous studies.
- Risk Assessment of heavy metal concentrations was done in very few studies and that too by applying just one or two sediment pollution indices.

Chapter 3
MATERIAL AND METHODS

3.1 Introduction

In this chapter, we provide a comprehensive overview of the study area and its key features, including historical background, population, climate, seasonal patterns, rainfall, and geomorphology. These details are critical for establishing the environmental and geographical context that influences sediment quality and the distribution of contaminants. The rationale behind the selection of sampling locations is elaborated, with detailed information on their names, identification codes, and precise GIS coordinates, ensuring the study's reproducibility and transparency.

The sampling period, along with the standardized methodology for collecting and preserving sediment samples, is thoroughly described. Special attention is given to protocols aimed at maintaining sample integrity and minimizing contamination risks during collection, transportation, and storage. These steps are vital for ensuring that subsequent analyses yield accurate and reliable results.

This chapter also presents the detailed procedures used to calculate various sediment quality indices, which are indispensable for assessing the levels and sources of contamination. These indices include the geoaccumulation index, enrichment factor, contamination factor, and pollution load index, all of which help quantify the extent of heavy metal contamination in sediments. Additionally, the chapter explores the methods for determining Anthropogenic Content and Lithogenic Content, enabling a distinction between human-induced and naturally occurring heavy metal sources.

To enhance the study's depth, steps for performing correlation analysis are included, helping establish relationships between different metals and identify potential contamination sources. The integration of these methods facilitates a comprehensive understanding of the sediment quality and the processes influencing it.

Finally, the overall methodology is summarized and visually represented through a flow diagram (Figure 3.1). This diagram serves as a clear guide to the research approach, ensuring that all aspects of the study from sampling to analysis are

methodically organized and easy to follow, providing a solid foundation for subsequent chapters.
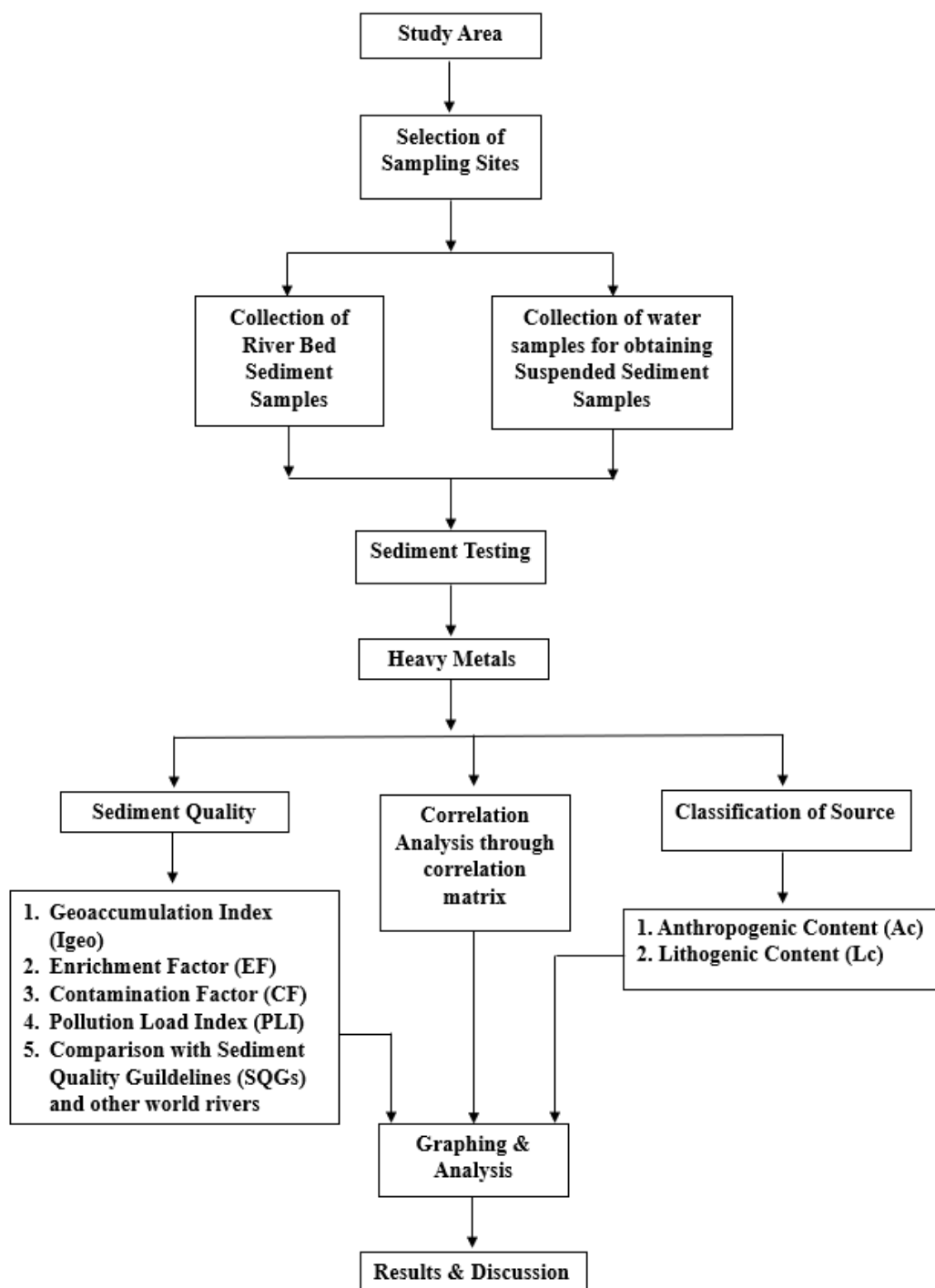
Figure 3.1 Flow diagram showing the overall methodology

3.2 Study Area

The entire study area is located between two main cities in the state of Uttar Pradesh of India. These two cities are Kanpur and Prayagraj (earlier known as Allahabad).

Kanpur, historically known as Cawnpore, stands as a prominent industrial city situated in the central-western region of the Indian state of Uttar Pradesh. Established in 1207, Kanpur evolved into a significant economic and military stronghold during the British India era. Functioning as Uttar Pradesh's financial hub, Kanpur, positioned along the Ganges River, has long served as a pivotal financial and industrial center in North India. It presently holds the status of being the ninth-largest metropolitan economy in the country. The city is renowned for its colonial architecture, lush gardens, parks, and the production of high-quality leather, plastic, and textile goods, primarily exported to Western markets. Geographically, Kanpur is situated at 26.449923°N 80.331874°E in the central-western part of Uttar Pradesh, approximately 475 kilometres from the national capital, New Delhi, and around 90 kilometres from the state capital, Lucknow. Its location is within the historical state of Awadh.

Kanpur is situated in the flat Indo-Gangetic Plains, at an elevation of 318 meters above sea level. The city is traversed by the Ganges, hosting various ghaats such as Sati Chaura Ghaat and Sarsaiya Ghaat. Another spiritually significant site, Brahmavart Ghaat in Bithoor (25 kilometres north), holds religious importance.

In 2011, Kanpur City and its suburbs had a population of 30,15,645, making it the largest urban agglomeration in Uttar Pradesh. Although the urban area of Kanpur City has expanded, its official bounds are yet to be approved by the government. As of 2023, the estimated populations for Kanpur City and the metropolitan region are 38,12,000 and 51,00,000, respectively.

The Ganga Pollution Control Unit in Kanpur received around Rs 200 crores in 2015 to operationalize four Sewage Treatment Plants (STPs). However, by 2017, only one STP handled tannery waste, a significant source of industrial pollution. This lone plant was set for replacement with a Rs 400 crore facility, as it could only manage a maximum of 9 million liters per day (MLD). Despite efforts, 823.1 MLD of untreated sewage and 212.42 MLD of industrial effluent still flowed into the river.

In 2019, plans were in progress for a new STP worth Rs 816.25 crore. However, as of 2020, eight out of the 48 drains in Kanpur lacked devices to prevent effluent discharge, indicating ongoing challenges in comprehensive pollution control measures.

Prayagraj, also known as Allahabad or Ilahabad, is a city in Uttar Pradesh. Serving as the administrative capital of the Prayagraj district and division, it is the most populated district in the state and the 13th most populous in India. Prayagraj is Uttar Pradesh's judicial center, with the Allahabad High Court being the top judicial authority. As of 2011, it had an estimated population of 1.53 million, ranking seventh in the state, thirteenth in Northern India, and thirty-sixth in the country. In 2011, it was recognized as the world's 40th fastest-growing city and the third most liveable urban agglomeration in the state in 2016. The city is located near Triveni Sangam, the confluence of the Ganges, Yamuna, and Sarasvati rivers, holding significance in Hindu texts as one of the world's oldest towns and revered as the sacred city of Prayag in the ancient Vedas.

3.2.1 Climate & Seasons

Climate of the study region is characterized as follows:

1. Summer (March to June):

   Summers in the study area are characterized by high temperatures and can be quite hot. Daytime temperatures often rise above 40 degrees Celsius (104 degrees Fahrenheit) during the peak summer months of May and June. The weather is dry and the city experiences intense heat.

2. Monsoon (July to September):

   The study area witnesses the monsoon season from July to September. The city receives a significant amount of rainfall during this period, providing relief from the summer heat. Monsoon rains are associated with the southwest monsoon winds, bringing moderate to heavy rainfall.

3. Autumn (October to November):

   After the monsoon season, temperatures gradually start to decrease during the autumn months. The weather becomes more comfortable as humidity levels decrease.

4. Winter (December to February):

Winters in the study area are cool and relatively dry. December and January are the coldest months, with temperatures sometimes dropping to around 5 degrees Celsius (41 degrees Fahrenheit) or lower. Foggy conditions, especially during the early mornings, are common in winter.

3.2.2 Rainfall

Study region receives a substantial portion of its annual rainfall during the monsoon season. The average annual rainfall in study area is around 1000 mm (39 inches), with most of the precipitation occurring in July and August. Monsoon rains are crucial for agriculture in the region, contributing to the fertility of the soil and the water supply for crops. Understanding of climate of a region is essential for various aspects of life, including agriculture, water management and planning outdoor activities. Keeping in mind that specific climate data can vary from year to year and the information provided is a general overview based on typical patterns.

3.2.3 Geomorphology of the study area

Geomorphology of Ganga River at study area is characterized as the Upland Terrace Surface (T2). The Upland Terrace Surface in the Ganga Basin is a level expanse with a gradual incline (average slope of 5-10 cm/km) towards the southeast. This surface is commonly referred to as Older Alluvium (Varanasi Older Alluvium) or Bangar, consisting of oxidized sediment that display signs of early soil development, including calcretization and ferrugenization. It exhibits a varied micro-geomorphology, featuring areas with centripetal drainage. Considered to be the oldest, the Upland Terrace Surface (T2) formed between 128-74 thousand years before present (ka BP) and serves as the base for the deposition of geomorphic surfaces (Singh 1996; Shukla et al. 2001). It is an accretionary surface with sections experiencing both erosion and sedimentation. Major and minor rivers deeply cut into this surface, forming narrow floodplains. Remarkably, this surface remains unaffected even during catastrophic floods in these rivers, exhibiting independent dynamics of sedimentation (Shukla & Singh 2004; Shukla 2009). Comprised mainly of fine-grained fine sand-silt and clay, the deposits on the T2 surface show distinct mottling, extensive calcrete development and a lack of preservation of primary physical structures and organic matter (Pl. II). Sediment transfer and deposition on this geomorphic surface primarily occur through

sheet flow processes during the monsoon season. These deposits are interpreted to have formed through interfluve (Doab) sedimentation (Singh, I.B. et al., 1999a; Shukla & Janardhana Raju 2008).

3.3 Selection of Sampling Sites

Kanpur is an industrial hub in India. Many industries work well here, yet many of them do not obey environmental standards. As a result, people dump a variety of waste into the Ganga River, thus polluting it.

Many religious ceremonies are done on the banks of the Ganga River, which contribute significantly to pollution. Based on these concerns, it was decided that the sampling location should comprise industrial, commercial sector, residential and agricultural sites.

A total of 10 sampling locations at approximate intervals of 20 kms were selected along the banks of the Ganga River covering a length of 225 kms between the two urban cities of Kanpur and Prayagraj in Uttar Pradesh state of India. (Table 3.1, Figure 3.2).

Table 3.1 Selected sampling locations, their codes, absolute location and distance from starting point

Name Of Site	Code	Absolute Location	Distance (Km)
Jajmau Bridge	L1	26˚26'17''N 80˚27'43''E	0
Maharajpur Village	L2	26˚22'42''N 80˚29'26''E	23.88
Sarsaul Village	L3	26˚18'13''N 80˚32'35''E	44.20
Dalmau Ganga Bridge	L4	26˚03'18''N 81˚01'56''E	89.18
Town Unchahar	L5	25˚53'22''N 81˚12'59''E	111.98
Nawabganj Ghaat	L6	25˚49'06''N 81˚19'46''E	134.01
Ganga Ghaat, Manikpur	L7	25˚46'03''N 81˚23'58''E	142.48
Shringverpur Ghaat	L8	25˚35'20''N 81˚38'01''E	181.12
Ganga Ghaat, Phaphamau	L9	25˚30'24''N 81˚51'59''E	213.46
Sangam Ghaat	L10	25˚25'41''N 81˚53'20''E	224.69
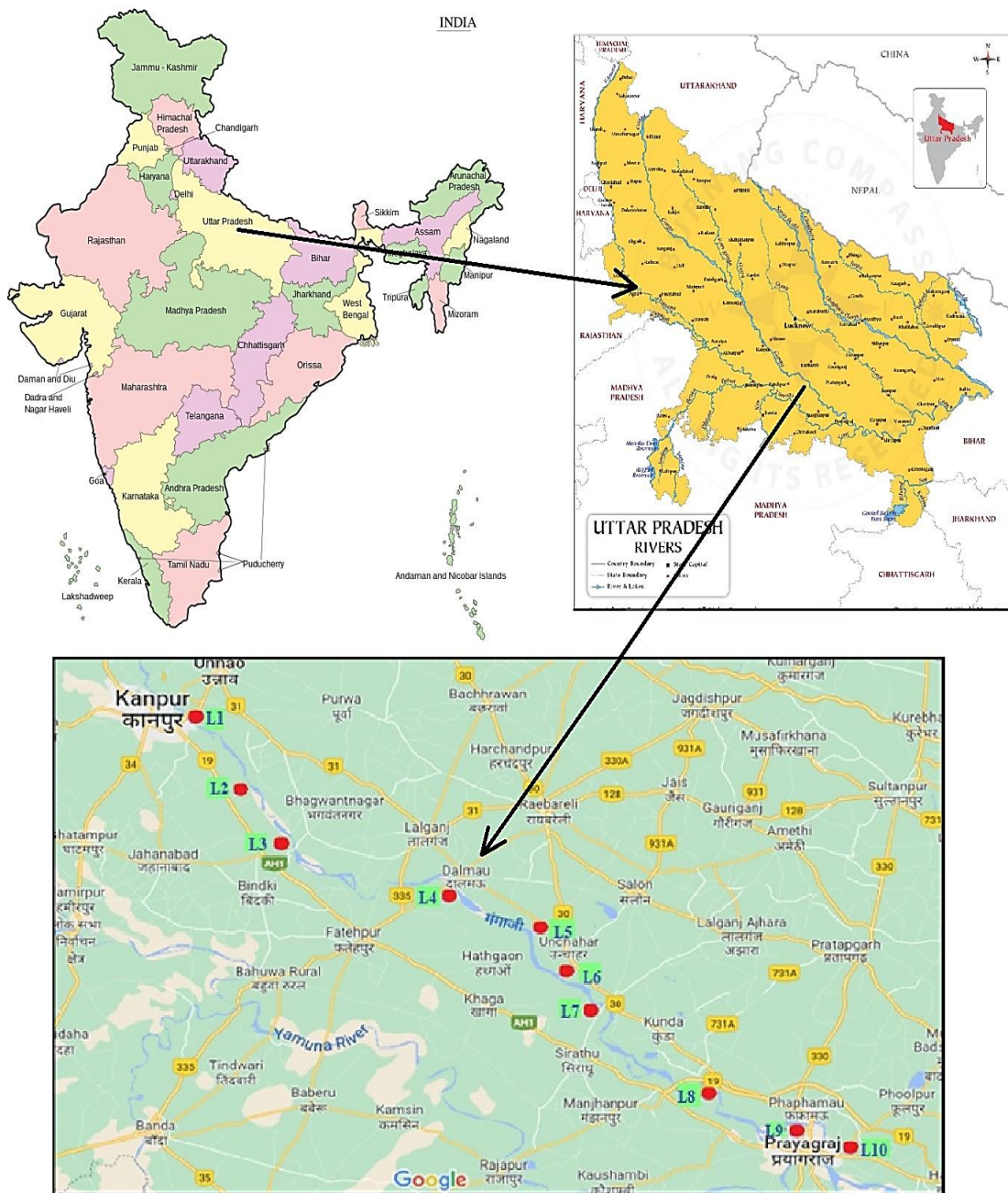
Figure 3.2 Sampling Locations between Kanpur & Prayagraj, U.P., India

3.4 Sampling Strategy and Sample Preparation

Riverbed sediment sampling was conducted on two occasions during the summer season in April 2019 and April 2021. Additionally, sampling for suspended sediment was carried out twice during the peak monsoon in July 2021 and July 2022, encompassing all selected sites. It is worth noting that all samples were collected

during daylight hours, specifically between 7:00 AM and 5:00 PM on the respective days.

Collection and handling of water samples for obtaining suspended sediment were conducted in accordance with standard methodology (ISO 5667-3,6,12; USEPA 2001). Water samples to were collected in polypropylene plastic bottles against the direction of flow. The suspension samples were acidified at the time of collection with nitric acid. Double distilled nitric acid is used for water sample conservation. The samples were stored and transported to the laboratory.

For riverbed sediment, samples were collected from each sampling location from a depth of 10-15 cm from the top surface of the river bank of the running river. In total 30 samples were collected from 10 selected sites using standard procedure. Each sediment sample of approximately 500g was collected with the help of a grab sampler and then packed in impermeable polythene bags (USEPA 2001). All sediment samples were then brought to the laboratory and were air dried for 72 hours before further analysis.

3.5 Analytical Aspect

The pH was determined for riverbed sediment with a pH meter by stirring a suspension of sediment and distilled water in a 1:2.5 ratio for 30 minutes using a glass rod in a beaker. The organic matter (OM) content was measured using the loss on ignition method, which involved drying the sediment for up to 24 hours and then igniting it in a muffle furnace at 600°C for up to 4 hours until the constant mass is reached.

According to APHA (2012), collected samples of sediment were digested and analysed to find the concentrations of heavy metals. Sediment samples were dried in the oven at 100 degree C for 1–2 hour to get the constant mass and then crumbled and ground to get < 63 μm fractions. Sediment samples each weighing 1 g were digested by adding 10 mL 1:2 solution of perchloric acid and nitric acid initially placed on a hot plate for 60 min at low temperature and then at 120°C temperature until fumes started arising and the solution became clear and transparent. Then digested samples were filtered using Whatman filter paper 42. Then 0.1 N HNO_3 is added to dilute the filtrate till the

final volume of 50 mL is reached. Finally, the concentrations of heavy metals namely Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn were measured in the digested samples.

The concentrations of heavy metals namely Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn were measured in the digested samples using atomic absorption spectroscopy (AAS) (Shimadzu AA-6300). In this technique concentration of metals is determined by measuring the absorption characteristics of radiation by the atomic vapour of the element. The major source of radiation is a hollow cathode lamp. Standard solutions in optimum range were prepared for each heavy metal (Cd, Cr, Cu, Fe, Ni, Pb, Zn) separately by their stock solutions. After that each standard was aspirated in turn into flame and absorbance was recorded. Calibration curve between absorbance and concentrations of standards were plotted and concentration of heavy metals in sediment samples was determined by using at respective wavelengths at 326.1 nm, 425.4 nm, 327.4 nm, 372 nm, 403.1 nm, 341.5 nm, 405.8 nm and 213.9 nm for cadmium, chromium, copper, iron, manganese, nickel, lead and zinc respectively.

Figure 3.3 Atomic Absorption Spectrophotometer (Shimadzu, AA-6300)

Table 3.2 Technical details of Atomic Absorption Spectrophotometer, Make-Shimadzu, Model- AA6300

Wavelength range	185 to 900 nm (Automated wavelength selection)
Mounting	Aberration-corrected Czerny-Turner mounting, Number of grating grooves:1800 lines/mm, Focal length: 298mm
Bandwidth	0.2 0.7 0.7 2.0(Low) nm (4 step automatic switching)
Detector	Photomultiplier (short wavelengths), semiconductor (long wavelength)
No. of lamps mounted	6 lamps, 2 user-selected lamps can be illuminated at the same time (1 for measurement, 1 warming up for next measurement)
Photometric Mode	Flame: Optical double beam. Furnace: Double beam
Background Correction	High-speed Self-Reversal method (BGC-SR), high-speed deuterium lamp method (BGC-D2)
Lamp Mode	Emission, Non-BGC, BGC-D2, BGC-SR
Burner Type	Air-cooled premix type
Burner Head	Made of titanium, 10cm slot (the 5cm slot for high temperature flames is optional)
Nebulizer	Pt-lr capillary with Teflon orifice and ceramic impact bead (Hydrofluoric acids can be used)
Chamber	Polypropylene
Positioning Control	Automatic search for the optimal burner height, automatic adjustment of vertical position, manual adjustment of back and forth position
Gas Control - Flow Control Unit	Fuel gas, support gas, automatic flow rate setting (0.1L/min step), automatic search for the optimal gas flow rate
Safety Measures	Safe ignition/ extinction sequence Automatic extinction in a power failure Flashback prevention through gas pressuring monitoring Burner misuse prevention Prevention of raw gas release when the flame dies out
Ignition	Push ignite button
Software	Software based on Microsoft Windows ™
Dimensions & Weight	835 (W) x 460 (H) x 545 (D) mm, 70 kg (not including the flue, protruding parts)
Power Requirements	AC100V±10% (no sudden voltage fluctuations) 230VA, 50/60HZ
Ambient Temperature and humidity range	Temperature: $10 \sim 35°C$ Humidity: $20\% \sim 80\%$ (less than 70% when temperature is greater than 30°C

Common Problems associated with AAS

1. **Lamp Issues:** The hollow cathode lamp (HCL) does not ignite or is unstable due to burnt-out lamp, loose connections, or incorrect lamp alignment which can be corrected by replacing the HCL if it is burnt out, checking and securing all electrical connections and ensuring the lamp is correctly aligned in its holder.

2. **Baseline Drift:** The baseline signal drifts over time, affecting measurement accuracy due to temperature fluctuations, aging of the detector, or unstable power supply which can be corrected by stabilizing the laboratory temperature, replacing or recalibrating the detector or by using a stable power supply with appropriate voltage regulation.

3. **Poor Sensitivity:** The instrument shows low sensitivity or high detection limits due to contaminated burner, clogged nebulizer, or improper gas flow rates which can be corrected by cleaning or replacing the burner and nebulizer, checking and adjust the gas flow rates to recommended levels or by ensuring that the sample introduction system is free of blockages.

4. **Noise in Readings:** The instrument shows noisy or erratic readings due to electrical interference, dirty optics, or unstable flame which can be corrected by eliminating sources of electrical interference, cleaning the optical components, including mirrors and lenses or adjusting the flame conditions to ensure stability.

5. **Calibration Issues:** Calibration curves are not linear or show unexpected behaviour due to incorrect standard preparation, contaminated reagents, or instrument misalignment which can be resolved by preparing standards carefully and verify their concentrations, using high-purity reagents and deionized water or checking and correcting the instrument alignment if necessary.

6. **Flame Extinguishment:** The flame extinguishes unexpectedly during analysis due to insufficient gas supply, blockage in the gas line, or malfunctioning safety interlock which can be resolved by ensuring adequate gas supply and check for leaks, clearing any blockages in the gas lines or inspecting and repairing or replacing faulty safety interlock components.

7. **Software or Communication Errors:** The instrument software crashes or cannot communicate with the computer due to Software bugs, outdated software version, or faulty communication cables. This can be resolved by updating the software to the latest version, reinstalling the software if necessary and checking and replacing communication cables if they are damaged.

Muffle Furnace

Muffle furnaces are commonly used in laboratories for various applications, including ashing, calcining, and thermal analysis. However, several potential issues and problems can arise when using these furnaces:

Figure 3.4 Muffle Furnace

Common Problems associated with Muffle Furnace

1. Temperature Control:

Muffle furnaces may experience fluctuations in temperature, leading to inconsistent heating. This can affect experimental results and the quality of the materials being processed. Ensuring accurate calibration and proper functioning of temperature control systems is crucial.

2. Heating Uniformity:

In some muffle furnaces, the distribution of heat may not be uniform, resulting in hot or cold spots within the chamber. This uneven heating can lead to incomplete reactions or uneven material properties.

3. Ventilation and Fume Management:

Muffle furnaces can produce harmful fumes and gases, especially when ashing organic materials or heating compounds that release volatile components. Proper ventilation systems must be in place to ensure safe operation and compliance with occupational health and safety regulations.

4. Energy Efficiency:

Muffle furnaces can consume significant amounts of energy, especially during extended heating periods. This can lead to high operational costs and environmental impacts. Using well-insulated models can improve energy efficiency.

5. Maintenance and Wear:

The internal components of a muffle furnace, such as heating elements and insulation, can degrade over time due to prolonged use at high temperatures. Regular maintenance and timely replacement of worn components are essential to ensure reliable performance.

6. Contamination:

If not properly cleaned, residues from previous experiments can contaminate new samples. This can lead to inaccurate results and affect the integrity of subsequent analyses.

7. Safety Hazards:

High temperatures pose risks of burns or fire hazards. Proper safety measures, including personal protective equipment (PPE) and safety training, are essential to prevent accidents.

8. Limitations in Material Types:

Certain materials may not be suitable for processing in muffle furnaces. For example, materials that release gases or expand significantly at high temperatures can cause damage to the furnace or affect results.

9. Cost and Space:

Muffle furnaces can be expensive to purchase and maintain. Additionally, their size may require significant laboratory space, which can be a limitation in smaller labs.

10. Startup and Cool Down Times:

Muffle furnaces can take considerable time to reach the desired operating temperature and to cool down afterward, which can limit throughput in high-demand environments.

pH Meter

pH meters are essential tools for measuring the acidity or alkalinity of solutions, but they can encounter various issues that may affect accuracy and reliability.

Figure 3.5 pH Meter

Here are some common problems with pH meters:

1. **Electrode Issues**

   Dirty or Contaminated Electrode: The electrode can become fouled by substances in the solution, leading to inaccurate readings.

   Dry Electrode: pH electrodes should be stored in a storage solution. If they dry out, the glass membrane can be damaged, resulting in poor readings.

   Clogged Junction: The reference junction can become clogged, especially when measuring samples with high solids or viscous solutions.

   Broken Glass Bulb: The glass membrane on the electrode tip is fragile. If it breaks or cracks, the pH meter will not work correctly.

   Aging Electrode: Over time, electrodes wear out and become less responsive, leading to sluggish or inaccurate readings.

2. **Calibration Problems**

   Improper Calibration: pH meters require regular calibration with standard buffer solutions. Inaccurate calibration will lead to erroneous measurements.

   Incorrect Buffer Solutions: Using expired or incorrect buffer solutions can affect the calibration accuracy.

   Not Calibrating to Multiple Points: Calibrating to only one point (instead of using both acidic and basic buffers) can reduce the accuracy across the full pH range.

3. **Temperature Effects**

   No Temperature Compensation: Many pH meters have automatic temperature compensation (ATC). If ATC is not functioning or not being used, temperature variations can affect pH readings.

   Incorrect Temperature Reading: If the temperature probe malfunctions, it can lead to incorrect pH results, especially when the sample temperature is significantly different from room temperature.

4. **Improper Handling**

   Rough Handling: Dropping or mishandling the meter or electrode can damage sensitive parts like the glass membrane, leading to poor readings.

Incorrect Storage: Storing the pH meter in water or dry conditions can damage the electrode. The meter should always be stored in a proper storage solution.

Cross-contamination: Not rinsing the electrode between samples can cause contamination, altering the readings.

5. **Electrical and Mechanical Issues**

Faulty Cables or Connections: Damaged cables or poor connections between the meter and electrode can cause erratic readings or failure to read.

Low Battery: If the pH meter uses batteries, low power can cause instability or inaccurate readings.

Software Errors: Digital pH meters with software or display malfunctions may display inaccurate or fluctuating readings.

6. **Sample Issues**

Inhomogeneous Sample: pH measurements can be inaccurate if the sample is not properly mixed or is too heterogeneous.

Improper Sample Volume: Insufficient sample volume can affect the immersion depth of the electrode, leading to false readings.

High or Low Ionic Strength Samples: Samples with extremely high or low ionic strengths (like ultrapure water) can yield unstable pH readings due to the low conductivity of the sample.

7. **Environmental Interference**

Electrical Interference: External sources of electrical interference, such as power lines or electronic equipment, can cause fluctuations or noise in pH readings.

Static or Air Bubbles: Air bubbles on the electrode can interfere with accurate measurements, especially in viscous or low-flow samples.

Proper maintenance, calibration, and handling are crucial to ensuring that pH meters function accurately and reliably.

3.6 Calculation of Sediment Quality Indices

To ascertain pollution levels, identify the natural and anthropogenic sources of metal pollution, and conduct risk assessments, many researchers have implemented the various sediment quality and pollution indices in the previous studies such as enrichment factor (EF) (Liaghaati et al. 2003; Wang et al. 2007; Fransco-Uria et al. 2009; Davutluoglu et al. 2011; Zhang et al. 2016), geoaccumulation index (Igeo) (Muller 1969; Buccolieri et al. 2006; Chakravarty & Patgiri 2009; Davutluoglu et al. 2011; Fu et al. 2013; Ma et al. 2016), contamination factor (CF) (Turekian and Wedephol 1961, Tomlinson et al. 1980; Fujita et al., 2014), pollution load index (PLI) (Fujita et al. 2014; Wazne & Korfali 2016) and sediment quality guidelines (SQGs) (Davutluoglu et al. 2011; Fu et al. 2013).

3.6.1 Geo-accumulation index

The Geoaccumulation Index (Igeo) is a widely used geochemical index that assesses the degree of metal contamination in sediment. It was introduced by Müller in 1969 and has since been applied to evaluate metal pollution in various environmental compartments, including river sediment. The geoaccumulation index (Igeo) enables the assessment of contamination by comparing the current and pre-industrial concentrations originally used with bottom sediment, it can also be applied to the assessment of soil contamination. The method assesses the degree of metal pollution in terms of seven classes (Table 3.3) based on the increasing numerical values of the index.

The geo-accumulation index (Igeo) for the metal concentrations was calculated by using the following formula proposed by Muller (1969):

$$\text{Igeo} = \text{Log}_2 \frac{Cn}{1.5 \times Bn} \tag{1}$$

where Cn is the measured concentration of metal n (in µg/g) in sediment, Bn is the geochemical background value (µg/g) of the element in the background sample and the factor 1.5 is introduced to minimize the effects of possible variations in the background values which may be attributed to lithogenic effects.

For riverbed sediment, background values of concentrations (in µg/g) of Fe, Ni, Cd, Cu, Cr, Mn, Pb and Zn were taken as 40346, 46, 0.58, 55, 147, 1764, 22 and 105 respectively from geometric mean values given by Singh et al. (2003). For suspended sediment analysis, background values of concentrations (in µg/g) of Fe, Ni, Cd, Cu, Cr, Mn, Pb and Zn were taken from world river average values drawn from Viers et al. (2009) as 58100, 74.5, 1.55,75.9, 130, 1679, 61.1 and 208 respectively.

Table 3.3 Classes of Igeo and pollution levels based on Igeo value, respectively

Igeo value	Igeo Class	Pollution level
<0	0	Unpolluted
0-1	1	Unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	Moderately to strongly polluted
3-4	4	Strongly polluted
4-5	5	Strongly to very strongly polluted
>5	6	Very strongly polluted

3.6.2 Enrichment factor

The enrichment factor (EF) is widely used as an appropriate approach to discriminate between natural and anthropogenic sources and to reflect the state of environmental pollution, based on the use of a standardization element to alleviate variations produced by heterogeneous sediment (Zhang et al. 2007; Zahra et al. 2014).

Metal concentrations normalized to the textural characteristic of sediment with respect to Fe, is used as reference material. According to Salati & Moore (2010), the EF of metals in the sediment for all sites is calculated as follows:

$$EF = \frac{[(X_x)/(X_{Fe})]s}{[(X_x)/(X_{Fe})]b} \tag{2}$$

where $[(X_x)/(X_{Fe})]_s$ is the ratio of metal (X) and Fe concentrations of the sample and $[(X_x)/(X_{Fe})]_b$ is the ratio of metal and Fe concentrations of background. The EF values are interpreted as mentioned in Table 3.4 (Salati and Moore, 2010).

Table 3.4 Classes of EF in relation to enrichment and pollution levels, respectively

EF value	Enrichment Level
<2	Depletion to mineral
2-5	Moderate
5-20	Significant
20-40	Very high
>40	Extremely high

3.6.3 Contamination factor & pollution load index

The method of the contamination factor (CF) evaluates the enrichment in metals in relation to the background concentrations of each metal in sediment. CF is the ratio obtained by dividing the concentration of each metal in the sediment by the background value (Hakanson 1980):

$$CFn = \frac{Cn}{Bn} \qquad (3)$$

where, CFn is the contamination factor of the metal 'n' in the sample. The level of contamination is classified as low: (CF less than 1); moderate: (CF between 1 & 3); considerable: (CF between 3 & 6) and very high contamination: (greater than 6)

Pollution load Index (PLI) is used to assess the overall metal load at each site by using the equation (Hakanson, 1980):

$$PLIn = (CF1 * CF2 * \ldots * CFn)^{\frac{1}{n}} \qquad (4)$$

Here, CFn represents the contamination factor of the nth metal

PLI value of 1 and below shows a baseline level of pollution whereas, above 1 shows progressive degradation.

3.7 Statistical investigation

For statistical investigation, concentrations of all identified metals are presented in micrograms per gram (µg/g). Correlation analysis was conducted by obtaining correlation matrix with the help of Weka Tool and Microsoft excel to see whether there was a significant association between metals, metals with pH and metal with OM. Correlation matrix is the statistical method of determining the relationship between two variables in a set of data. The matrix is a tabular representation wherein each cell represents a correlation coefficient. A value of 1 indicates a strong relationship between variables, a value of 0 as neutral, while a value of -1 indicates a weak relationship. A value between 0.1 – 0.3 indicate weak positive correlation, 0.3 – 0.5 indicate moderate positive correlation whereas 0.5 – 1.0 indicate strong positive correlation.

Heavy metal concentrations are also compared to corresponding values of SQGs given by MacDonald et al. (2000) as mentioned in Table 3.5. SQGs are helpful in the assessment of the level upto which heavy metal concentrations in suspended sediment may adversely influence aquatic plants & animals and are depicted to judge suspended sediment quality (Wenning 2005). SQGs of two categories i.e. Threshold Effect Concentration (TEC) and probable Effect Concentration (PEC) are established for the freshwater ecosystem (MacDonald et al. 2000). TEC values indicate that concentration less than which adverse effects are expected to happen rarely and PEC value indicate the concentration beyond which adverse effects are expected to happen likely.

Table 3.5 Sediment quality guidelines (SQGs) values (in µg/g)

		Fe	Mn	Cr	Zn	Pb	Ni	Cu	Cd
SQGs	**TEC**	20000	460	43.4	121	35.8	22.7	31.6	0.99
	PEC	40000	1100	111	459	128	48.6	149	4.98

3.8 Classification of source of metals

All metal sources were classified into two categories as natural and anthropogenic. The anthropogenic impact on metals is computed as follows:

$$\text{Anthropogenic Content, } A_c \text{ (\%)} = \frac{(C_n - B_n)}{C_n} \times 100 \tag{5}$$

where C_n is the concentration of metal at a particular location and B_n is the baseline concentration of that metal sediment of the Ganga River at Hastinapur location taken from Singh et al. (2003). Negative values of A_c were considered to be as zero which indicates no anthropogenic content in the sample.

The following formula was used to calculate the impact of lithogenic inputs to metals:

$$\text{Lithogenic Content, } L_c \text{ (\%)} = (100 - A_c) \tag{6}$$

where A_c is the Anthropogenic content in percentage.

Chapter 4
RESULTS AND DISCUSSION

4.1 Introduction

This chapter presents the results of the heavy metal concentrations obtained from the testing of sediment samples, encompassing both riverbed sediment and suspended sediment. The analysis and discussion of these concentrations are supported by graphical representations. Additionally, sediment quality indices, namely the Geoaccumulation index, enrichment factor, contamination factor, and pollution load index, are systematically evaluated, reported, and discussed in this section. The origins of heavy metal contamination are categorized through an assessment of Anthropogenic content and Lithogenic content. Furthermore, a correlation matrix is employed to establish the correlations between various heavy metals.

4.2 Heavy Metals Risk Assessment for Riverbed Sediment

Riverbed sediment samples were collected on two occasions during the pre-monsoon season in April, 2019, and April, 2021. During the pre-monsoon, there is less turbulence in the river due to low discharge which results in less temporal variations in the concentrations of heavy metals. The concentrations of heavy metals in the riverbed sediment are detailed and discussed in the subsequent sub-sections. These concentrations are then compared with sediment quality guidelines to assess the level by which the sediment can harm aquatic plants & animals. Additionally, sediment quality indices are computed to ascertain the level of the contamination.

4.2.1 pH, organic matter, metal concentrations and their spatial distribution in the riverbed sediment of the selected sites

The pH, organic matter, concentrations of heavy metals in the riverbed sediment samples during April, 2019 & April, 2021 with their averages, standard deviation, minimum and maximum values are reported in Table 4.1. The baseline concentrations of metals for sediment of Ganga River established by Singh et al. (2003) mentioned in Table 4.1 are taken as the background concentrations (Bn) in this study and are used for the calculations of sediment quality indices.

Table 4.1 pH, OM (%) and Metals concentrations (in μg/g) in riverbed sediment of Ganga River at various points on the study area, their SQGs values, IRS and WSR averages in the sediment

April, 2019										
Code	**pH**	**OM**	**Fe**	**Mn**	**Cr**	**Zn**	**Pb**	**Ni**	**Cu**	**Cd**
L1	7.88	8.88	19503	482	31.4	34.8	35.8	33.4	5.7	1.15
L2	7.92	7.81	19352	541	100.2	39.1	31.5	33.4	8.55	2.31
L3	7.57	7.32	15110	367	42.5	29.6	29.5	32.2	4.75	2.39
L4	7.75	9.08	23038	654	65.8	33.8	36.6	32.2	4.75	3.45
L5	8.02	8.56	20725	568	61.7	37	34.5	34.5	9.5	2.32
L6	8.14	9.37	30017	679	85.0	56.9	37.8	40.8	17.1	1.15
L7	8.32	9.82	29017	462	95.1	58.1	39.6	42.6	15.2	2.34
L8	7.81	7.56	19700	352	38.5	35.9	30.5	35.7	6.65	2.31
L9	7.67	7.32	17286	349	34.4	30.6	29.5	33.4	5.7	0.95
L10	7.59	7.81	16974	457	56.7	27.5	31.5	33.4	3.8	1.15
Average	7.87	8.35	21072	491	61.13	38.33	33.7	35.2	8.17	1.94
Std. Deviation	0.24	0.91	4956	118	25.28	10.70	3.66	3.62	4.57	0.80
Minimum	7.57	7.31	15110	349	31.4	27.5	29.5	32.2	3.8	0.95
Maximum	8.32	9.82	30017	679	100.2	58.1	39.6	42.6	17.1	3.45
April, 2021										
Code	**pH**	**OM**	**Fe**	**Mn**	**Cr**	**Zn**	**Pb**	**Ni**	**Cu**	**Cd**
L1	7.40	6.39	22602	502.9	48.69	26.27	25.79	25.13	25.31	1.01
L2	7.43	5.97	23782	495.1	45.17	25.38	24.09	29.82	23.56	1.58
L3	7.39	6.29	24088	512.8	58.13	24.30	25.37	31.73	19.09	1.22
L4	7.59	6.57	24430	521.7	45.93	29.32	26.48	33.69	21.88	1.19
L5	7.44	6.12	23580	524.3	52.45	25.38	24.67	30.78	22.18	0.84
L6	7.63	5.83	24014	526.8	54.25	36.40	23.51	31.41	21.12	1.09
L7	7.61	5.47	23214	486.5	48.84	35.55	22.06	28.01	25.88	1.14
L8	7.55	5.51	25760	444.9	52.73	34.32	22.23	27.86	24.32	1.27
L9	7.49	5.05	24829	452.2	59.24	31.26	20.37	29.80	23.71	0.85
L10	7.31	4.73	26579	421.9	58.20	29.29	19.09	28.88	22.47	0.78
Average	7.48	5.79	24288	488.9	52.36	29.75	23.36	29.71	22.95	1.10
Std. Deviation	0.11	0.60	1183	37.1	5.13	4.49	2.41	2.40	2.03	0.24
Minimum	7.31	4.73	22602	421.9	45.17	24.30	19.09	25.13	19.09	0.78
Maximum	7.63	6.57	26579	526.8	59.24	36.40	26.48	33.69	25.88	1.58
Background Values (Bn)[a]			40346	1764	147	105	22	46	55	0.58
Indian River System Average[b]			-	607	87	16	-	37	28	-
World Surface Rock Average[c]			35900	720	71	127	16	49	32	0.20
SQGs[d]	**TEC**		20000	460	43.4	121	35.8	22.7	31.6	0.99
	PEC		40000	1100	111	459	128	48.6	149	4.98

[a] Values taken from Singh et al. (2003)
[b] Values taken from Subramanian et al. (1985)
[c] Values taken from Martin & Maybeck (1979)
[d] Values taken from MacDonald et al. (2000)

From table 4.1, it has been observed that for year 2019, the pH of the riverbed sediment varies from 7.57 to 8.32, with a mean of 7.87 ± 0.24 indicating a mild alkaline condition whereas in 2021, pH of the riverbed sediment varies from 7.31 to 7.63, with a mean of 7.48 ± 0.11 indicating again a mild alkaline condition.

The pH of river sediments significantly influences the behaviour, mobility, and bioavailability of anionic contaminants, such as phosphates, arsenates, and chromates. The solubility of these contaminants is highly dependent on pH; for instance, phosphates tend to remain soluble in acidic conditions, but as pH increases, they can precipitate as insoluble metal phosphates, which reduces their bioavailability to aquatic organisms. Similarly, arsenates (AsO_4^{3-}) are more stable in neutral to alkaline conditions, where they remain soluble, while in acidic environments, they may transform into less soluble forms, affecting their mobility and potential for bioaccumulation.

Moreover, pH affects the charge characteristics of sediment particles and organic matter, influencing adsorption processes. In acidic conditions, sediments generally have fewer negatively charged sites available for anionic contaminants to bind, leading to increased mobility in the water column. In contrast, neutral to alkaline conditions enhance the negative charge on sediment surfaces, promoting the adsorption of anionic contaminants and effectively immobilizing them, which reduces their bioavailability.

As pH changes, the concentration and speciation of competing anions, such as sulphates and carbonates, can also vary, influencing the behaviour of anionic contaminants. Higher pH levels may increase competition for adsorption sites, potentially reducing the retention of contaminants like arsenate and phosphate in sediments. Additionally, pH influences redox conditions that can affect the transformation of certain contaminants; for example, in acidic environments, some anionic contaminants may undergo reduction or other chemical transformations, altering their overall mobility and toxicity.

The toxicity of anionic contaminants can also vary with pH, as certain metal complexes, such as chromates, can become more or less toxic depending on their speciation. Overall, the interplay between pH and anionic contaminants is critical for understanding their fate and transport in river sediments. Effective management

strategies must consider these pH-related effects to mitigate the impacts of anionic contamination and protect water quality and aquatic ecosystems.

In 2019, the OM (%) in the riverbed sediment varies from 7.31 to 9.82, with a mean of 8.35 ± 0.91 whereas in 2021 OM in the riverbed sediment varies from 4.73 to 6.57, with a mean of 5.79 ± 0.60.

In 2019, the averages of metal concentrations were observed in the following order: Fe > Mn > Cr > Zn > Ni > Pb > Cu > Cd and in year 2021 as Fe > Mn > Cr > Zn > Ni > Pb > Cu > Cd. From the above order for both the sampling periods, it has been found that Fe is found to be highest in concentrations and Cd is in scarce in the collected riverbed sediment samples.

In 2021, average concentrations of Mn, Cr, Ni, Zn, Pb & Cd metal reduced by 0.45%, 14.35%, 15.50%, 22.38%, 30.61% & 43.43% respectively whereas the average concentrations of Fe and Cu increased by 15.26% and 180.91%. Except Cu & Fe, average concentrations of all other metals reduced in the riverbed sediment collected in 2021 as compared to that in riverbed sediment collected in 2019 indicating increase in the anthropogenic input of Cu & Fe from the upstream areas whereas reduction in the fresh inputs of other metals in the study area.

In 2021, metals concentrations were more uniform and showed less variations along the sampling sites whereas in 2019, metal concentrations showed huge variations which indicate that the sources of metal contamination at local level have reduced in 2021which were giving sudden spikes in concentrations in 2019 at various locations.

The concentration of carbonate in river sediments significantly influences the distribution and mobility of heavy metals. Carbonates can form complexes with heavy metals, altering their chemical speciation; at higher carbonate concentrations, metals like lead, cadmium, and zinc may form stable carbonate complexes, which can affect their solubility and mobility. This interaction may lead to increased retention in sediments or enhanced release into the water column, depending on the specific circumstances. Additionally, carbonates can promote the precipitation of certain heavy metals as carbonate minerals, elevated carbonate levels can cause metals like copper and nickel to precipitate as carbonates (e.g., malachite for copper), effectively immobilizing them in sediments and reducing their bioavailability and potential toxicity to aquatic organisms.

Moreover, carbonate concentration can influence the pH of river sediments. Higher levels of carbonates often lead to increased pH, which in turn affects metal solubility and speciation; many heavy metals become less soluble at higher pH, resulting in reduced mobility and increased adsorption to sediment particles. This adsorption is facilitated by the alkaline conditions created by carbonates, which enhance the negative charge on sediment surfaces and provide more sites for cationic heavy metals to bind, further immobilizing them.

Carbonates can also compete with other anions in solution for binding sites on sediments, influencing the distribution of heavy metals. For example, high carbonate concentrations may compete with sulphates or phosphates, potentially altering the availability and retention of heavy metals. Additionally, carbonates can impact redox conditions in sediments; by promoting reducing environments, they can facilitate transformations of certain heavy metals, such as the reduction of chromium from its hexavalent (Cr(VI)) to trivalent (Cr(III)) forms, leading to decreased mobility and toxicity.

The variations in concentrations of each heavy metal in riverbed sediment have been discussed individually in detail:

Iron (Fe)

The variation in concentrations of Fe along the selected stretch are depicted with the help of Figure 4.1.

Fe concentrations were found to be highest among all elements in riverbed sediment due to many natural reasons like weathering, erosion, etc., and human activities such as urban discharge, industrial effluent, construction and demolition wastes, municipal solid waste, and agricultural activities.

In 2019, Fe concentration ranged between 15,110 and 30,017 µg/g with an average value of 21072.2 µg/g. Fe concentration in the sites followed this order L3 < L10 < L9 < L2 < L1 < L8 < L5 < L4 < L7 < L6 being highest at L6 and lowest at L3.

In 2021, Fe concentration ranged between 22602 and 26579 µg/g with an average value of 24288 µg/g. Fe concentration in the sites followed this order L1 < L7 < L5 < L2 < L6 < L3 < L4 < L9 < L8 < L10 being highest at L10 and lowest at L1. Fe

concentrations in all samples were recorded less than the world surface rock average of 35900 µg/g.

Fe concentrations in all samples collected during both sampling events were consistently below the World Surface Rock average of 35900 µg/g and the Bn value of 40346 µg/g. This suggests that Fe concentrations in the riverbed sediment are within safer levels and do not exhibit significant contributions from anthropogenic sources.

The average concentration of Fe in 2021 experienced a noticeable uptick of 15.26% when compared to that observed in 2019. Across the sampling locations within the study area, the concentrations of iron in 2021 exhibited less variability, implying a reduction in fluctuations compared to those in 2019. This suggests a potential rise in the influx of iron from upstream areas.

Figure 4.1 Variation in Fe concentrations in the riverbed sediment of Ganga River along the sampling points on the study area

The adsorption and precipitation of iron (Fe) in river sediments are critical processes that regulate the mobility, bioavailability, and cycling of iron in aquatic environments. Adsorption occurs when dissolved iron (Fe^{2+} or Fe^{3+}) binds to the surface of sediment

particles, such as clays, organic matter, or iron oxides, and is influenced by factors like pH, redox conditions, sediment composition, and ionic strength. Higher pH and oxygen levels Favour the adsorption of ferric iron (Fe^{3+}), while low pH and reducing conditions promote the mobility of ferrous iron (Fe^{2+}). Precipitation, on the other hand, occurs when dissolved iron forms insoluble minerals, such as iron hydroxides, oxides, or sulphides, which then settle in the sediment. This process is also strongly influenced by pH, redox conditions, and the availability of other ions like hydroxide (OH^-) or sulphide (S^{2-}). In oxygen-rich environments, Fe^{2+} oxidizes to Fe^{3+}, forming solid minerals like ferrihydrite or goethite, while in anoxic conditions, Fe^{2+} may precipitate as iron sulphides, such as pyrite. Adsorption and precipitation are interconnected, with iron initially adsorbing onto sediment surfaces and later precipitating as solid minerals under favourable conditions. These processes also play a role in nutrient cycling and contaminant transport, as iron can bind to and immobilize elements like phosphorus or toxic metals. Changes in redox conditions, such as during flooding, can remobilize previously adsorbed or precipitated iron, impacting water chemistry and sediment quality. Understanding the balance between these processes is essential for managing the ecological health of river systems and addressing issues like water quality and sediment contamination.

The concentration and behaviour of Fe in river sediments are significantly influenced by pH, along with factors like redox potential, organic matter, and the presence of other ions. In neutral to alkaline conditions (pH > 6.5), Fe, especially in its oxidized form (Fe^{3+}), tends to precipitate as iron hydroxides ($Fe(OH)_3$) and oxides. These precipitates are generally stable and lead to the removal of iron from the water phase, trapping it in the sediment. The iron precipitates ($Fe(OH)_3$, Fe_2O_3) that form at higher pH act as strong adsorbents for other metals, such as lead (Pb), arsenic (As), and chromium (Cr), reducing the mobility of these metals. In alkaline or neutral conditions, iron exists predominantly as Fe(III) in the form of oxides and hydroxides, which are insoluble and tend to accumulate in sediments. These iron oxides form stable complexes and play a key role in binding heavy metals, thus acting as a natural filter in river systems.

Organic matter forms stable complexes with Fe^{2+} and Fe^{3+}, increasing iron's solubility and mobility in sediments. Organic matter supports microbial reduction of Fe^{3+} to Fe^{2+},

enhancing iron's solubility, particularly in anoxic conditions. Organic matter inhibits the precipitation of iron oxides, keeping iron in a dissolved state. Organic matter promotes redox cycling between Fe^{2+} and Fe^{3+}, influencing iron's speciation and distribution. Organic matter decomposition can lower pH, increasing iron solubility and concentration. Overall, the presence of organic matter in river sediments tends to increase the concentration of dissolved iron, primarily by complexation, microbial reduction, and inhibiting precipitation of iron minerals.

Manganese (Mn)

The variation in concentrations of Mn along the selected stretch are depicted with the help of Figure 4.2.

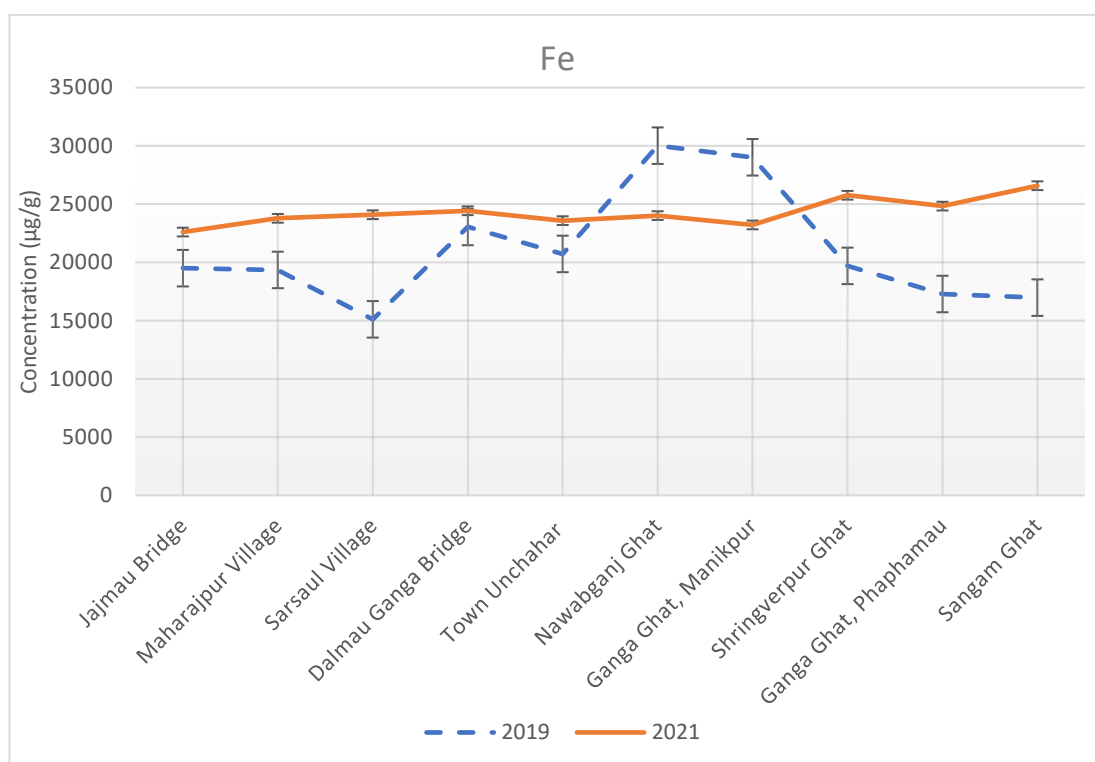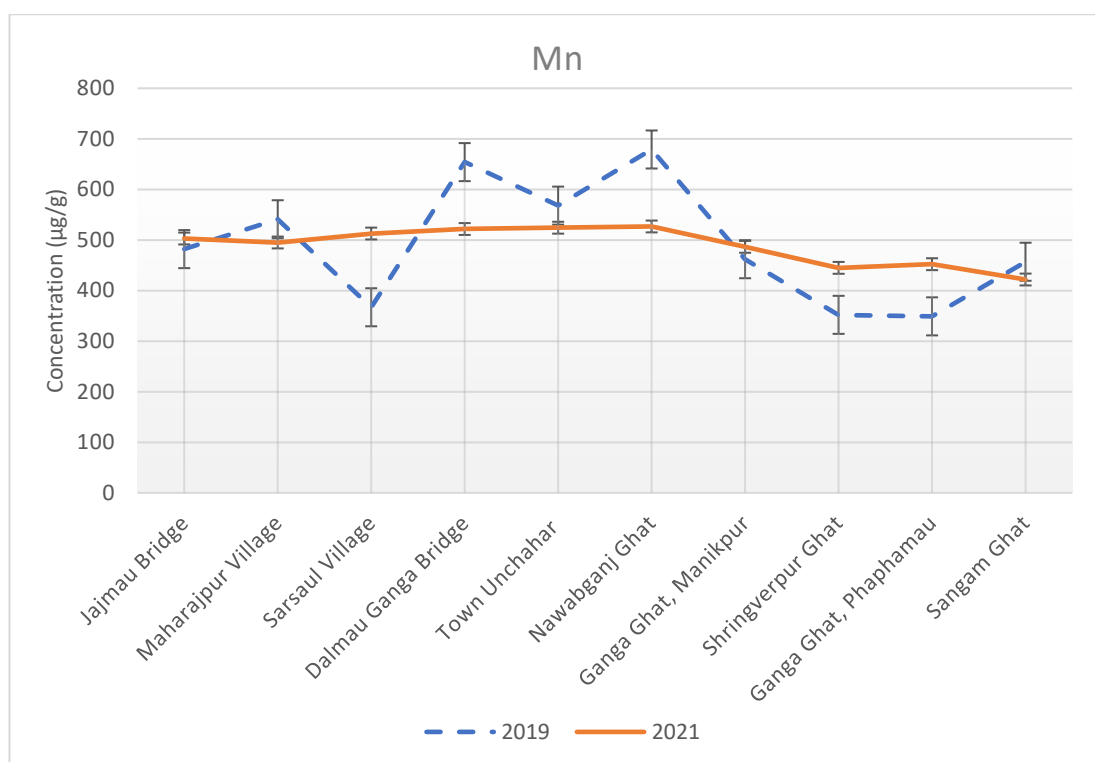**Figure 4.2** Variation in Mn concentrations in the riverbed sediment of Ganga River along the sampling points on the study area

In 2019, Mn concentration lies between 349 to 679 µg/g with a mean value of 491.1 µg/g. Mn concentration in the sites followed this order L9 < L8 < L3 < L10 < L7 < L1 < L2 < L5 < L4 < L6 being highest at L6 and lowest at L9.

In 2021, Mn concentration lies between 421.9 to 526.8 µg/g with a mean value of 488.9 µg/g. Mn concentration in the sites followed this order L10 < L8 < L9 < L7 < L2 < L1 < L3 < L4 < L5 < L6 being highest at L6 and lowest at L10.

In 2019, the Mn concentration at locations L4 and L6 surpassed the IRS average of 607 µg/g, while concentrations in all samples during both sampling periods remained below the global surface rock average of 720 µg/g. This indicates that the Mn concentration in the sediment of the riverbed has a minimal contribution from anthropogenic sources.

The average Mn concentration in 2021 closely resembled the levels recorded in 2019, with a marginal difference of only 0.45%. Throughout the sampling locations in the study area, Mn concentrations in 2021 exhibited greater consistency, signifying decreased variability compared to 2019. This suggests that there has been a cessation of new Mn input into the river. Interestingly, during the COVID-19 lockdown, Mn concentrations did not significantly decrease but rather became evenly distributed in the sediment of the riverbed.

The adsorption and precipitation of manganese (Mn) in river sediments are essential processes that influence the mobility, bioavailability, and geochemical cycling of manganese in aquatic environments. Adsorption occurs when dissolved manganese (typically Mn^{2+}) adheres to the surfaces of sediment particles like clay minerals, organic matter, or iron and manganese oxides. This process is affected by factors such as pH, redox conditions, and sediment composition. Under alkaline conditions, manganese ions are more likely to adsorb onto sediment particles, while in acidic conditions, manganese remains more mobile in its dissolved state. Redox conditions play a crucial role, as manganese exists in different oxidation states. In oxygen-rich (oxic) environments, Mn^{2+} is oxidized to Mn^{3+} or Mn^{4+}, which form insoluble manganese oxides that can adsorb to sediments or precipitate out of the water column. In reducing (anoxic) environments, Mn^{2+} is the dominant form, which is more soluble and less likely to adsorb, leading to increased mobility.

Precipitation of manganese occurs when dissolved Mn^{2+} is converted into solid manganese oxides, such as MnO_2, under favourable chemical conditions, particularly in the presence of oxygen. In toxic environments, manganese readily precipitates as

Mn oxides, whereas in anoxic conditions, it remains in dissolved form unless it reacts with other ions like sulphide to form manganese sulphides. Similar to iron, precipitation of manganese is influenced by pH, with higher pH levels promoting the formation of solid manganese compounds. Adsorption and precipitation of manganese often occur together, as adsorbed Mn^{2+} can be further oxidized and precipitate as manganese oxides. Manganese cycling in sediments is also dynamic, as changing environmental conditions, such as shifts in oxygen levels due to seasonal changes or organic matter degradation, can release previously adsorbed or precipitated manganese back into the water column.

These processes are significant for regulating the concentration of manganese in river systems, affecting the transport of other trace metals and nutrients. Manganese oxides in sediments can also adsorb or co-precipitate with contaminants, influencing water quality and sediment chemistry. The interplay between adsorption, precipitation, and redox conditions determines the fate of manganese in river ecosystems, with implications for both natural processes and human activities, such as pollution control and environmental management.

The concentration of Mn in river sediments is strongly influenced by both pH and organic matter. Mn behaviour in sediments is driven by its oxidation states-Mn^{2+} (soluble) and Mn^{4+} (insoluble in oxides)-and is sensitive to changes in pH, redox conditions, and interactions with organic matter. At higher pH (neutral to alkaline, pH > 7), Mn^{2+} is less soluble. In these conditions, Mn tends to oxidize and precipitate as insoluble MnO_2 or other Mn oxides, reducing the concentration of dissolved manganese in the sediment. In alkaline conditions, Mn^{2+} is readily oxidized to Mn^{4+} and precipitates as manganese dioxide (MnO_2), an insoluble form. This leads to lower concentrations of manganese in the sediment pore water, as manganese is effectively trapped in the sediment in solid oxide forms.

Organic matter, particularly humic and fulvic acids, can form complexes with Mn^{2+}. These complexes can increase the solubility of manganese in sediments by stabilizing Mn^{2+}, even in conditions where it might otherwise precipitate. This means that the presence of organic matter can maintain manganese in its dissolved, mobile form. Organic matter can also help solubilize Mn^{2+} by preventing the formation of manganese oxides. This keeps manganese in a more bioavailable and mobile state

within the sediment pore water, leading to higher manganese concentrations in organic-rich sediments.

In conclusion, pH and organic matter together play a crucial role in controlling manganese concentration and mobility in river sediments, with low pH and high organic content promoting manganese solubility, while high pH leads to precipitation unless organic matter interferes.

Chromium (Cr)

The variation in concentrations of Cr along the selected stretch are depicted with the help of Figure 4.3.

Figure 4.3 Variation in Cr concentrations in the riverbed sediment of Ganga River along the sampling points on the study area

In 2019, Cr ranged from 31.4 to 100.2 µg/g with an average of 61.13 µg/g and followed the order L1 < L9 < L8 < L3 < L10 < L5 < L4 < L6 < L7 < L2 with lowest at L1 and highest at L2 site.

In 2021, Cr ranged from 45.17 to 59.24 µg/g with an average value of 52.36 µg/g and followed the order L2 < L4 < L1 < L7 < L5 < L8 < L6 < L3 < L10 < L9 with lowest at L2 and highest at L9.

In 2019, Cr concentrations at sites L2, L6 and L7 exceeded both IRS average value and world surface rock average of 87 µg/g and 71 µg/g respectively whereas concentrations at all other samples were less than the IRS average value and the world surface rock average. Cr concentrations at some sites are alarming that can cause lethality to some aquatic species in the river system.

During 2021, there was a notable 14.35% decrease in the average concentration of Cr compared to the levels documented in 2019. Across various sampling locations within the study area, Cr concentrations in 2021 exhibited increased uniformity, indicating decreased variability when contrasted with observations from 2019. This suggests a reduction in the input of Cr both from upstream and at the local level. The decline in metal concentrations is likely a result of decreased industrial activities during the COVID-19 lockdown in the country, reflecting a natural rejuvenation process taking place in the riverbed sediment of the Ganga River over time.

The adsorption and precipitation of chromium (Cr) in river sediments are key processes that influence its mobility, toxicity, and environmental behavior in aquatic systems. Chromium exists primarily in two oxidation states, Cr (III) and Cr (VI), which exhibit very different behaviors. Cr (III) is less mobile and less toxic, whereas Cr (VI) is highly soluble, toxic, and mobile. These processes are influenced by various factors such as pH, redox conditions, sediment composition, and the presence of competing ions or organic matter.

Adsorption of Cr in river sediments primarily involves Cr(III), which tends to strongly adsorb onto sediment particles such as clay minerals, organic matter, and iron or manganese oxides. This process is influenced by pH, with higher adsorption occurring at neutral to slightly alkaline pH levels. Cr(III) forms stable complexes with hydroxides and organic ligands, which enhances its adsorption capacity. On the other hand, Cr(VI) in the form of chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$) is less likely to adsorb onto sediments due to its negative charge, making it more mobile and bioavailable in the water column, especially under alkaline conditions. However, Cr(VI) can adsorb onto positively charged surfaces of minerals, especially in acidic environments, though its adsorption is generally weaker compared to Cr(III).

Precipitation of Cr mainly occurs when Cr(III) forms insoluble hydroxides or oxides, such as $Cr(OH)_3$ or Cr_2O_3, which precipitate out of the water column and accumulate in sediments. This precipitation is favoured at higher pH levels (alkaline conditions), where Cr(III) becomes less soluble. In contrast, Cr(VI) does not readily precipitate under natural water conditions unless it is reduced to Cr(III), which can occur in reducing (anoxic) environments, often facilitated by organic matter or microbial activity. Once reduced to Cr(III), the chromium can then precipitate as solid phases. The reduction of Cr(VI) to Cr(III) is a crucial process that controls the detoxification and immobilization of chromium in sediments.

In redox-sensitive environments, Cr(VI) can be reduced to Cr(III) under anoxic conditions, leading to its adsorption onto sediments or its precipitation as solid chromium hydroxides. This transformation significantly reduces its mobility and toxicity. Conversely, under oxic conditions, Cr(III) is generally stable and tends to remain adsorbed or precipitated, while Cr(VI) can remain in the dissolved phase, increasing its mobility.

The interplay between adsorption and precipitation of chromium in sediments is critical for controlling its transport, bioavailability, and potential environmental impact. Factors such as pH, redox conditions, and the composition of sediment particles determine the extent to which chromium is adsorbed or precipitated. Sediments rich in iron or manganese oxides, for example, can promote the adsorption of Cr(III), while organic-rich or reducing sediments can enhance the reduction of Cr(VI) to Cr(III), facilitating its immobilization. Changes in environmental conditions, such as flooding, oxygen fluctuations, or human-induced pollution, can cause previously adsorbed or precipitated chromium to be released back into the water, posing a risk to aquatic ecosystems and human health.

Understanding the behavior of chromium in river sediments is essential for managing its environmental risks, especially in regions affected by industrial pollution, where Cr(VI) contamination is a concern. Effective management requires monitoring the conditions that favour either the adsorption and precipitation of Cr(III) or the mobility

of Cr(VI), as these processes govern the fate and transport of chromium in aquatic systems.

Chromium can exist in two main oxidation states: Cr(III) (trivalent, less toxic, and less mobile) and Cr(VI) (hexavalent, more toxic, and more mobile). The speciation, solubility, and mobility of chromium in sediments depend on the redox conditions, pH, and interactions with organic matter.

At higher pH (neutral to alkaline conditions, pH > 7), Cr(III) tends to precipitate as chromium hydroxides (Cr $(OH)_3$), making it less soluble and reducing its concentration in the dissolved phase. This means Cr(III) is less mobile in alkaline sediments. In contrast, Cr (VI) is more stable and soluble in alkaline conditions, existing as chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$). This increases the mobility and concentration of Cr(VI) in the sediment pore water, especially in oxidizing environments where Cr(VI) is more stable.

Organic matter plays a key role in reducing toxic Cr(VI) to the less toxic and less mobile Cr(III). Organic compounds, particularly those rich in functional groups like carboxyls and hydroxyls, can act as electron donors, facilitating the reduction of Cr(VI) to Cr(III), especially in reducing (anoxic) environments. This process decreases the mobility and toxicity of chromium by converting it to the less soluble Cr(III) form. Humic and fulvic acids, which are components of organic matter, are particularly effective at reducing Cr(VI) to Cr(III). Organic matter can also form stable complexes with Cr(III), increasing its solubility and mobility in certain conditions. These Cr(III)-organic complexes prevent the immediate precipitation of Cr(III) as hydroxides or oxides, allowing it to remain dissolved in sediment pore water. Organic matter, by forming complexes with Cr(III), can inhibit its precipitation as Cr$(OH)_3$. This keeps Cr(III) in a dissolved form in the sediment, particularly in organic-rich environments, which can increase its concentration in sediment pore water. In conclusion, pH and organic matter play a key role in determining the speciation, mobility, and toxicity of chromium in river sediments. Acidic and organic-rich conditions tend to stabilize Cr(III) and reduce Cr(VI), while alkaline environments increase the stability and mobility of Cr(VI) unless organic matter facilitates its reduction.

Zinc (Zn)

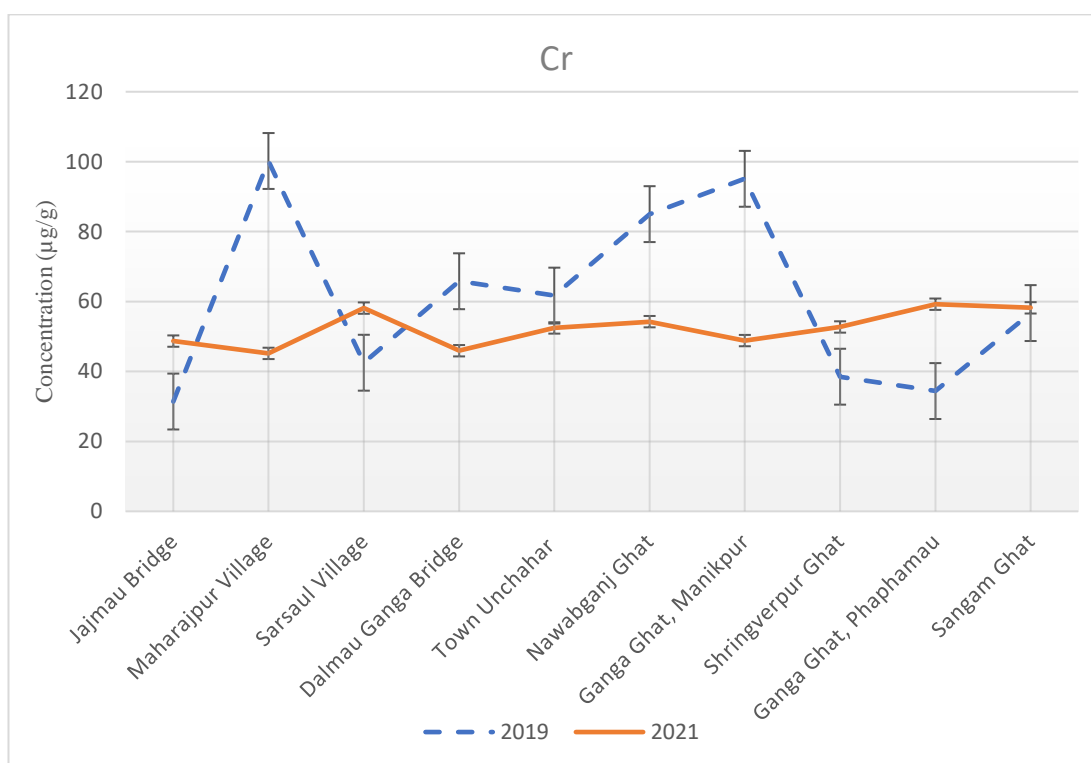The variation in concentrations of Zn along the selected stretch are depicted with the help of Figure 4.4.
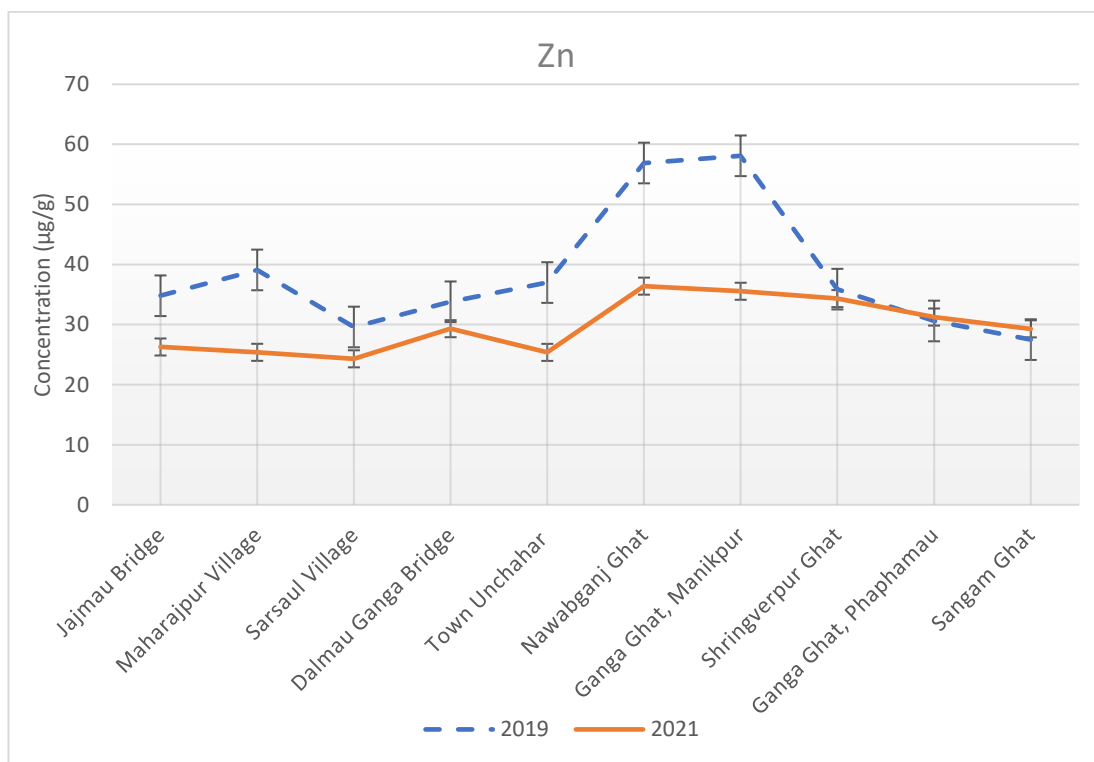
Figure 4.4 Variation in Zn concentrations in the riverbed sediment of Ganga River along the sampling points on the study area

In 2019, concentrations of Zn ranged from 27.5 to 58.1 µg/g with an average value of 38.33 µg/g. Cu concentration in the sites followed this order L10 < L3 < L9 < L4 < L1 < L8 < L5 < L2 < L6 < L7 with highest at L7 and lowest at L10.

In 2021, concentrations of Zn ranged from 24.3 to 36.4 µg/g with an average value of 29.75 µg/g. Cu concentration in the sites followed this order L3 < L5 < L2 < L1 < L10 < L4 < L9 < L8 < L7 < L6 with highest at L6 and lowest at L3.

Zn concentrations in all samples were observed less than the World Surface Rock Average of 127 µg/g but exceeded the IRS average value of 16 µg/g which shows the possible input of Zn from anthropogenic sources may cause adverse effect on aquatic biota.

The average concentration of Zn in 2021 experienced a notable decrease of 22.38% compared to that in 2019. Across the sampling locations in the study area, Zn concentrations in 2021 displayed more uniformity, indicating less variation than observed in 2019. This implies a reduction in fresh zinc input from upstream and at the local level. The decline in metal concentrations is likely attributable to a decrease in industrial activities during the COVID-19 lockdown in the country, signifying a natural rejuvenation process of the riverbed sediment in the Ganga River over time.

The adsorption and precipitation of zinc in river sediments are key processes that control its mobility, bioavailability, and environmental impact in aquatic systems. Zinc primarily exists in the form of Zn^{2+} in water and can interact with sediment particles and dissolved components, affecting its distribution between the water column and the sediment.

Adsorption of Zn onto river sediments is influenced by factors such as pH, sediment composition, ionic strength, and redox conditions. In general, Zn^{2+} adsorbs onto sediment particles, including clays, organic matter, and metal oxides (like iron and manganese oxides). Adsorption increases under alkaline conditions, as higher pH levels promote the formation of hydroxyl complexes (e.g., $ZnOH^+$), which are more readily adsorbed onto negatively charged sediment surfaces. Under acidic conditions, Zn remains more soluble and mobile, as fewer negatively charged binding sites are available. Sediments rich in organic matter, iron oxides, and manganese oxides provide a high surface area and reactive sites for Zn adsorption, making these sediments particularly effective at immobilizing zinc.

Precipitation of Zn occurs when dissolved Zn^{2+} reacts with other anions in the water, such as carbonate (CO_3^{2-}), hydroxide (OH^-), or sulphide (S^{2-}), to form insoluble zinc compounds that settle into the sediment. Under neutral to alkaline conditions, Zn^{2+} can precipitate as zinc hydroxide ($Zn(OH)_2$) or zinc carbonate (smithsonite, $ZnCO_3$), which are relatively insoluble and accumulate in the sediment. In reducing (anoxic) environments, Zn^{2+} can precipitate as zinc sulphide (ZnS), especially in areas with high organic matter and sulphide concentrations, such as the bottom of rivers or in wetlands. Precipitation is generally more effective at immobilizing Zn than adsorption, as the

solid phases formed are more stable and less prone to re-dissolution under varying conditions.

Redox conditions in sediments also play a critical role in controlling zinc behavior. In oxidizing environments, Zn^{2+} tends to remain dissolved or adsorbed to iron and manganese oxides. In contrast, in reducing environments, zinc may co-precipitate with sulphides or be released from oxides as redox-sensitive metals (such as iron and manganese) undergo dissolution, potentially mobilizing previously adsorbed or precipitated Zn.

The interplay between adsorption and precipitation determines the extent to which zinc is immobilized or remains mobile in river sediments. Adsorbed zinc can remain on sediment surfaces and be exchanged between the water and sediments depending on environmental conditions. However, if zinc concentrations in the water become too high or pH and redox conditions change, Zn may precipitate as a solid phase, further reducing its mobility. In particular, sediments that are rich in reactive metal oxides or organic matter can serve as both adsorbents and precipitating agents for zinc, enhancing its retention in the sediment.

Changes in environmental conditions, such as fluctuations in pH, redox potential, or sediment disturbance (e.g., during flooding or dredging), can cause previously adsorbed or precipitated zinc to be released back into the water, making it bioavailable again and posing a potential environmental hazard. Zinc, while an essential trace element for living organisms, can become toxic at high concentrations, making the processes that control its cycling in river sediments important for water quality and ecosystem health.

Overall, the adsorption and precipitation of Zn in river sediments are governed by a complex interplay of chemical and physical factors, with adsorption dominating under certain conditions and precipitation occurring when favourable geochemical conditions (such as high pH or the presence of sulphides) are met. Understanding these processes is important for managing zinc contamination in aquatic systems, especially in areas impacted by industrial pollution or natural geochemical processes.

The concentration and behavior of zinc (Zn) in river sediments are strongly influenced by both pH and organic matter. Zinc exists primarily as Zn^{2+} in natural environments, and its mobility, bioavailability, and concentration are controlled by the pH of the environment and the presence of organic matter, which can form complexes with zinc and affect its solubility and precipitation.

In neutral to alkaline conditions (pH > 7), zinc solubility decreases significantly as Zn^{2+} tends to precipitate as zinc hydroxide ($Zn(OH)_2$), zinc carbonate ($ZnCO_3$), or other zinc minerals like smithsonite. This leads to lower concentrations of dissolved zinc in sediment pore water. As pH increases, Zn^{2+} has a higher affinity for adsorption onto sediment particles, such as iron and manganese oxides, clay minerals, and organic matter. This reduces the mobility of zinc, leading to its sequestration in sediments. In neutral to alkaline conditions, zinc is more likely to precipitate and adsorb to sediments, reducing the concentration of dissolved Zn^{2+} and limiting its mobility.

Organic matter, especially humic and fulvic acids, contains functional groups (e.g., carboxyl, hydroxyl) that can form complexes with Zn^{2+}. These organic-zinc complexes increase zinc solubility in some cases, as the complexes can remain dissolved even when inorganic zinc would precipitate or adsorb to particles. Organic matter can enhance zinc mobility by preventing its precipitation as zinc hydroxides or carbonates. These complexes may also reduce zinc adsorption onto mineral surfaces, keeping it in the dissolved phase in sediment pore water. Organic matter increases the solubility and mobility of zinc in sediments by forming complexes with Zn^{2+}, allowing zinc to remain in the dissolved phase, especially in organic-rich environments. In addition to complexing with Zn^{2+}, organic matter itself can adsorb zinc ions onto its surface. In organic-rich sediments, zinc may be sequestered in the solid phase, reducing its bioavailability and mobility. The strength of this adsorption depends on the specific composition of the organic matter and the pH. In some cases, zinc adsorbed to organic matter becomes immobilized, especially under neutral to alkaline conditions, where the binding between organic matter and zinc is stronger. Organic matter can reduce zinc mobility by adsorbing it, especially in environments where organic matter is abundant and where pH conditions support stronger adsorption. In conclusion, pH and organic matter jointly influence the mobility, bioavailability, and concentration of zinc

in river sediments. Low pH increases zinc solubility, while high pH promotes zinc precipitation and adsorption. Organic matter can enhance zinc solubility through complexation or immobilize zinc through adsorption, depending on the specific sediment conditions.

Lead (Pb)

The variation in concentrations of Pb along the selected stretch are depicted with the help of Figure 4.5.
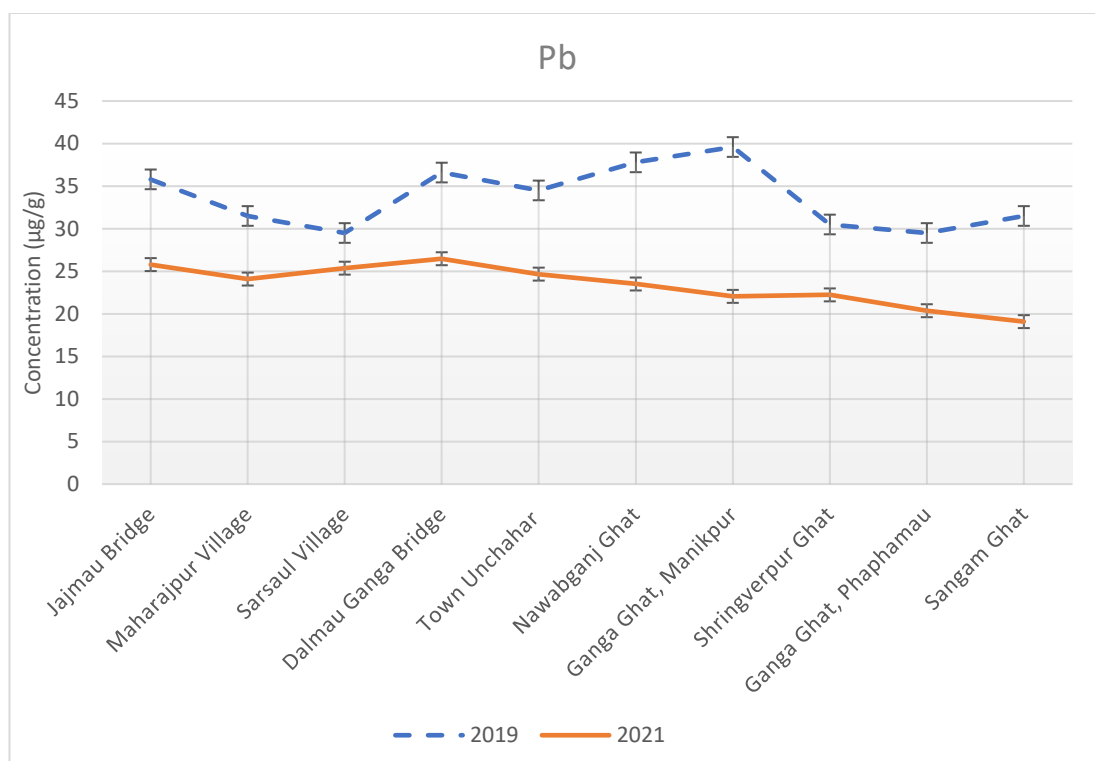
Figure 4.5 Variation in Pb concentrations in the riverbed sediment of Ganga River along the sampling points on the study area

In 2019, Pb concentrations ranged from 29.5 to 39.6 µg/g, with an average value of 33.68 µg/g. The order of Pb concentration at the sites is as follows: L3 < L9 < L8 < L2 < L10 < L5 < L1 < L4 < L6 < L7, with the highest value recorded at site L7 and the lowest at site L3.

In 2021, Pb concentrations ranged from 19.09 to 26.48 µg/g, with an average value of 23.36 µg/g. The order of Pb concentration at the sites is as follows: L10 < L9 < L7 <

L8 < L6 < L2 < L5 < L3 < L1 < L4, with the highest value recorded at site L4 and the lowest at site L10.

Pb concentrations in all samples during both sampling period exceeded the world WSR average of 16 µg/g indicating possible input of Pb metal from anthropogenic sources. Also, Pb concentrations in most samples exceeded the Bn value of 22 µg/g. Higher levels of Pb is a threat to fisheries resources, whereas, in plants, it initially results in enhanced growth, but from a concentration of 5 µg/g onwards, this is counteracted by severe growth retardation, discoloration, and morphological abnormalities.

The average concentration of lead in 2021 decreased by 30.61% compared to that in 2019. In the study area, Pb concentrations across sampling locations exhibited greater uniformity in 2021, with less variation than observed in 2019. This suggests a reduction in fresh Pb input from upstream and at the local level. The decrease in metal concentrations can be attributed to a decline in industrial activities during the COVID-19 lockdown in the country, indicating a self-rejuvenation of the riverbed sediment in the Ganga River over time.

The adsorption and precipitation of lead in river sediments are crucial processes that influence its mobility, bioavailability, and potential toxicity in aquatic environments. Lead typically exists as Pb^{2+} in water, and its interaction with sediment particles is determined by factors such as pH, redox conditions, sediment composition, and the presence of competing ions and organic matter. Adsorption occurs when Pb^{2+} binds to sediment particles, including clay minerals, organic matter, and metal oxides like iron and manganese oxides. This process is highly dependent on pH, with lead adsorbing more effectively in neutral to alkaline conditions, while remaining more soluble and mobile under acidic conditions. Organic matter can also bind lead through complexation, enhancing its immobilization. Redox conditions further influence adsorption, as Pb^{2+} can strongly adsorb to metal oxides in oxygen-rich environments, but may be released if these oxides dissolve under reducing conditions. Precipitation of lead occurs when dissolved Pb^{2+} reacts with anions such as hydroxide, carbonate, sulphate, or sulphide to form insoluble compounds like lead carbonate (cerussite, $PbCO_3$), lead hydroxide ($Pb(OH)_2$), or lead sulphide (galena, PbS), depending on

environmental conditions. In neutral to alkaline conditions, lead carbonate or hydroxide tends to precipitate, while in anoxic, sulphide-rich environments, lead sulphide becomes the dominant precipitate, providing stable and long-term immobilization of lead. Adsorption and precipitation often work together, with lead initially adsorbing onto sediment surfaces and later precipitating as stable minerals. These processes help control the fate of lead in river sediments, limiting its mobility and reducing its toxicity. However, environmental changes such as pH shifts or redox fluctuations can remobilize lead, posing risks to water quality and aquatic ecosystems. Understanding the balance between adsorption and precipitation is crucial for managing lead contamination in river systems, particularly in areas impacted by industrial pollution or natural geochemical processes.

The concentration and behavior of Pb in river sediments are strongly influenced by pH and organic matter. Lead exists primarily in its divalent form (Pb^{2+}) in natural environments, and its solubility, mobility, and bioavailability depend on sediment pH, redox conditions, and the presence of organic matter.

At neutral to alkaline pH (pH > 7), lead's solubility decreases significantly. Lead tends to precipitate as lead hydroxide [$Pb(OH)_2$], lead carbonate ($PbCO_3$, cerussite), or lead phosphate ($Pb_3(PO_4)_2$) in alkaline environments. These insoluble compounds reduce the concentration of dissolved Pb^{2+} in sediment pore water, limiting lead's mobility. As pH increases, lead has a higher affinity for adsorption onto sediment particles, such as iron and manganese oxides, clay minerals, and organic matter. Lead becomes strongly bound to these particles, which immobilizes it in sediments and reduces its potential for leaching. At neutral to alkaline pH, lead is more likely to precipitate and adsorb onto sediments, resulting in lower concentrations of dissolved Pb^{2+} and reduced mobility.

Organic matter, especially humic and fulvic acids, contains functional groups (e.g., carboxyl, hydroxyl, phenolic groups) that can form strong complexes with Pb^{2+}. These lead-organic complexes can increase the solubility of lead in some cases, keeping lead in the dissolved phase even under conditions where inorganic lead might otherwise precipitate. The complexation of Pb^{2+} with organic matter can prevent it from

adsorbing onto sediment particles or precipitating, leading to higher concentrations of dissolved lead in organic-rich sediments. Organic matter can increase the solubility and mobility of lead in sediments by forming stable lead-organic complexes, preventing lead precipitation and keeping lead in the dissolved phase in organic-rich environments. Organic matter can also adsorb lead directly, especially in its particulate form. Lead strongly binds to the organic matter in sediments, particularly under neutral and alkaline conditions. This adsorption process can effectively immobilize lead, reducing its mobility and bioavailability in sediments. In sediments rich in organic material, lead can become sequestered in the solid phase, reducing its potential for leaching into the water column. The strength of this adsorption depends on the pH and the type of organic matter present. Organic matter can immobilize lead by adsorbing it, especially under neutral to alkaline conditions, reducing the mobility and bioavailability of lead in sediments.

In conclusion, pH and organic matter jointly control the mobility, bioavailability, and concentration of lead in river sediments. Low pH enhances lead solubility, while high pH promotes lead precipitation and adsorption. Organic matter can either increase lead mobility by forming soluble complexes or immobilize lead through adsorption, depending on the environmental conditions.

Nickel (Ni)

The variation in concentrations of Ni along the selected stretch are depicted with the help of Figure 4.6.

In 2019, Ni concentration remained below its baseline concentration (46 μg/g) ranging between 32.2 to 42.6 μg/g with a mean value of 35.16 μg/g, indicating a less contaminated condition by this metal. In 2019, Ni concentration in the sites followed the order L3 < L4 < L1 < L2 < L9 < L10 < L5 < L8 < L6 < L7 with lowest at L3 and highest at L7.

In 2021, Ni concentration remained below its baseline concentration (46 μg/g) ranging between 25.13 to 33.69 μg/g with a mean value of 29.71 μg/g, indicating a less contaminated condition by this metal. In 2021 Ni concentration in the sites followed

the order L1 < L8 < L7 < L10 < L9 < L2 < L5 < L6 < L3 < L4 with lowest at L1 and highest at L4.

In 2019, Ni concentrations at sites L6 and L7 exceeded the IRS average value of 37 µg/g whereas Ni concentrations in all samples during both sampling period were recorded less than the world surface rock average of 49 µg/g.

In 2021, the average Ni concentration witnessed a significant decline of 15.50% compared to the levels recorded in 2019. Throughout the sampling locations within the study area, Ni concentrations in 2021 demonstrated greater uniformity, suggesting reduced variability when compared to the observations in 2019. This indicates a decrease in Ni input both from upstream and at the local level. The drop in metal concentrations can be attributed to a reduction in industrial activities during the COVID-19 lockdown in the country, indicating a natural rejuvenation process occurring in the sediment of the Ganga River over time.

Figure 4.6 Variation in Ni concentrations in the riverbed sediment of Ganga River along the sampling points on the study area

The adsorption and precipitation of nickel (Ni) in river sediments are important processes that control its mobility, bioavailability, and potential environmental impact in aquatic systems. Nickel primarily exists in its divalent form (Ni^{2+}) in water, and its behavior is influenced by factors such as pH, redox conditions, sediment composition, and the presence of other ions or organic matter.

Adsorption of Ni^{2+} onto sediment particles, including clays, organic matter, and metal oxides (such as iron and manganese oxides), is a key mechanism that regulates its distribution between the water column and the sediment. The adsorption process is highly dependent on pH, with higher adsorption occurring at neutral to alkaline pH levels. In acidic conditions, Ni remains more soluble and mobile, making it less likely to adsorb to sediment particles. In contrast, at higher pH, the negatively charged surfaces of sediment particles bind Ni^{2+} more effectively, immobilizing it in the sediment. Metal oxides, particularly iron and manganese oxides, are especially effective in adsorbing nickel, as they provide numerous reactive sites for metal binding. Organic matter also plays a significant role, as it can complex with Ni^{2+} and enhance its adsorption.

Precipitation of nickel occurs when Ni^{2+} reacts with other ions in the water, forming insoluble nickel compounds that settle into the sediment. This process is influenced by pH and the availability of anions such as carbonate (CO_3^{2-}), hydroxide (OH^-), or sulphide (S^{2-}). At neutral to alkaline pH, Ni^{2+} can precipitate as nickel hydroxide ($Ni(OH)_2$) or nickel carbonate ($NiCO_3$), which are relatively insoluble and help reduce nickel's mobility. In reducing (anoxic) environments, where organic matter or microbial activity promotes sulphide production, Ni^{2+} can precipitate as nickel sulphide (NiS), which is highly stable and insoluble. This precipitation process, especially in sulphide-rich environments, effectively immobilizes nickel in the sediment.

Redox conditions significantly influence nickel's behavior. In oxidizing environments, Ni^{2+} is more likely to adsorb onto metal oxides, while in reducing conditions, nickel may co-precipitate with sulphides or be released from metal oxides as they dissolve.

Redox fluctuations can cause previously adsorbed or precipitated nickel to be remobilized, making it bioavailable and increasing the risk of contamination.

The interplay between adsorption and precipitation is essential for controlling the fate of nickel in river sediments. Adsorption tends to dominate at lower Ni concentrations or under conditions where immediate precipitation is not favourable. As conditions such as pH, redox state, or Ni concentration change, nickel can precipitate as solid compounds, further stabilizing it in the sediment. This immobilization is critical in preventing the remobilization of nickel under changing environmental conditions. However, disturbances such as sediment reworking, pH shifts, or redox changes can lead to the release of previously immobilized nickel, posing potential environmental risks.

Overall, the adsorption and precipitation of Ni in river sediments are complex processes influenced by chemical and environmental factors. These processes are essential for managing nickel contamination, reducing its bioavailability, and protecting aquatic ecosystems from its potentially harmful effects, especially in areas impacted by industrial pollution or natural geochemical changes.

The concentration and behavior of nickel (Ni) in river sediments are influenced by pH and organic matter. Nickel predominantly exists in the form of Ni^{2+} in natural environments, and its mobility, bioavailability, and tendency to adsorb to sediments are controlled by these factors.

As pH increases (pH > 7), nickel solubility decreases. Nickel tends to precipitate as nickel hydroxide [$Ni(OH)_2$] and other nickel compounds (such as $NiCO_3$ in carbonate-rich waters) at higher pH. These minerals are less soluble, causing a reduction in the concentration of dissolved Ni^{2+} in sediment pore water. At neutral and alkaline pH, nickel adsorption onto sediment particles, such as clay, iron oxides, and organic matter, increases. Higher pH favours the binding of Ni^{2+} to negatively charged sediment surfaces, resulting in less mobile nickel and more nickel being retained in the solid phase. In neutral to alkaline conditions, nickel becomes less soluble and more likely to precipitate or adsorb onto sediment particles, leading to lower concentrations of dissolved Ni^{2+} and reduced mobility.

Organic matter, particularly humic and fulvic acids, contains functional groups (e.g., carboxyl and hydroxyl groups) that can form stable complexes with Ni^{2+}. These organic complexes can keep nickel in the dissolved phase, even when the conditions would otherwise favour precipitation or adsorption. The formation of nickel-organic complexes can enhance the solubility of nickel in sediments, especially in organic-rich environments. When organic matter forms complexes with nickel, it can increase the mobility of nickel by preventing it from precipitating or adsorbing onto sediment particles. This is especially important in environments with high levels of dissolved organic carbon (DOC), where complexation can lead to higher concentrations of dissolved nickel in the sediment pore water. Organic matter increases nickel solubility and mobility by forming nickel-organic complexes, preventing nickel from precipitating or adsorbing onto sediments in organic-rich environments. Organic matter can also act as an adsorbent for nickel, particularly under neutral to alkaline conditions. Nickel ions can bind to the negatively charged functional groups on organic matter, which reduces nickel's mobility in sediments. The adsorption of nickel onto organic matter effectively sequesters it in the solid phase, reducing its bioavailability. In organic-rich sediments, nickel may be immobilized by adsorption onto organic particles. The strength of this adsorption depends on the type of organic matter and environmental conditions, such as pH. Organic matter can reduce nickel mobility by adsorbing it onto its surfaces, especially under neutral to alkaline conditions, sequestering nickel in the sediment and reducing its bioavailability.

In conclusion, both pH and organic matter play a critical role in controlling the concentration, mobility, and bioavailability of nickel in river sediments. At low pH, nickel remains more soluble and mobile, while at high pH, nickel is more likely to precipitate and adsorb onto sediments, reducing its mobility. Organic matter can increase nickel mobility through complexation, especially under acidic conditions, or immobilize nickel through adsorption, particularly in neutral to alkaline environments.

Copper (Cu)

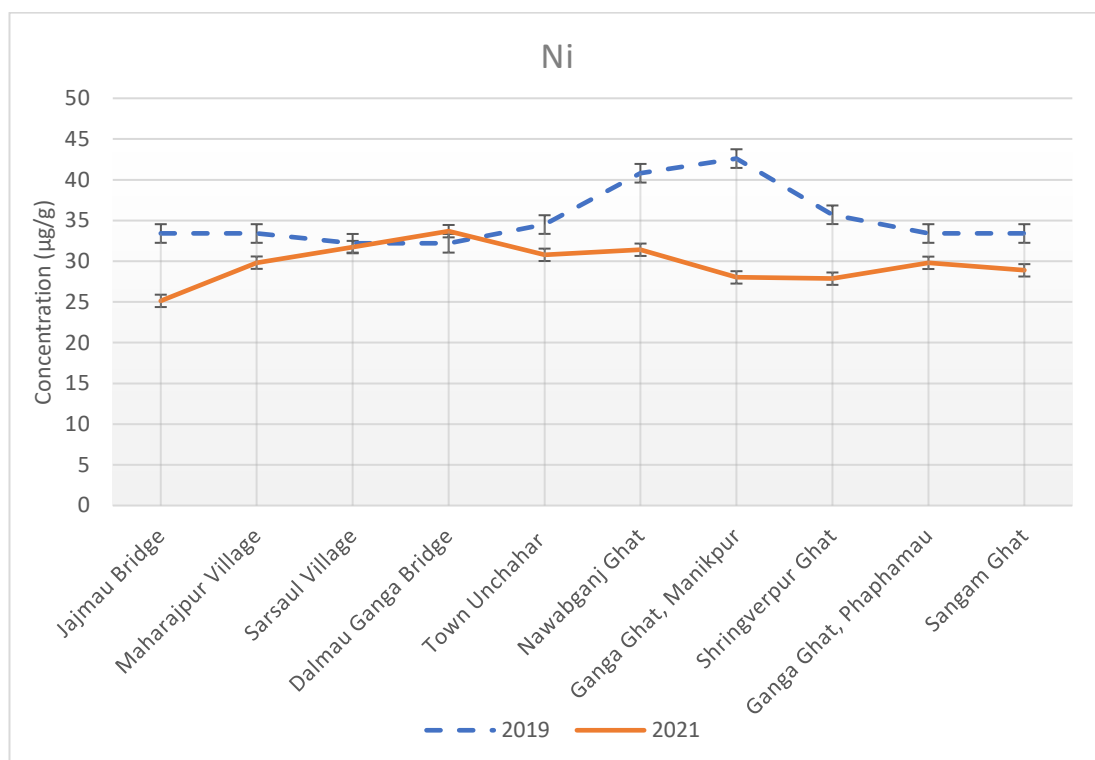The variation in concentrations of Cu along the selected stretch are depicted with the help of Figure 4.7.
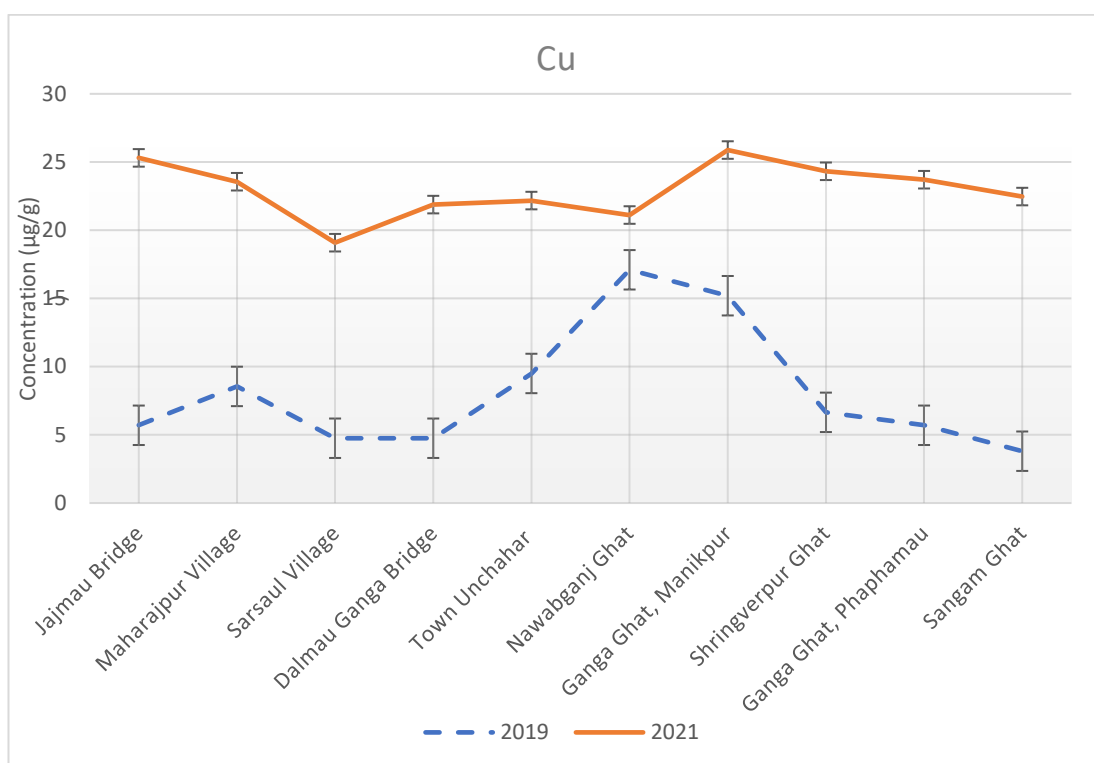
Figure 4.7 Variation in Cu concentrations in the riverbed sediment of Ganga River along the sampling points on the study area

In 2019, Cu concentration ranged from 3.8 to 17.1 µg/g with an average value of 8.17 µg/g. Cu concentration in the sites followed this order L10 < L3 < L4 < L1 < L9 < L8 < L2 < L5 < L7 < L6 with highest at L6 and lowest at L10.

In 2021, Cu concentration ranged from 19.09 to 25.88 µg/g with an average value of 22.95 µg/g. Cu concentration in the sites followed the order L3 < L6 < L4 < L5 < L10 < L2 < L9 < L8 < L1 < L7 with highest at L7 and lowest at L3.

Cu concentrations in all samples collected during both sampling events were consistently below the World Surface Rock average of 32 µg/g and the IRS average value of 28 µg/g. This suggests that copper concentrations in the riverbed sediment are within safer levels and do not exhibit significant contributions from anthropogenic sources.

The average copper concentration in 2021 witnessed a substantial increase of 180.91% compared to that in 2019. In the sampling locations across the study area, copper concentrations in 2021 showed greater uniformity, suggesting reduced variability

compared to 2019. This indicates a potential increase in the source of copper from upstream areas. Moreover, the riverbed sediment in 2021 appeared to adsorb more of copper during the lower concentrations of other metals, possibly associated with a reduction in industrial activities, due to the COVID-19 lockdown.

The adsorption and precipitation of copper (Cu) in river sediments are critical processes that regulate its mobility, bioavailability, and potential toxicity in aquatic environments. Copper primarily exists as Cu^{2+} in water, and its interaction with sediment particles is influenced by factors such as pH, redox conditions, sediment composition, and the presence of other ions and organic matter. Adsorption occurs when Cu^{2+} binds to sediment particles like clay minerals, organic matter, and metal oxides, especially iron and manganese oxides, which have a high affinity for copper. Adsorption is more effective at neutral to alkaline pH levels, where copper hydroxide complexes form and bind to negatively charged sediment surfaces, immobilizing the metal. In contrast, acidic conditions increase copper's solubility and mobility. Organic matter also plays a key role in binding Cu^{2+} through complexation, further reducing its mobility.

Precipitation of copper occurs when dissolved Cu^{2+} reacts with anions like hydroxide, carbonate, or sulphide to form solid mineral phases that settle into the sediment. Under neutral to alkaline conditions, copper can precipitate as copper hydroxide ($Cu(OH)_2$) or copper carbonate (malachite), which are insoluble and effectively trap the metal in the sediment. In reducing (anoxic) environments, often rich in organic matter, copper can precipitate as copper sulphide (CuS), a highly stable and insoluble compound. This precipitation process is especially important in areas with high sulphide production due to microbial activity, further enhancing copper immobilization.

The interplay between adsorption and precipitation controls copper's fate in river sediments. Initially, Cu^{2+} may adsorb onto sediment particles, especially in oxygen-rich environments, and later precipitate as solid compounds when conditions favour it. Precipitation is more permanent and stable, but environmental changes such as shifts in pH or redox conditions can cause previously adsorbed or precipitated copper to be

remobilized. Such changes can dissolve metal oxides or sulphides, releasing copper back into the water and increasing its bioavailability and toxicity.

Copper is an essential micronutrient but becomes toxic at elevated concentrations, making these processes essential for managing copper contamination in aquatic systems. Adsorption and precipitation help immobilize copper in sediments, protecting water quality and aquatic life, but these mechanisms can be disrupted by environmental changes. Understanding these processes is crucial for managing copper pollution, particularly in areas affected by industrial activities or natural geochemical changes.

The concentration and behavior of copper in river sediments are heavily influenced by pH and the presence of organic matter. Copper primarily exists as Cu^{2+} in natural environments, and its solubility, mobility, and adsorption to sediments are affected by these environmental factors.

At neutral to alkaline pH (pH > 7), copper tends to precipitate as copper hydroxide $[Cu(OH)_2]$, copper carbonate $(CuCO_3)$, or copper sulphide (CuS) under reducing conditions. These copper compounds are relatively insoluble, leading to lower concentrations of dissolved copper in the sediment pore water. At higher pH, copper ions are more likely to adsorb onto sediment particles, such as clays, iron oxides, and organic matter. As pH increases, sediment surfaces become more negatively charged, favouring the adsorption of Cu^{2+} and decreasing its mobility. Copper becomes more tightly bound to sediments, reducing its bioavailability. In neutral to alkaline conditions, copper is less soluble and more likely to adsorb onto sediments, reducing its mobility and bioavailability in river sediments.

Organic matter, especially humic and fulvic acids, contains functional groups (e.g., carboxyl, hydroxyl, and phenolic groups) that can bind strongly with Cu^{2+}. These copper-organic complexes can increase copper solubility and keep it in the dissolved phase, even under conditions that would otherwise promote precipitation or adsorption. Organic matter, particularly dissolved organic carbon (DOC), can form stable complexes with Cu^{2+}, enhancing its solubility and mobility in sediments. This means copper may remain in the dissolved phase and can be transported through

sediments, especially in organic-rich environments. Organic matter can increase copper solubility and mobility by forming copper-organic complexes, preventing copper from precipitating or adsorbing onto sediments. Organic matter can also adsorb copper, particularly in its particulate form. Copper binds strongly to organic matter, particularly under neutral to alkaline conditions, where the functional groups on organic matter readily attract Cu^{2+}. This process can sequester copper in sediments, reducing its mobility and bioavailability. In sediments rich in organic matter, copper is often immobilized by binding to organic particles, such as humic substances. This reduces the concentration of dissolved copper in sediment pore water, particularly in neutral to alkaline conditions. Organic matter can immobilize copper by adsorbing it, particularly in neutral to alkaline conditions, reducing copper's mobility and bioavailability in sediments.

Both pH and organic matter play a crucial role in determining the concentration, mobility, and bioavailability of copper in river sediments. Low pH enhances copper solubility, while high pH promotes copper precipitation and adsorption to sediments, reducing its mobility. Organic matter can increase copper mobility by forming complexes with Cu^{2+}, particularly under acidic conditions, or immobilize copper through adsorption, especially in neutral to alkaline conditions.

Cadmium (Cd)

The variation in concentrations of Cd along the selected stretch are depicted with the help of Figure 4.8.

In 2019, Cd concentrations ranged from 0.95 to 3.45 µg/g, with an average value of 1.94 µg/g. The order of Cd concentration at the sites was as follows: L9 < L1 < L6 < L10 < L2 < L3 < L5 < L7 < L8 < L4, with the highest concentration recorded at site L4 and the lowest at site L9.

In 2021, Cd concentrations ranged from 0.78 to 1.58 µg/g, with a mean value of 1.10 µg/g. The order of Cd concentration at the sites was as follows: L10 < L5 < L9 < L1 < L6 < L7 < L4 < L3 < L8 < L2, with the highest concentration recorded at site L2 and the lowest at site L10.
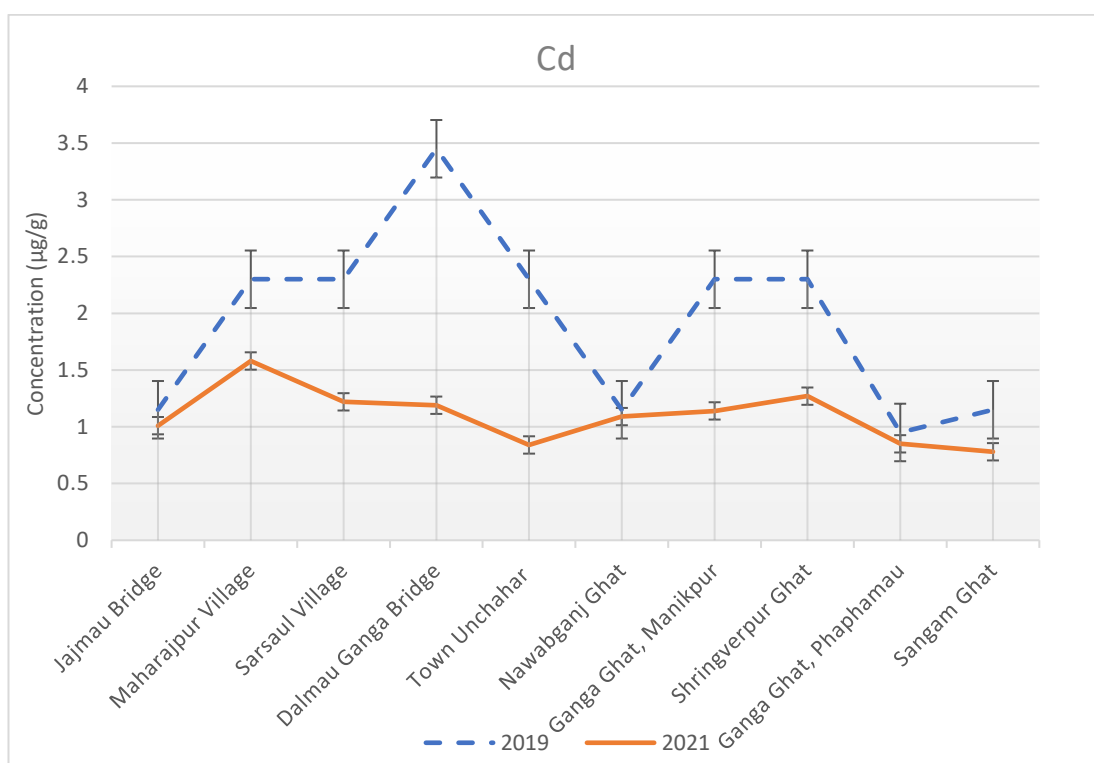
Figure 4.8 Variation in Cd concentrations in the riverbed sediment of Ganga River along the sampling points on the study area

Cd concentrations in all samples collected during both sampling surpassed both the World Surface Rock Average of 0.2 µg/g and the Bn value of 0.58 µg/g, suggesting an elevation in anthropogenic activities. This heightened Cd presence poses a potential toxicity risk to aquatic species in the surrounding area.

The average concentration of Cd in 2021 experienced a significant 43.43% decrease compared to 2019. Across the study area's sampling locations, cadmium concentrations in 2021 were more consistent, indicating reduced variability as compared to that in 2019. This implies a decrease in cadmium entering the river from upstream and local sources. The decline in metal concentrations is linked to reduced industrial activities during the COVID-19 lockdown, showcasing a natural renewal process of the Ganga River's riverbed sediment over time.

The adsorption and precipitation of cadmium (Cd) in river sediments are critical processes that influence its mobility, bioavailability, and environmental toxicity. Cadmium primarily exists in its divalent form (Cd^{2+}) in aquatic environments, and its

behavior is shaped by factors such as pH, redox conditions, sediment composition, and the presence of organic matter and competing ions.

Adsorption of Cd^{2+} occurs when it binds to sediment particles, including clays, metal oxides (such as iron and manganese oxides), and organic matter. This process is highly dependent on pH, with adsorption generally increasing under neutral to alkaline conditions, where Cd^{2+} can form hydroxyl complexes that more readily adhere to negatively charged surfaces. In acidic conditions, cadmium remains more soluble and mobile, making it less likely to adsorb effectively. Organic matter also plays a significant role in enhancing the adsorption of cadmium by forming stable complexes, which further reduces its mobility in the water column.

Precipitation of cadmium occurs when dissolved Cd^{2+} reacts with other ions to form solid cadmium compounds that settle into the sediment. This process is influenced by environmental factors such as pH and the presence of anions like carbonate (CO_3^{2-}), hydroxide (OH^-), and sulphide (S^{2-}). Under neutral to alkaline conditions, cadmium can precipitate as cadmium carbonate (smithsonite, $CdCO_3$) or cadmium hydroxide ($Cd(OH)_2$), both of which are relatively insoluble and help immobilize cadmium in the sediment. In reducing environments, particularly those rich in organic matter, cadmium can precipitate as cadmium sulphide (CdS), which is highly insoluble and stable, providing effective immobilization of cadmium under these conditions.

The interplay between adsorption and precipitation is essential for controlling the fate of cadmium in river sediments. Initially, cadmium may adsorb onto sediment particles, especially in environments where metal oxides and organic matter are abundant. As conditions shift—such as increases in cadmium concentration or changes in pH and redox potential—cadmium may transition from being adsorbed to precipitating as stable solid phases. Precipitation typically provides a more permanent form of immobilization compared to adsorption, but environmental changes, such as fluctuations in pH or redox conditions, can lead to the remobilization of previously immobilized cadmium, posing risks to aquatic ecosystems.

Cadmium is a toxic heavy metal, and its presence in river sediments can have significant implications for water quality and aquatic life. While adsorption and

precipitation help mitigate the mobility and bioavailability of cadmium, disturbances in the environment such as sediment resuspension or changes in chemical conditions can lead to the release of cadmium back into the water column, increasing the risk of contamination. Understanding the mechanisms of adsorption and precipitation is vital for managing cadmium pollution in aquatic systems, particularly in areas affected by industrial discharge or natural mineralization processes.

The concentration and behavior of cadmium (Cd) in river sediments are influenced significantly by pH and organic matter. Cadmium typically exists as Cd^{2+} in natural environments, and its solubility, mobility, and adsorption are sensitive to both these environmental factors.

As pH increases (pH > 7), cadmium tends to precipitate as cadmium hydroxide $[Cd(OH)_2]$ or cadmium carbonate $(CdCO_3)$. These cadmium compounds are relatively insoluble, resulting in lower concentrations of dissolved Cd^{2+} in sediment pore water. At higher pH, sediment surfaces become more negatively charged, favouring the adsorption of Cd^{2+} onto particles such as clays, iron oxides, and organic matter. Cadmium adsorption increases with pH, which decreases its mobility and bioavailability in river sediments. In neutral to alkaline conditions, cadmium becomes less soluble and is more likely to precipitate or adsorb onto sediments, reducing its mobility and bioavailability.

Organic matter, especially dissolved organic carbon (DOC) such as humic and fulvic acids, contains functional groups (e.g., carboxyl, hydroxyl, and phenolic groups) that can form stable complexes with Cd^{2+}. These complexes can increase cadmium solubility, keeping it in the dissolved phase even when pH conditions would otherwise favour precipitation or adsorption. Organic matter, particularly in dissolved form, can enhance cadmium mobility in sediments by forming cadmium-organic complexes. These complexes can prevent cadmium from precipitating or adsorbing onto sediment particles, allowing cadmium to remain mobile and increasing its potential to be transported through sediment layers. Organic matter increases cadmium solubility and mobility by forming stable cadmium-organic complexes, particularly in organic-rich environments. Organic matter can also adsorb cadmium, especially in its particulate

form. Cadmium binds to organic matter through functional groups, particularly under neutral to alkaline conditions. This adsorption can immobilize cadmium, reducing its mobility and bioavailability in the sediment. In sediments rich in organic matter, cadmium can be sequestered by binding to organic particles such as humic substances. This reduces the concentration of dissolved cadmium in sediment pore water, especially in neutral to alkaline environments where adsorption is stronger. Organic matter can immobilize cadmium by adsorbing it onto its surfaces, reducing cadmium's mobility and bioavailability, especially in organic-rich sediments.

Both pH and organic matter play a significant role in determining the concentration, mobility, and bioavailability of cadmium in river sediments. Low pH increases cadmium solubility and mobility, while high pH promotes cadmium precipitation and adsorption to sediment particles, reducing its mobility. Organic matter can either enhance cadmium mobility by forming cadmium-organic complexes, particularly in acidic conditions, or immobilize cadmium through adsorption, especially in neutral to alkaline environments.

4.2.2 Comparison with Sediment Quality Guidelines (SQGs)

SQGs are used to assess the level upto which heavy metal concentrations in suspended sediment may adversely influence aquatic plants & animals and are depicted to judge suspended sediment quality. The reference SQGs values of TEC and PEC for river sediment are mentioned in Table 4.1.

In 2019, though the average concentrations of all metals remained below their PEC values but the average concentrations of Fe, Mn, Cr, Pb, Ni, and Cd metal exceeded the TEC level by 48.6, 44.7, 128, 8.93, 63, and 200% indicating harmful effects of these metals may occur on the aquatic plants and animals.

In 2021, the average concentrations of all metals remained below their PEC values but the average concentrations of Fe, Mn, Cr, Ni, and Cd exceeded the TEC level by 21.43, 6.28, 20.65, 30.88 and 11.11% respectively indicating that they may have harmful effects on the aquatic plants and animals.

Based on the SQGs values, it can be stated that riverbed sediment of selected stretch of Ganga River had higher concentrations of Fe, Mn, Cr, Ni, and Cd which can adversely affect aquatic plants and animals.

4.2.3 Estimation of sediment quality indices for riverbed sediment

Geo-Accumulation Index (Igeo)

The Igeo class was determined with reference to the classification, as mentioned in Table 3.3 in chapter 3. This index is used to assess the anthropogenic impact of metals on the riverbed sediment of Ganga River. The Igeo values for the studied 8 heavy metals for each sampling location are shown in Table 4.2.

Table 4.2 Geoaccumulation index (Igeo) of metals for riverbed sediment of Ganga River

Code	Fe	Mn	Cr	Zn	Pb	Ni	Cu	Cd
April, 2019								
L1	-1.63	-2.46	-2.81	-2.18	0.12	-1.08	-3.86	0.40
L2	-1.64	-2.29	-1.14	-2.01	-0.07	-1.08	-3.27	1.40
L3	-2.00	-2.85	-2.38	-2.41	-0.16	-1.13	-4.12	1.40
L4	-1.39	-2.02	-1.74	-2.22	0.15	-1.13	-4.12	1.99
L5	-1.55	-2.22	-1.84	-2.09	0.06	-1.03	-3.12	1.40
L6	-1.01	-1.96	-1.38	-1.47	0.20	-0.79	-2.27	0.40
L7	-1.06	-2.52	-1.21	-1.44	0.26	-0.73	-2.44	1.40
L8	-1.62	-2.91	-2.52	-2.13	-0.11	-0.98	-3.63	1.40
L9	-1.81	-2.92	-2.68	-2.36	-0.16	-1.08	-3.86	0.13
L10	-1.83	-2.53	-1.96	-2.52	-0.07	-1.08	-4.44	0.40
Mean	-1.56	-2.47	-1.97	-2.08	0.02	-1.01	-3.51	1.03
April, 2021								
L1	-1.42	-2.40	-2.18	-2.58	-0.36	-1.49	-1.70	0.22
L2	-1.35	-2.42	-2.29	-2.63	-0.45	-1.24	-1.81	0.86
L3	-1.33	-2.37	-1.92	-2.70	-0.38	-1.15	-2.11	0.49
L4	-1.31	-2.34	-2.26	-2.43	-0.32	-1.07	-1.91	0.45
L5	-1.36	-2.34	-2.07	-2.63	-0.42	-1.20	-1.90	-0.05
L6	-1.33	-2.33	-2.02	-2.11	-0.49	-1.17	-1.97	0.33
L7	-1.38	-2.44	-2.17	-2.15	-0.58	-1.33	-1.67	0.39
L8	-1.23	-2.57	-2.06	-2.20	-0.57	-1.34	-1.76	0.55
L9	-1.29	-2.55	-1.90	-2.33	-0.70	-1.24	-1.80	-0.03
L10	-1.19	-2.65	-1.92	-2.43	-0.79	-1.29	-1.88	-0.16
Mean	-1.32	-2.44	-2.08	-2.42	-0.51	-1.25	-1.85	0.30

In 2019, the Igeo values for Cr, Cu, Fe, Mn, Ni, and Zn were less than zero for all sites which lie in class 0, indicating that the sediment of Ganga River at these sampling sites are unpolluted by these metals and the average value of Igeo for Pb is calculated to be as 0.02 µg/g which lies in class 1 (i.e Igeo value between 0 and 1) indicate unpolluted stage to moderately pollution stage. Igeo value of Cd at most sites falls in class 2 (i.e Igeo value lies between 1 and 2) with a mean value of 1.03 which indicates moderate pollution by this metal.

In 2021, except for Cd, Igeo values for all other metals for all sampling sites lies in class 0 (Igeo < 0) which revealed that sediment was uncontaminated by these metals. Igeo values of Cd for sites L1, L2, L3, L4, L6, L7 & L8 lies in Class 1 (0 < Igeo < 1) which indicate unpolluted to moderate level of Cd pollution at these sites and for site L5, L9, L10 Igeo lies in Class 0 (Igeo < 0).

The values of Igeo revealed that in 2019, riverbed sediment had moderate contamination by Pb and Cd metal whereas in 2021, showed moderate contamination by Cd metal only.

Enrichment Factor (EF)

EF depicts the contamination levels of heavy metals and their source of contamination in a specific environment (Feng et al. 2004; Chen et al. 2007). EF < 2 indicates the crustal source of the elements in the sediment, whereas EF > 2 reflects the high levels of anthropogenic pollution as classified in Table 3.4. The EF values of studied heavy metals in this study are presented in Table 4.3.

In 2019, the EF values range for Mn (0.36 - 0.64), Cr (0.44 - 1.42), Zn (0.56 – 0.78), Pb (2.50 -3.40), Ni (1.17 -1.83), Cu (0.15 - 0.42) & Cd (2.67 – 10.59). Enrichment levels are identified using Table 3.4 based on calculated values of EF. The EF values for all heavy metals at all sites except for Cd and Pb are less than 2 which indicates the enrichment is at mineral depletion level by the other metals. For most sites, the EF values of Cd show significant contamination (i.e 5 < EF < 20) of which, site L3 and L4 were the most significant sites with EF value of 10.59 and 10.42 respectively indicating high pollution due to anthropogenic activities. Cd has high geochemical activity in the environment and can be transported for a long distance as it is mobile

and soluble in water compared to other heavy metals. The values of EF for Pb are between 2 and 5 for all sites which indicates moderate contamination.

Table 4.3 Enrichment factor (EF) of metals in riverbed sediment of Ganga River

April, 2019							
Site	**Mn**	**Cr**	**Zn**	**Pb**	**Ni**	**Cu**	**Cd**
L1	0.57	0.44	0.69	3.37	1.47	0.21	4.10
L2	0.64	1.42	0.78	2.99	1.48	0.32	8.27
L3	0.56	0.77	0.75	3.58	1.83	0.23	10.59
L4	0.65	0.78	0.56	2.91	1.20	0.15	10.42
L5	0.63	0.82	0.69	3.05	1.43	0.34	7.72
L6	0.52	0.78	0.73	2.31	1.17	0.42	2.67
L7	0.36	0.90	0.77	2.50	1.26	0.38	5.51
L8	0.41	0.54	0.70	2.84	1.56	0.25	8.12
L9	0.46	0.55	0.68	3.13	1.66	0.24	3.82
L10	0.62	0.92	0.62	3.40	1.69	0.16	4.71
April, 2021							
Site	**Mn**	**Cr**	**Zn**	**Pb**	**Ni**	**Cu**	**Cd**
L1	0.51	0.59	0.45	2.09	0.95	0.82	3.11
L2	0.48	0.52	0.41	1.86	1.08	0.73	4.62
L3	0.49	0.66	0.39	1.93	1.13	0.58	3.52
L4	0.49	0.52	0.46	1.99	1.18	0.66	3.39
L5	0.51	0.61	0.41	1.92	1.12	0.69	2.48
L6	0.50	0.62	0.58	1.80	1.12	0.65	3.16
L7	0.48	0.58	0.59	1.74	1.04	0.82	3.42
L8	0.40	0.56	0.51	1.58	0.93	0.69	3.43
L9	0.42	0.65	0.48	1.50	1.03	0.70	2.38
L10	0.36	0.60	0.42	1.32	0.93	0.62	2.04

In 2021, the EF values range for Mn (0.36 - 0.51), Cr (0.52 – 0.66), Zn (0.39 – 0.59), Pb (1.32 -2.09), Ni (0.93 -1.18), Cu (0.58 - 0.82) & Cd (2.04 – 4.62). The values of EF reduced in 2021. EF values for Cd at all sites lies between 2 and 5 which indicate moderate enrichment level of Cd metal at sites. EF values for Pb at some sites is near to 2 which indicate present enrichment at mineral level which may become moderate in the coming years. For other metals, the values of EF are less than 2, which indicate enrichment at mineral level.

The variations in the values of EF for various heavy metals in riverbed sediment of selected locations was probably because of variation in input of each metal or the

variation in the removal rate of each heavy metal from the riverbed sediment (Ghrefat et al. 2011).

Contamination Factor (CF) and Pollution Load Index (PLI)

The calculated values of CF are reported in Table 4.4, In 2019, CF values for Fe, Mn, Cr, Zn, Ni & Cu in all riverbed sediment samples were found to be < 1 with an average of 0.52, 0.28, 0.42, 0.37, 0.75 & 0.15 respectively which shows that the Ganga River sediment is not polluted by these metals. CF values for Pb at all locations lie between 1 & 3 with an average of 1.53 which indicates moderate contamination by Pb at all sites. The maximum CF value of for Pb was measured as 1.80 for site L7 (Manikpur) while the minimum value measured was 1.34 for site L3 (Sarsaul) & L9 (Phaphamau). The average value of CF for Cd is calculated as 3.34 which shows river sediment are contaminated by Cd in considerable amount. CF values of Cd for sites L1, L6, L9 & S10 lie between 1 & 3 which indicate moderate contamination by Cd at these sites whereas CF value for Cd at sites L2, L3, L4, L5, L7 & L8 lies between 3 & 6 which indicate a considerable amount of contamination by Cd at these sites. The maximum CF value of 5.95 for Cd was computed for site L4 while the minimum value of 1.64 was recorded at site L9.

In 2021, CF values for Fe, Mn, Cr, Zn, Ni & Cu in all sediment samples were found to be < 1 with an average of 0.60, 0.28, 0.36, 0.28, 0.63 & 0.42 respectively which shows that the Ganga River sediment is not polluted by these metals. CF values for Cd at all locations lie between 1 & 3 with an average of 1.89 which indicates moderate contamination by Cd at all sites. The maximum value of CF for Cd metal was calculated as 2.72 at site L2 followed by site L8 (2.19), L3 (2.10), L4 (2.05), L7 (1.97), L6 (1.88), L1 (1.74), L9 (1.47), L5 (1.45) & L10 (1.34). CF values of Pb for sites L1, L2, L3, L4, L5, L6, L7, L8 lie between 1 & 3 with an average of 1.06 which indicate moderate contamination by Pb metal at these sites whereas CF value for Pb at sites L9 & L10 is less than 1 which indicate a low level of contamination by Pb at these sites.

The general outcome from calculated values of CF demonstrates that the concentrations of Fe, Mn, Cr, Zn, Ni & Cu metal in the riverbed sediment are not in disturbing condition at present. However, riverbed sediment have moderate

contamination of Pb and Cd metal which may increase in the future and may be alarming to the river ecosystem with the rapidly increasing population in the river basin.

Pollution load index (PLI) indicates the overall heavy metal pollution at any site. The calculated values of PLI for all selected sites are reported in Table 4.4.

Table 4.4 Contamination Factor (CF) and Pollution Load Index (PLI) of metals for riverbed sediment of Ganga River

Site	Fe	Mn	Cr	Zn	Pb	Ni	Cu	Cd	PLI
April, 2019									
L1	0.48	0.27	0.21	0.33	1.63	0.71	0.10	1.98	0.018
L2	0.48	0.31	0.68	0.37	1.43	0.71	0.16	3.97	0.187
L3	0.37	0.21	0.29	0.28	1.34	0.69	0.09	3.97	0.016
L4	0.57	0.37	0.45	0.32	1.66	0.69	0.09	5.95	0.143
L5	0.51	0.32	0.42	0.35	1.57	0.73	0.17	3.97	0.154
L6	0.74	0.38	0.58	0.54	1.72	0.87	0.31	1.98	0.660
L7	0.72	0.26	0.65	0.55	1.80	0.91	0.28	3.97	0.964
L8	0.49	0.20	0.26	0.34	1.39	0.76	0.12	3.97	0.035
L9	0.43	0.20	0.23	0.29	1.34	0.71	0.10	1.64	0.007
L10	0.42	0.26	0.39	0.26	1.43	0.71	0.07	1.98	0.012
AVG	0.52	0.28	0.42	0.37	1.53	0.75	0.15	3.34	0.100
April, 2021									
Site	Fe	Mn	Cr	Zn	Pb	Ni	Cu	Cd	PLI
L1	0.56	0.29	0.33	0.25	1.17	0.53	0.46	1.74	0.534
L2	0.59	0.28	0.31	0.24	1.10	0.63	0.43	2.72	0.562
L3	0.60	0.29	0.40	0.23	1.15	0.68	0.35	2.10	0.555
L4	0.61	0.30	0.31	0.28	1.20	0.72	0.40	2.05	0.569
L5	0.58	0.30	0.36	0.24	1.12	0.65	0.40	1.45	0.532
L6	0.60	0.30	0.37	0.35	1.07	0.67	0.38	1.88	0.574
L7	0.58	0.28	0.33	0.34	1.00	0.60	0.47	1.97	0.561
L8	0.64	0.25	0.36	0.33	1.01	0.59	0.44	2.19	0.569
L9	0.62	0.26	0.40	0.30	0.93	0.63	0.43	1.47	0.538
L10	0.66	0.24	0.40	0.28	0.87	0.61	0.41	1.34	0.517
AVG	0.60	0.28	0.36	0.28	1.06	0.63	0.42	1.89	0.551

In 2019, PLI value indicate the highest metal pollution at L7-Manikpur site (0.964) followed by L6-Nawabganj (0.66), L2-Maharajpur (0.187), L5-Unchahar (0.154), L4-Dalmau-Fatehpur Bridge (0.143), L8-Shringverpur (0.035), L1-Jajmau (0.018), L3-Sarsaul (0.016), L10- Sangam (0.012), whereas the lowest polluted was L9-

Phaphamau site (0.007). In 2019, PLI value for site L7-Manikpur (0.964) was approximately 1 which was close to baseline level of pollution.

In 2021, the values of PLI have reduced and were recorded less than 1 for all sites which indicate pollution at baseline levels only. Nawabganj site L6 recorded the highest PLI value of 0.574 followed by L4-Dalmau-Fatehpur Bridge (0.569), L8-Shringverpur (0.569), L2- Maharajpur (0.562), L7- Manikpur (0.561), L3- Sarsaul (0.555), L9- Phaphamau (0.538), L1- Jajmau (0.534), L5- Unchahar (0.532), whereas the lowest polluted site was L10-Sangam (0.517).

Based on the PLI, it can be concluded that the reduction in values of PLI in 2021 indicate the improvement of sediment quality in the entire selected stretch.

4.2.4 Classification of source of metal pollution

The values of anthropogenic content (Ac) and lithogenic content (Lc) in riverbed sediment samples collected in April 2019 and April 2021 were analyzed and represented using charts displayed in Figures 4.9 and 4.10. The analysis of Ac and Lc values revealed that the metals lead (Pb) and cadmium (Cd) were primarily influenced by anthropogenic sources, while other metals originated predominantly from lithogenic sources during both 2019 and 2021.

A comparison of data from the two years indicated a noticeable reduction in the Ac values for Pb and Cd in 2021, suggesting a decrease in anthropogenic inputs of these specific metals over time. This decline may be attributed to improved environmental management practices, regulatory measures, or changes in industrial or agricultural activities contributing to the river system.

In contrast, the consistent lithogenic content of other metals across both years highlights their natural origin, unaffected by human activities. The findings underscore the importance of monitoring both anthropogenic and lithogenic contributions to understand environmental changes and assess the effectiveness of pollution control measures. This data serves as a valuable indicator for sustainable riverine ecosystem management and planning future mitigation strategies for anthropogenic pollution.
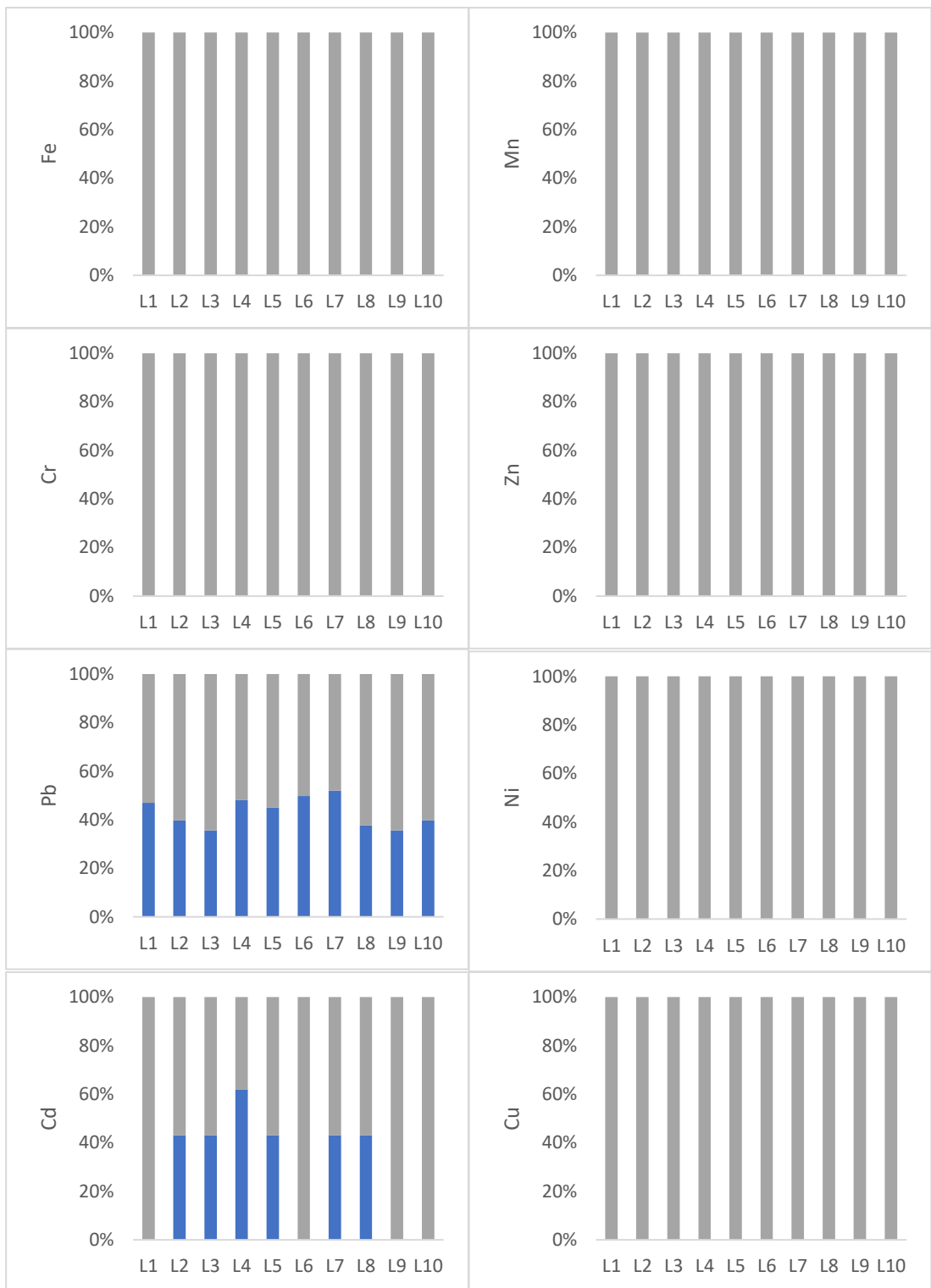
Figure 4.9 Anthropogenic & Lithogenic content in riverbed sediment of Ganga River collected in April, 2019
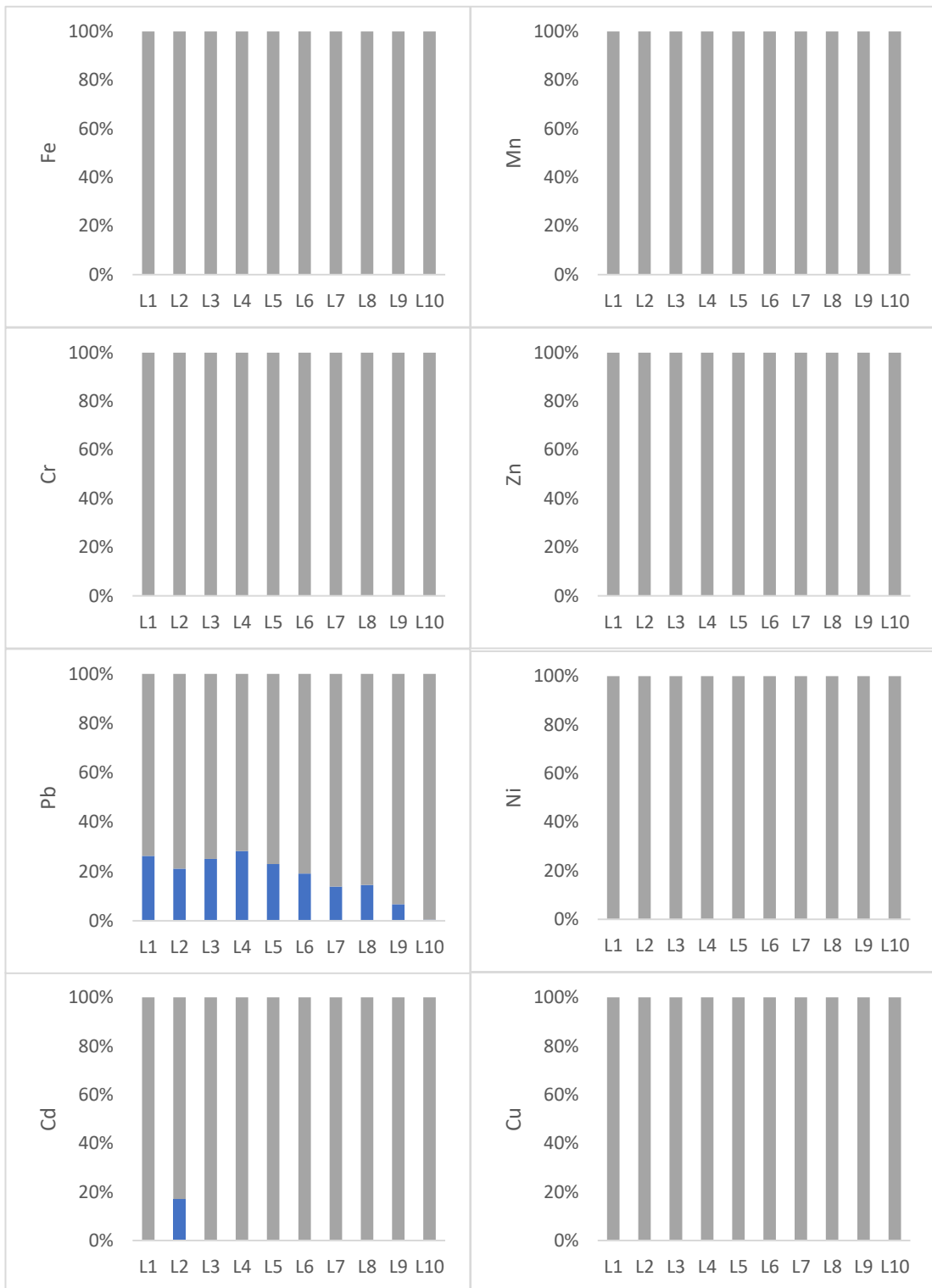
Figure 4.10 Anthropogenic & Lithogenic content in riverbed sediment of Ganga River collected in April, 2021

4.2.5 Correlation analysis of metals with pH & OM in riverbed sediment

The observed metal concentrations which are mentioned in Table 4.1 are used to identify correlation between various metals, pH & OM in riverbed sediment of Ganga River using correlation matrix as shown in Table 4.5. For samples collected in 2019, the correlation matrix showed a perfect correlation of Fe-Zn, Fe-Pb, Fe-Ni & Fe-Cu, Zn-Ni, Zn-Cu and Ni-Cu suggesting that they have similar geochemical nature or their input from same source. Cd showed weak or no correlation with all other metals. All other metals were less correlated with each other. All metals showed positive correlation with pH where Fe, Cr, Zn, Pb and Cu showed perfect, Mn showed moderate and Cd showed weak positive correlation. All metals showed positive correlation with OM where Fe, Mn, Cr, Zn, Pb, Ni & Cu showed perfect and Cd showed weak positive correlation.

In 2021, the correlation matrix showed a perfect positive correlation between Mn-Pb only and strong correlation of Fe-Cr suggesting that they have similar geochemical nature or their input from a same source. Mn-Ni, Pb-Cd and Zn-Cu had moderate correlation with each other. Other metals were either weakly correlated or had negative correlation. Mn, Zn, Pb, Ni, Cu & Cd showed positive correlation with pH whereas Fe & Cr showed negative correlation with pH. Zn showed perfect, Mn showed moderate and Pb, Ni, Cu & Cd showed weak positive correlation. Mn, Pb, Ni & Cd showed positive correlation with OM whereas Fe, Cr, Zn & Cu showed negative correlation with OM. Mn & Pb showed perfect, Cd showed moderate and Ni showed weak positive correlation with OM.

Based on the current study, it was revealed that high organic content generally leads to the accumulation of heavy metals in sediments, potentially reducing their bioavailability and toxicity. However, changes in environmental conditions can alter these interactions, affecting the mobility and bioavailability of heavy metals. Understanding these dynamics is crucial for effective management and remediation of polluted river systems.

Table 4.5 Correlation Matrix for metals, pH and OM in riverbed sediment of Ganga River

April, 2019										
	Fe	**Mn**	**Cr**	**Zn**	**Pb**	**Ni**	**Cu**	**Cd**	**pH**	**OM**
Fe	1	0.62	0.65	0.94	0.88	0.87	0.89	0.1	0.87	0.88
Mn	0.62	1	0.59	0.44	0.68	0.22	0.45	0.25	0.45	0.68
Cr	0.65	0.59	1	0.7	0.52	0.55	0.68	0.29	0.66	0.52
Zn	0.94	0.44	0.7	1	0.77	0.94	0.97	0	0.93	0.77
Pb	0.88	0.68	0.52	0.77	1	0.67	0.68	0.16	0.8	0.99
Ni	0.87	0.22	0.55	0.94	0.67	1	0.92	-0.13	0.85	0.67
Cu	0.89	0.45	0.68	0.97	0.68	0.92	1	-0.09	0.91	0.68
Cd	0.1	0.25	0.29	0	0.16	-0.13	-0.09	1	0.07	0.17
pH	0.87	0.45	0.66	0.93	0.8	0.85	0.91	0.07	1	0.8
OM	0.88	0.68	0.52	0.77	0.99	0.67	0.68	0.17	0.8	1
April, 2021										
	Fe	**Mn**	**Cr**	**Zn**	**Pb**	**Ni**	**Cu**	**Cd**	**pH**	**OM**
Fe	1	-0.76	0.52	0.22	-0.67	0.15	-0.21	-0.22	-0.21	-0.67
Mn	-0.76	1	-0.44	-0.24	0.86	0.44	-0.37	0.26	0.33	0.86
Cr	0.52	-0.44	1	0.08	-0.57	0.06	-0.42	-0.6	-0.33	-0.57
Zn	0.22	-0.24	0.08	1	-0.45	-0.09	0.32	-0.06	0.76	-0.45
Pb	-0.67	0.86	-0.57	-0.45	1	0.28	-0.27	0.42	0.15	0.99
Ni	0.15	0.44	0.06	-0.09	0.28	1	-0.77	0.12	0.27	0.28
Cu	-0.21	-0.37	-0.42	0.32	-0.27	-0.77	1	0.01	0.17	-0.27
Cd	-0.22	0.26	-0.6	-0.06	0.42	0.12	0.01	1	0.26	0.42
pH	-0.21	0.33	-0.33	0.76	0.15	0.27	0.17	0.26	1	0.15
OM	-0.67	0.86	-0.57	-0.45	0.99	0.28	-0.27	0.42	0.15	1

4.3 Heavy Metals Risk Assessment for Suspended Sediment

Suspended sediment samples were collected twice during the monsoon season in July, 2021, and July, 2022. During the monsoon season, the suspended load is high and sufficient amount of sediment samples are obtained for heavy metal analysis. The concentrations of heavy metals in the suspended sediment are detailed and discussed in the subsequent sub-sections. These concentrations are then compared with sediment quality guidelines to assess their harmful effects of aquatic plants & animals. Additionally, sediment quality indices are computed to ascertain the quality of the suspended sediment based to level of contamination.

4.3.1 Concentrations and spatial distribution of heavy metals in the suspended sediment of the selected sites

The concentrations (in µg/g) of studied heavy metals in the collected suspended sediment samples, suspended sediment concentration (mg/l), SQGs values and concentrations of metals in sediment of Ganga River observed in past studies are reported in Table 4.6.

In 2021, the average concentrations of all 8 heavy metals in suspended sediment of Ganga River followed this order: Fe (51939µg/g) > Mn (1048µg/g) > Zn (215µg/g) > Cr (129µg/g) > Pb (71.8µg/g) > Ni (69.5µg/g) > Cu (68.9µg/g) > Cd (1.70µg/g). Fe, Mn, and Zn with the highest concentrations of 73987,1449 & 312 µg/g respectively are the most abundant metals present in the suspended sediment, and Cd with a maximum value of 2.14 µg/g at the Nawabganj Village (L6) is in lowest concentration among the identified heavy metals. The mean concentrations of Pb, Zn & Cd are observed to be elevated than the background values (world river average) adopted for the present study.

In 2022, the average concentrations of all 8 heavy metals in suspended sediment of Ganga River followed this order: Fe (50230µg/g) > Mn (1283µg/g) > Cr (201µg/g) > Zn (183µg/g) > Pb (55.1µg/g) > Ni (50.9µg/g) > Cu (42.8µg/g) > Cd (1.01µg/g). The average concentrations of Cr are observed to be elevated than the background values (world river average) adopted for the present study.

In 2022, average concentrations of Fe, Zn, Pb, Ni, Cu & Cd metal reduced by 3.29 %, 14.88 %, 23.26 %, 26.76 %, 37.88 % & 40.59 % respectively whereas the average concentrations of Mn and Cr increased by 22.42 % and 55.81 %. Except Mn & Cr, average concentrations of all other metals reduced in the suspended sediment collected in 2022 as compared to that in suspended sediment collected in 2021 indicating increase in the input of Mn & Cr from the upstream areas whereas reduction in the fresh inputs of other metals in the study area.

In 2022, metals concentrations were more uniform and showed less variations along the sampling sites whereas in 2021, metal concentrations showed huge variations

which indicate that the sources of metal contamination at local level have reduced in 2022 which were giving sudden spikes in concentrations in 2021 at various locations. The variations in concentrations of each heavy metal in suspended sediment have been discussed individually in subsequent sections below:

Table 4.6. Suspended sediment concentration (SSC) (mg/l), metals concentrations (in µg/g) in suspended sediment, their SQGs values, and past concentrations in the sediment of Ganga River.

Site Name	Code	SSC	Fe	Cr	Mn	Cu	Zn	Ni	Cd	Pb
July, 2021										
Jajmau Bridge	L1	137	48071	66	1028	48.1	187	66.0	1.26	76.3
Maharajpur	L2	184	47699	211	1154	72.1	210	65.9	2.06	67.1
Sarsaul Village	L3	131	37243	89	783	40.5	159	63.7	1.98	62.9
Dalmau Ganga	L4	124	56785	138	1395	40.0	181	63.6	2.08	78.0
Town Unchahar	L5	211	51083	130	1212	80.1	288	68.2	1.87	73.5
Nawabganj Ghaat	L6	256	73987	179	1449	144.2	305	80.6	2.14	80.6
Ganga Ghaat,	L7	234	71522	200	986	128.1	312	84.2	1.79	84.4
Shringverpur	L8	152	48557	81	751	56.1	193	70.6	1.63	65.0
Ganga Ghaat,	L9	131	42607	72	745	48.1	164	64.0	0.99	62.9
Sangam Ghaat	L10	116	41838	119	975	32.0	148	68.0	1.21	67.1
Average		167	51939	129	1048	68.9	215	69.5	1.70	71.8
Std. Deviation		50.33	12217	53	254	38.5	63	7.22	0.41	7.79
Min		116	37243	66	745	32.0	148	63.6	0.99	62.9
Max		256	73987	211	1449	144.2	312	84.2	2.14	84.4
July, 2022										
Jajmau Bridge	L1	145	49081	206	1190	43.8	192	52.4	1.19	56.6
Maharajpur	L2	139	48701	202	1335	41.7	172	50.3	1.06	58.6
Sarsaul Village	L3	156	50026	219	1415	36.9	163	48.6	1.09	54.9
Dalmau Ganga	L4	171	57977	228	1614	36.5	186	50.6	0.98	50.1
Town Unchahar	L5	159	52156	216	1402	45.3	201	52.0	1.01	49.2
Nawabganj Ghaat	L6	166	55540	219	1376	48.5	196	51.5	0.97	55.3
Ganga Ghaat,	L7	160	53024	198	1140	46.9	202	54.3	0.93	63.7
Shringverpur	L8	149	49577	181	1098	45.1	198	53.8	0.98	56.8
Ganga Ghaat,	L9	129	43502	172	1131	43.8	169	48.8	0.99	54.9
Sangam Ghaat	L10	127	42716	167	1128	39.2	151	46.9	0.94	50.6
Average		150	50230	201	1283	42.8	183	50.9	1.01	55.1
Std. Deviation		15.02	4779	21	171	4.09	18	2.36	0.08	4.37
Min		127	42716	167	1098	36.5	151	46.9	0.93	49.2
Max		171	57977	228	1614	48.5	202	54.3	1.19	63.7
Background Conc. (Bn)[a]			58100	130	1679	75.9	208	74.5	1.55	61.1
(SQGs)[b]	**TEC**		20000	43.4	460	31.6	121	22.7	0.99	35.8
	PEC		40000	111	1100	149	456	48.6	4.98	128
GR Sediment, Hastinapur 2003[c]			39200	136	1250	53	104	50	1.31	19
GR Sediment, Kanpur 2017[d]			-	83	-	35.6	-	-	9.7	12.5
GR Sediment, Kanpur 2018[e]			5882.1	135.9	-	19.17	66.35	22.74	3.89	6.55

[a] World River Average values are drawn from Viers et al. (2009)
[b] Values are given by MacDonald et al. (2000)
[c] Values are taken from Singh et al. (2003)
[d] Values taken from Kumar, D et al. (2020)
[e] Values taken from Kumar, M et al., (2020)

Iron (Fe)

The variation in concentrations of Fe along the selected stretch are depicted with the help of Figure 4.11.
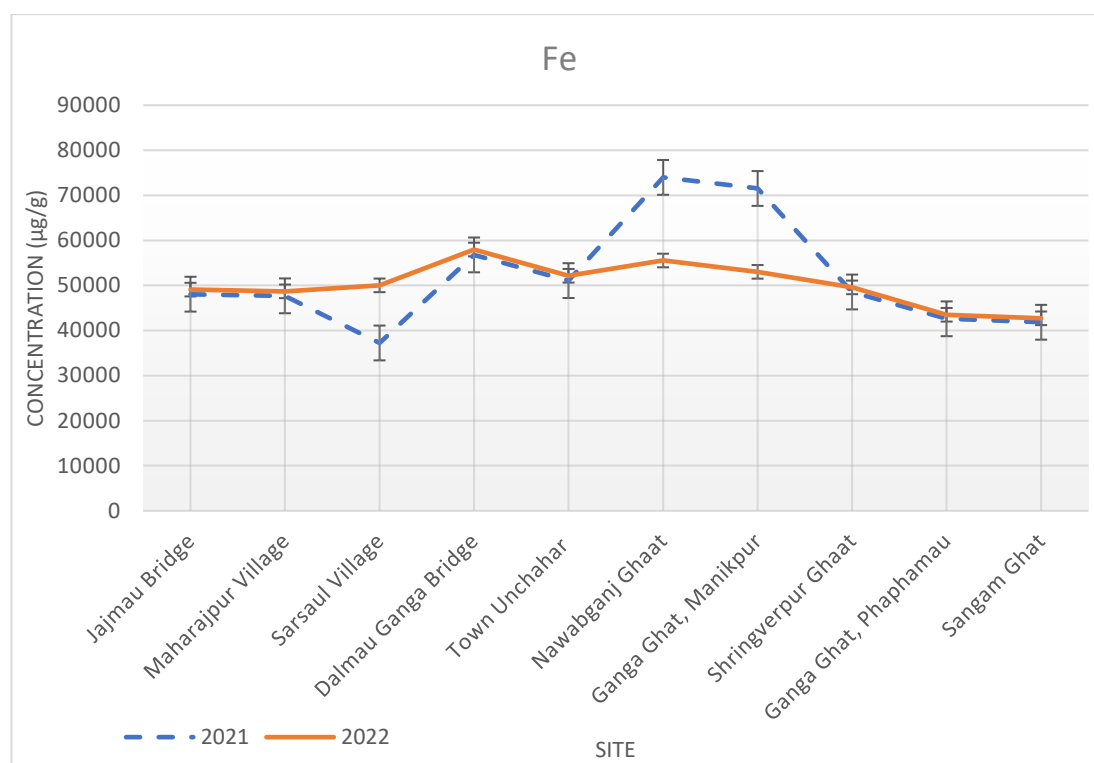
Figure 4.11 Variation in Fe concentrations in the suspended sediment of Ganga River along the sampling points on the study area

In 2021, Fe concentrations in the samples ranged between 37243 to 73987 µg/g with the highest at the Nawabganj Village L6 site followed by L7, L4, L5, L8, L2, L9, L10, and lowest at Sarsaul Village L3. Fe concentrations at all sites except L3 were found to be more than the PEC value of 40000 µg/g which indicates Fe metal in suspended sediment will have an adverse effect on aquatic plants & animals. Fe concentrations in the suspended sediment at all locations except at L3 are recorded higher than those reported in the riverbed sediment of Ganga River in the past studies as mentioned in Table 4.6.

In 2022, Fe concentrations in the samples ranged between 42716 to 57977 µg/g with the highest at site Dalmau Ganga Bridge-L4 followed by L6, L7, L5, L3, L8, L1, L2, L9 and lowest at Sangam Ghaat L10. Fe concentrations at all sites were found to be more than the PEC value of 40000 µg/g which indicates Fe metal in suspended sediment will have an adverse effect on aquatic plants & animals. Fe concentrations in the suspended sediment at all locations are recorded higher than those reported in the riverbed sediment of Ganga River in the past studies as mentioned in Table 4.6 which indicates more affinity of Fe metal in suspended sediment and an increase in Fe input from anthropogenic activities.

Average concentration of Fe was higher in 2022 in comparison to 2021. Except at Nawabganj and Manikpur site, Fe concentrations were recorded higher at most sites in 2022 as compared to that in 2021. Concentrations of Fe in 2022 were more uniform whereas large variations were seen in 2021.

Manganese (Mn)

The variation in concentrations of Mn along the selected stretch are depicted with the help of Figure 4.12.

In 2021, Mn concentrations in suspended sediment samples ranged between 745 to 1449 µg/g with the highest at Nawabganj village L6 site followed by L4, L5, L2, L1, L7, L10, L3, L8 and lowest at Phaphamau bridge site L9. As per SQG values for concentrations of Mn at all locations are higher compared to the TEC value of 460 µg/g while for sites L6, L4, L5 & L2 concentrations are beyond the PEC value of 1100 µg/g which indicates Mn metal in suspended sediment are likely to cause adverse effect to aquatic plants & animals at these sites. Mn concentrations in the suspended sediment at locations L4 & L6 are recorded higher than those reported in the riverbed sediment of Ganga River in the past studies which indicate increase of Mn concentrations from anthropogenic activities at site L4 & L6.

In 2022, Mn concentrations in suspended sediment samples ranged between 1098 to 1614 µg/g with the highest at Dalmau Ganga Bridge-L4 followed by L3, L5, L6, L2, L1, L7, L9, L10 and lowest at site Shringverpur Ghaat-L8. As per SQG values for concentrations of Mn at all locations are higher as compared to the TEC value of 460

μg/g. For all sites except site L8 Mn concentrations are also observed beyond the PEC value of 1100 μg/g which indicates Mn metal in suspended sediment are likely to cause adverse effect to aquatic plants & animals at these sites. Mn concentrations in the suspended sediment at locations L2, L3, L4, L5 & L6 are recorded higher than those reported in the riverbed sediment of Ganga River in the past studies which indicate increase of Mn concentrations from anthropogenic activities at these sites.

Figure 4.12 Variation in Mn concentrations in the suspended sediment of Ganga River along the sampling points on the study area

Average concentrations of Mn were observed to be more in 2022 than that in 2021. But at Nawabganj site, Mn conc. was recorded higher in 2021. Concentrations of Mn in 2022 were more uniform whereas large variations were recorded in 2021 along the selected stretch of Ganga River.

Chromium (Cr)

The variation in concentrations of Cr along the selected stretch are depicted with the help of Figure 4.13.

In 2021, Cr concentrations of various sampling sites ranged between 66 to 211 µg/g with the highest at Maharajpur Village site L2 site followed by L7, L6, L4, L5, L10, L3, L8, L9 and lowest at site L1- Jajmau Bridge. As per SQG values for concentrations of Cr at all locations are observed to be higher than the TEC value of 43.4 µg/g while at sites L2, L4, L5, L6, L7 & L10 are higher than the PEC values of 111 µg/g which indicate Cr metal in suspended sediment are likely to affect aquatic plants & animals at these sites.

Figure 4.13 Variation in Cr concentrations in the suspended sediment of Ganga River along the sampling points on the study area

In 2022, Cr concentrations of various sampling sites ranged between 167 to 228 µg/g with the highest at Dalmau Ganga Bridge site L4 site followed by L3, L6, L5, L1, L2, L7, L8, L9 and lowest at Sangam Ghaat site L10. As per SQG values, concentrations of Cr at all locations are observed above the TEC and PEC values of 43.4 µg/g and 111 µg/g respectively which indicate Cr metal in suspended sediment are likely to affect aquatic plants & animals at these sites. The Cr concentrations at all sites in suspended sediment are observed higher than that recorded in the past studies which indicate that the input of Cr metal has increased in the selected stretch of Ganga River.

At most sites Cr concentrations was recorded higher in 2022 as compared to that in 2021. Variations in concentrations of Cr within the stretch in 2022 were less whereas large variations were recorded in 2021. Average concentration of Cr increased in 2022 in comparison to that in 2021.

Zinc (Zn)

The variation in concentrations of Zn along the selected stretch are depicted with the help of Figure 4.14.
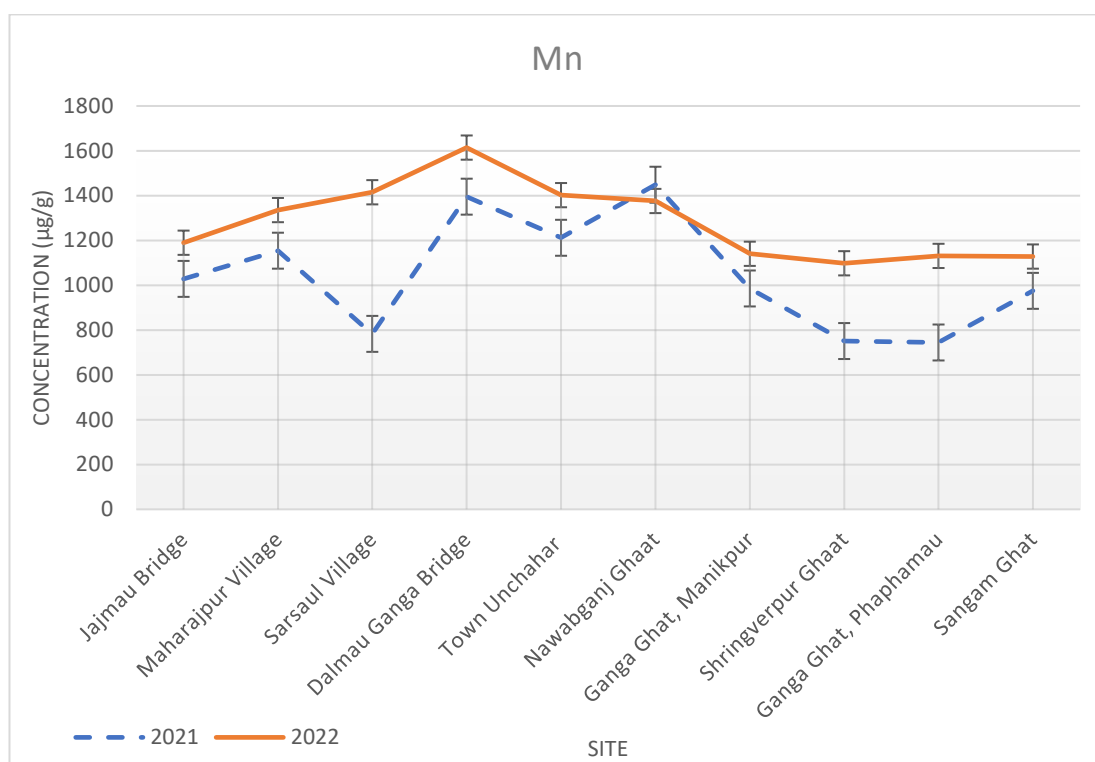

Figure 4.14 Variation in Zn concentrations in the suspended sediment of Ganga River along the sampling points on the study area

In 2021, Zn concentrations of various sampling sites ranged between 148 to 312 µg/g with the highest at the Manikpur site L7 site followed by L6, L2, L5, L8, L1, L4, L9, L3, and the lowest at Sangam site L10. As per SQG values, concentrations of Zn at all locations are above the TEC value of 121 µg/g while concentrations of Zn at all locations are below the PEC value of 456 µg/g which indicates Zn metal in suspended sediment are not likely to harm aquatic plants & animals. Average Zn concentration in the suspended sediment has almost doubled the concentration reported in the riverbed

sediment of Ganga River in the past studies which indicates more affinity of Zn metal in suspended sediment and an increase in Zn input from anthropogenic activities.

In 2022, Zn concentrations of various sampling sites ranged between 151 to 202 µg/g with the highest at the Manikpur site L7 site followed by L5, L8, L6, L1, L4, L2, L9, L3, and the lowest at Sangam site L10. As per SQG values, concentrations of Zn at all locations are above the TEC value of 121 µg/g while concentrations of Zn at all locations are below the PEC value of 456 µg/g which indicates Zn metal in suspended sediment are not likely to harm aquatic plants & animals. Average of Zn concentrations in the suspended sediment has almost doubled the concentration reported in the riverbed sediment of Ganga River in the past studies which indicate increase in Zn input from anthropogenic activities.

Average concentration of Zn was observed to be lower in 2022 in comparison to that in 2021. Zn concentrations at Jajmau, Unchahar, Nawabganj and Manikpur were recorded higher in 2021 than the concentrations recorded in 2022. Variations of Conc. of Zn in 2022 were less whereas large variations were recorded in 2021 along the selected stretch of Ganga River.

Lead (Pb)

The variation in concentrations of Pb along the selected stretch are depicted with the help of Figure 4.15.

In 2021, Pb concentrations of various sampling sites ranged between 62.9 to 84.4 µg/g with the highest at the L7 site (Manikpur) followed by L6, L4, L1, L5, L2, L10, L8, L3, and lowest at L9 site (Phaphamau). As per SQG values for Pb, concentrations at all locations are found above the TEC value of 35.8 µg/g and found below the PEC value of 128 µg/g which indicates Pb metal in suspended sediment are not likely to cause an adverse effect on aquatic plants & animals. The average Pb concentration in the suspended sediment exceeded more than 3 times the previous concentration reported in the riverbed sediment of Ganga River in the past studies which indicate high affinity of Pb metal in suspended sediment and strong input of Pb metal.
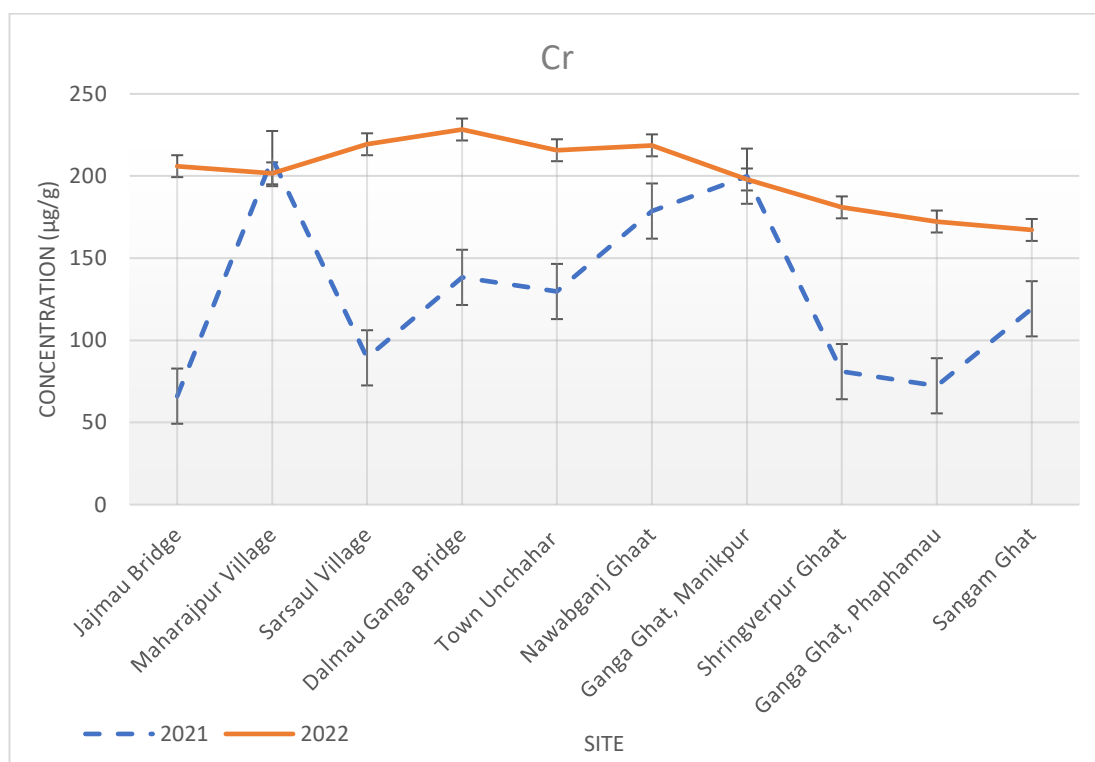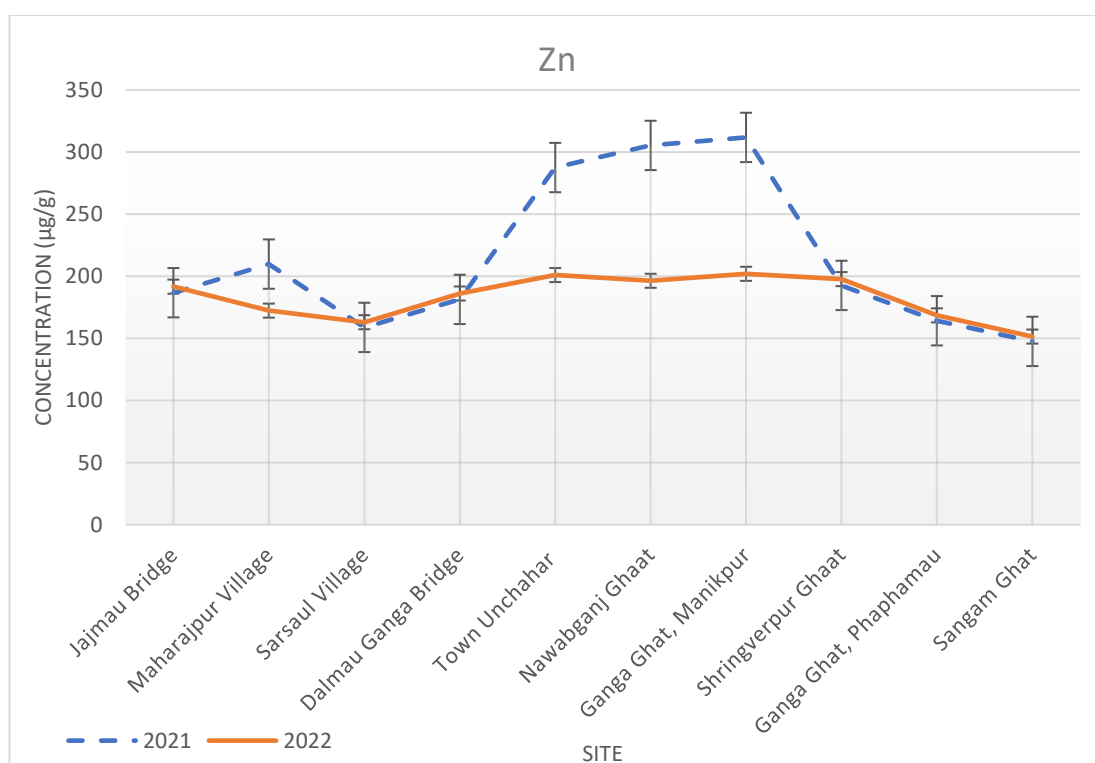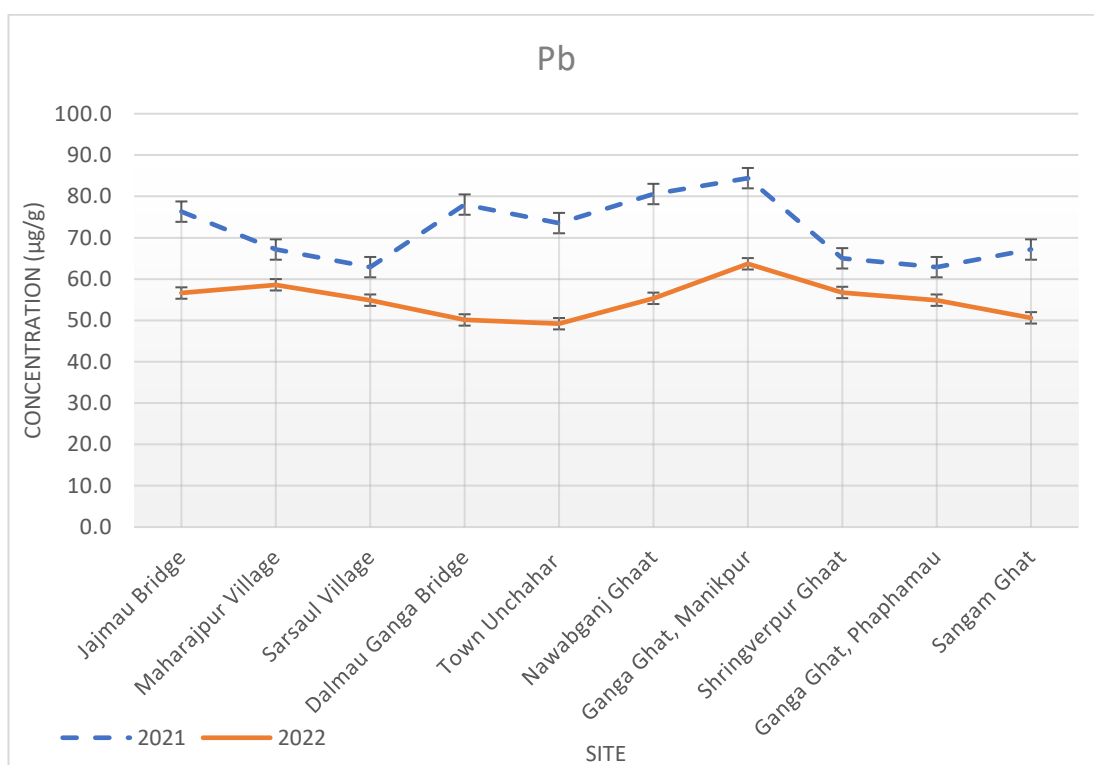
Figure 4.15 Variation in Pb concentrations in the suspended sediment of Ganga River along the sampling points on the study area

In 2022, Pb concentrations of various sampling sites ranged between 49.2 to 63.7 µg/g with the highest at the L7 site (Manikpur) followed by L2, L8, L1, L6, L3, L9, L10, L4 and lowest at L5 site (Unchahar). As per SQG values for Pb, concentrations at all locations are found above the TEC value of 35.8 µg/g and found below the PEC value of 128 µg/g which indicates Pb metal in suspended sediment are not likely to cause an adverse effect on aquatic plants & animals. The average of Pb concentrations in the suspended sediment exceeded more than 3 times the previous concentration reported in the riverbed sediment of Ganga River in the past studies which indicate high affinity of Pb metal in suspended sediment and strong input of Pb metal in the selected stretch.

Concentrations of Pb in 2022 at all sampling locations were recorded lesser than the concentrations in 2021. Conc. of Pb in 2022 showed more uniformity whereas large variations were recorded in 2021 along the selected stretch of Ganga River.

Nickel (Ni)

The variation in concentrations of Ni along the selected stretch are depicted with the help of Figure 4.16.

Figure 4.16 Variation in Ni concentrations in the suspended sediment of Ganga River along the sampling points on the study area

In 2021, Ni concentrations of various sampling sites ranged between 63.6 to 84.2 μg/g with the highest at the L7 site (Ganga Ghaat, Manikpur) followed by L6, L8, L5, L10, L1, L2, L9, L3 and lowest at site L4 (Dalmau Ganga Bridge). As per SQG values for Ni, concentrations at all locations are found above the PEC value of 48.6 μg/g which indicates Ni metal in suspended sediment is most likely to cause adverse effects on aquatic plants & animals. The average Ni concentration in the suspended sediment is observed 20% more than the previous concentration reported in the riverbed sediment of Ganga River in the past studies which indicates more affinity of Ni metal in suspended sediment and increase in anthropogenic source of Ni metal.

In 2022, Ni concentrations of various sampling sites ranged between 46.9 to 54.3 μg/g with the highest at the L7 site (Ganga Ghaat, Manikpur) followed by L8, L1, L5, L6,

L4, L2, L9, L3 and lowest at site L10 (Dalmau Ganga Bridge). As per SQGs values for Ni, concentrations at all locations expect L10 are found above the PEC value of 48.6 µg/g which indicates Ni metal in suspended sediment is most likely to cause adverse effects on aquatic plants & animals. The average Ni concentration in the suspended sediment is observed 20% more than the previous concentration reported in the riverbed sediment of Ganga River in the past studies which indicates more affinity of Ni metal in suspended sediment and increase in anthropogenic source of Ni metal.

Average concentration of Ni was observed to reduce in 2022 in comparison to that in 2021.

Concentration of Ni at sampling locations were recorded lesser in 2022 than the concentrations in 2021. Variations in concentrations of Ni in 2022 were more uniform whereas little more variation were recorded in 2021 along the selected stretch of Ganga River.

Copper (Cu)

The variation in concentrations of Cu along the selected stretch are depicted with the help of Figure 4.17.

In 2021, Cu concentrations of various sampling sites ranged between 32 to 144.2 µg/g with the highest at site L6 (Nawabganj) followed by L7, L5, L2, L8, L1, L9, L3, L4 and lowest at site L10 (Sangam). As per SQG values for Cu, concentrations of Cu at all locations are found above the TEC value of 31.6 µg/g and lower than the PEC value of 149 µg/g which indicates Cu metal in suspended sediment are not expected to cause harmful effects on aquatic plants & animals. The average Cu concentration in the suspended sediment is observed 17% more than the previous concentration reported in the riverbed sediment of Ganga River in the past studies which indicates more affinity of Cu metal in suspended sediment and increased in anthropogenic source of Cu metal.

In 2022, Cu concentrations of various sampling sites ranged between 36.5 to 48.5 µg/g with the highest at site L6 (Nawabganj Ghaat) followed by L7, L5, L8, L1, L9, L2, L10, L3 and lowest at site L4 (Dalmau Ganga Bridge). As per SQG values for Cu,

concentrations of Cu at all locations are found above the TEC value of 31.6 µg/g and lower than the PEC value of 149 µg/g which indicates Cu metal in suspended sediment are not likely to cause harmful effects on aquatic plants & animals. The average Cu concentration in the suspended sediment is observed more than the Cu concentration reported in the riverbed sediment of Ganga River in the past studies which indicates more affinity of Cu metal in suspended sediment and increased in anthropogenic source of Cu metal.

Figure 4.17 Variation in Cu concentrations in the suspended sediment of Ganga River along the sampling points on the study area

Average concentration of Cu was much lesser in 2022 in comparison to that in 2021. Concentrations of Cu at all sampling locations except at Sangam site were recorded less in 2022 than the concentrations in 2021. Variations of Conc. of Cu in 2022 were less whereas large variations were recorded in 2021 along the selected stretch of Ganga River.

Cadmium (Cd)

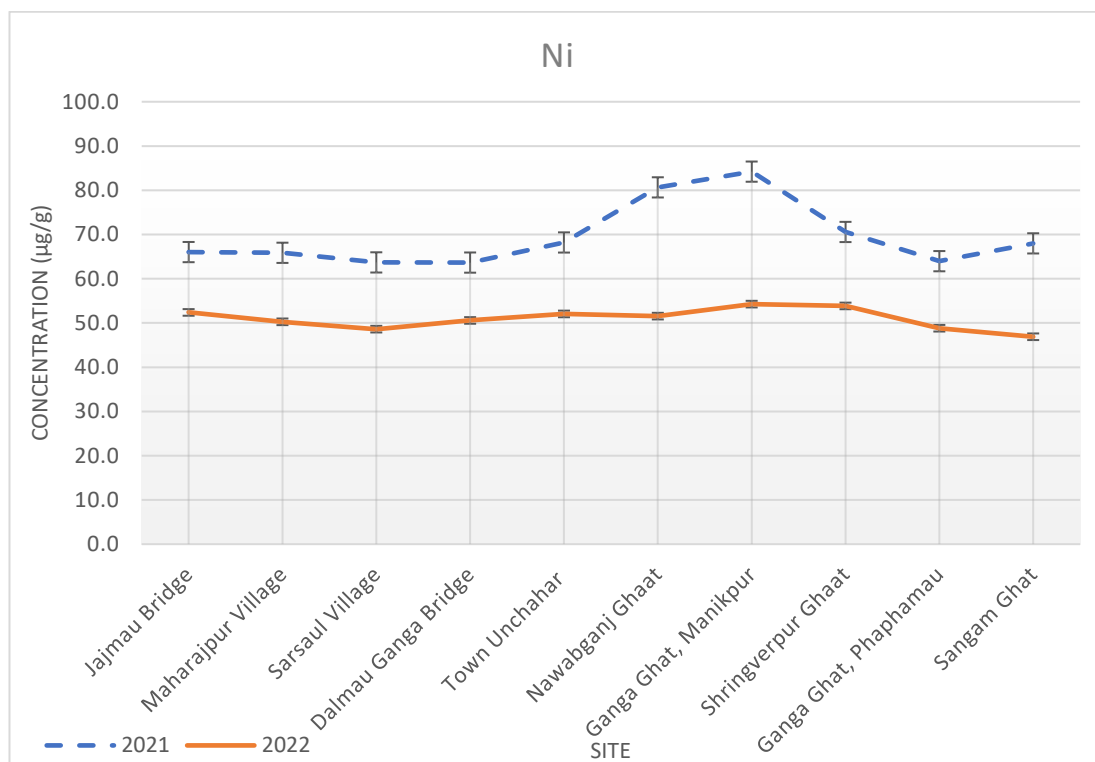The variation in concentrations of Cd along the selected stretch are depicted with the help of Figure 4.18.

In 2021, Cd concentrations of various sampling sites ranged between 0.99 to 2.14 µg/g with the highest at Nawabganj site L6 site followed by L4, L2, L3, L5, L7, L8, L1, L10 and lowest at site L9. As per SQG values, Cd concentrations at all locations are observed above the TEC value of 0.99 µg/g and lower than the PEC value of 4.98 µg/g which indicate Cd metal in suspended sediment are not much likely to cause adverse effects on aquatic plants & animals. The average Cd concentration in suspended sediment is observed to be much lower as compared to that in sediment from past studies which indicate less affinity of Cd metal towards suspended solid as that in riverbed sediment.
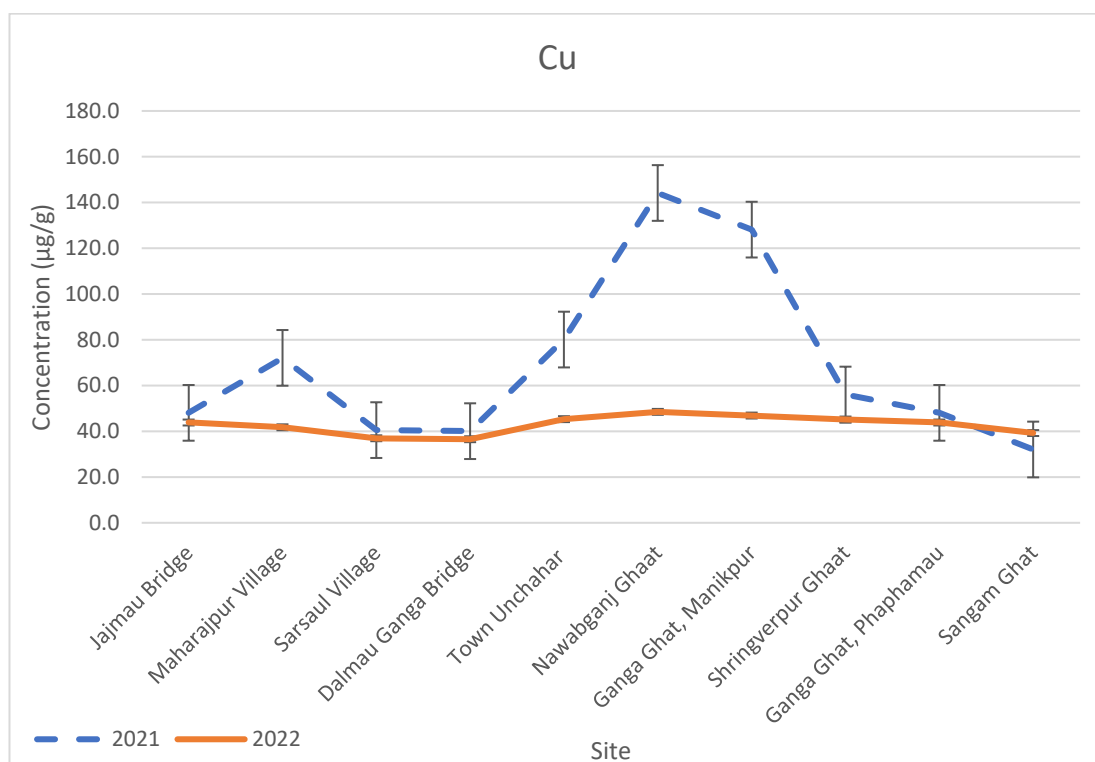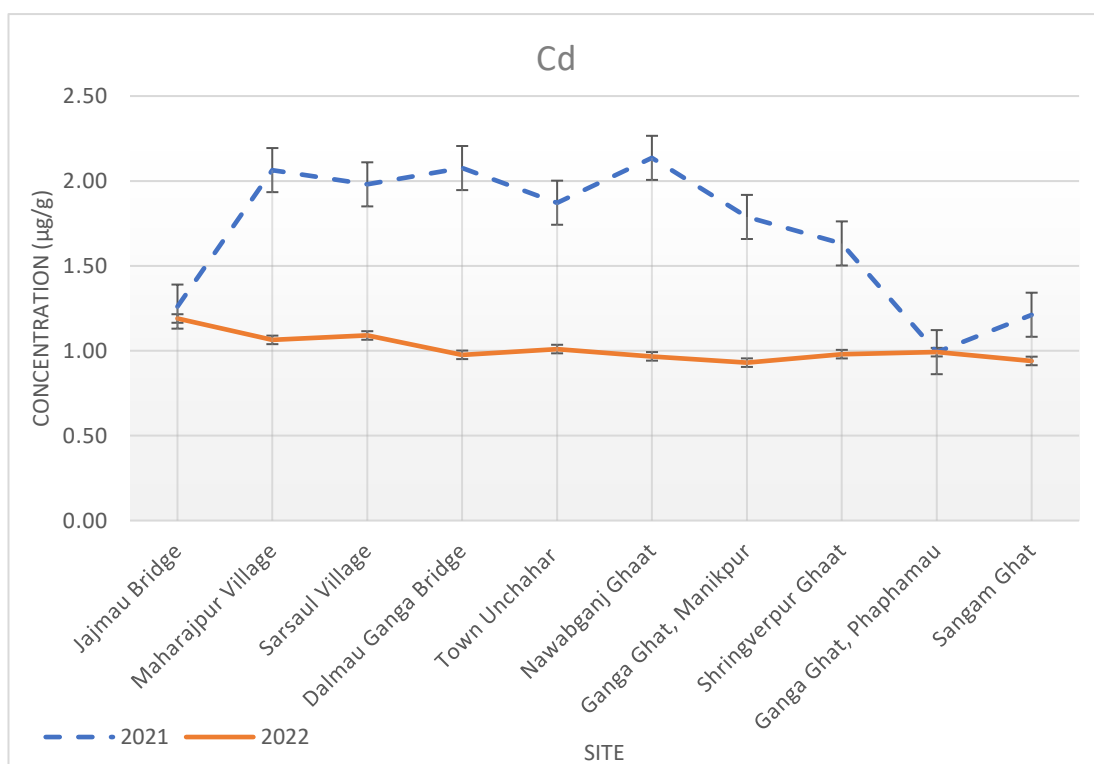

Figure 4.18 Variation in Cd concentrations in the suspended sediment of Ganga River along the sampling points on the study area

In 2022, Cd concentrations of various sampling sites ranged between 0.93 to 1.19 µg/g with the highest at Jajmau site L6 site followed by L3, L2, L5, L9, L4, L8, L6, L10

and lowest at site L7. As per SQG values, Cd concentrations at locations L1, L3, L2, L5, L9 are observed above the TEC value of 0.99 µg/g and observed lower than the PEC value of 4.98 µg/g at all locations which indicate Cd metal in suspended sediment are not likely to cause adverse effects on aquatic plants & animals. The average Cd concentration in suspended sediment is observed to be much lower as compared to that in sediment from past studies which indicate less affinity of Cd metal towards suspended solid as that in riverbed sediment.

Average concentration of Cd reduced in 2022 in comparison to that in 2021. Concentrations of Cd at all sampling locations recorded in 2022 were observed to be less at most locations or approximately similar at some location to the concentrations in 2021. Variations of Conc. of Cd in 2022 was uniform whereas large variations were recorded in 2021 along the selected stretch of Ganga River.

4.3.2 Comparison with river averages of various continents

Average concentrations of heavy metals recorded in consecutive two years in the present study are compared with the other continental river averages as mentioned in Table 4.7.

Table 4.7 Comparative study of metal concentrations in suspended sediment with Continental Rivers Averages

Metal	Ganga River (Present Study)	World River Average	South America River Average	North America River Average	Asia (Russia) River Average	Asia (China) River Average	Africa River Average	Europe River Average
Cd	1.35	1.55	-	-	-	-	-	-
Cr	165	130	79	115	260	117	130	164
Cu	55.8	75.9	59	34	145	53	53	172
Fe	51084	58100	52900	45000	78800	46000	75000	43000
Mn	1165	1679	700	1430	5767	970	1478	1884
Ni	60.1	74.5	46	50	123	68	78	66
Pb	63	61.1	76	22	35	64	46	71
Zn	199	208	184	137	300	145	130	346

Note: Values of continental rivers averages are taken from Viers et al. (2009); - Data not available

Cr concentrations are much higher as compared to the world river average, and Pb concentrations are close to the world river average, while Cu, Mn, Fe, Cd, Zn and Ni concentrations are lesser than the world river average. On comparing with neighbouring regions i.e., the river average of Asia (China), except Ni & Pb, the

average concentrations of all metals are higher indicating the suspended sediment of the Ganga River are affected by human activities whereas, except Pb, concentrations of all other metals are observed to be lesser than those in Asia (Russia) whereas metal concentrations are lesser or close to Europe Rivers which indicates the influence of economic growth on the river environment.

4.3.3 Estimation of sediment quality indices for suspended sediment

Geoaccumulation Index (Igeo)

Igeo values are mentioned in table 4.8 below.

Table 4.8 Geoaccumulation index (Igeo) of metals for suspended sediment of Ganga River

July 2021								
Code	**Fe**	**Mn**	**Cr**	**Zn**	**Pb**	**Ni**	**Cu**	**Cd**
L1	-0.86	-1.29	-1.56	-0.74	-0.26	-0.76	-1.24	-0.88
L2	-0.87	-1.13	0.11	-0.57	-0.45	-0.76	-0.66	-0.17
L3	-1.23	-1.69	-1.13	-0.97	-0.54	-0.81	-1.49	-0.23
L4	-0.62	-0.85	-0.5	-0.78	-0.23	-0.81	-1.51	-0.16
L5	-0.77	-1.06	-0.59	-0.12	-0.32	-0.71	-0.51	-0.31
L6	-0.24	-0.80	-0.13	-0.03	-0.19	-0.47	0.34	-0.12
L7	-0.29	-1.35	0.04	0.00	-0.12	-0.41	0.17	-0.38
L8	-0.84	-1.75	-1.27	-0.70	-0.50	-0.66	-1.02	-0.51
L9	-1.03	-1.76	-1.43	-0.93	-0.54	-0.80	-1.24	-1.23
L10	-1.06	-1.37	-0.71	-1.08	-0.45	-0.72	-1.83	-0.94
July 2022								
Code	**Fe**	**Mn**	**Cr**	**Zn**	**Pb**	**Ni**	**Cu**	**Cd**
L1	-0.83	-1.08	0.08	-0.70	-0.70	-1.09	-1.38	-0.97
L2	-0.84	-0.92	0.05	-0.86	-0.65	-1.15	-1.45	-1.13
L3	-0.80	-0.83	0.17	-0.94	-0.74	-1.20	-1.62	-1.09
L4	-0.59	-0.64	0.23	-0.74	-0.87	-1.14	-1.64	-1.25
L5	-0.74	-0.85	0.15	-0.63	-0.90	-1.10	-1.33	-1.20
L6	-0.65	-0.87	0.17	-0.67	-0.73	-1.12	-1.23	-1.27
L7	-0.72	-1.14	0.02	-0.63	-0.52	-1.04	-1.28	-1.32
L8	-0.81	-1.20	-0.11	-0.66	-0.69	-1.05	-1.33	-1.25
L9	-1.00	-1.15	-0.18	-0.89	-0.74	-1.20	-1.38	-1.23
L10	-1.03	-1.16	-0.22	-1.04	-0.86	-1.25	-1.54	-1.31

In 2021, for metal Fe, Zn, Mn, Pb, Cd & Ni, the Igeo values were less than zero which indicate that all locations are uncontaminated by the particular metals whereas Igeo values for Cr metal at site L2 & L7 lies just above zero indicating a stage of

"uncontaminated to moderate contamination" by Cr metal (Igeo between 0 & 1) and Igeo values for Cu metal at site L6 & L7 are also found above zero indicating that the suspended sediment at these locations are in "uncontaminated to moderately contaminated" stage by Cu metal.

In 2022, Igeo values for Cr for some sites lies in Class 1 (0< Igeo <1) which indicate unpolluted to moderate pollution level of Cr metal. Igeo values for all other metals for all sampling sites lies in Class 0 (Igeo < 0) which revealed that sediment were uncontaminated by other metals.

Enrichment Factor (EF)

The enrichment factor for suspended sediment is calculated and reported in Table 4.9.

Table 4.9 Enrichment Factor (EF) of metals for suspended sediment of Ganga River

July 2021							
Code	Mn	Cr	Zn	Pb	Ni	Cu	Cd
L1	0.74	0.61	1.09	1.51	1.07	0.77	0.98
L2	0.84	1.97	1.23	1.34	1.08	1.16	1.62
L3	0.73	1.07	1.19	1.61	1.33	0.83	1.99
L4	0.85	1.09	0.89	1.31	0.87	0.54	1.37
L5	0.82	1.13	1.57	1.37	1.04	1.20	1.37
L6	0.68	1.08	1.15	1.04	0.85	1.49	1.08
L7	0.48	1.25	1.22	1.12	0.92	1.37	0.94
L8	0.54	0.74	1.11	1.27	1.13	0.88	1.26
L9	0.60	0.76	1.08	1.40	1.17	0.86	0.87
L10	0.81	1.27	0.99	1.53	1.27	0.59	1.09
July 2022							
Code	Mn	Cr	Zn	Pb	Ni	Cu	Cd
L1	0.84	1.88	1.09	1.10	0.83	0.68	0.91
L2	0.95	1.85	0.99	1.14	0.80	0.66	0.82
L3	0.98	1.96	0.91	1.04	0.76	0.57	0.82
L4	0.96	1.76	0.90	0.82	0.68	0.48	0.63
L5	0.93	1.85	1.08	0.90	0.78	0.66	0.73
L6	0.86	1.76	0.99	0.95	0.72	0.67	0.65
L7	0.74	1.67	1.06	1.14	0.80	0.68	0.66
L8	0.77	1.63	1.11	1.09	0.85	0.70	0.74
L9	0.90	1.77	1.08	1.20	0.88	0.77	0.85
L10	0.91	1.75	0.99	1.13	0.86	0.70	0.82

In 2021, the mean of EF of studied metals observed in the decreasing order: Pb (1.35) > Cd (1.26) > Zn (1.15) > Cr (1.10) > Ni (1.07) > Cu (0.97) > Mn (0.71). The values of EF at all sites were calculated less than 2 indicating no enrichment in suspended sediment of Ganga River from human influence.

Whereas in 2022, The values of Enrichment Factor for all heavy metals at all sites are less than 2 which indicates the enrichment of these metals is at mineral depletion level. Average value of EF was calculated above 1 for Cr (1.30), Zn (1.02) and Pb (1.19) which may reach above 2 in the level of moderate enrichment in upcoming years.

Contamination factor (CF) & Pollution load index (PLI)

The calculated values of CF & PLI are reported in Table 4.10.

Table 4.10 Contamination Factor (CF) and Pollution Load Index (PLI) of metals for suspended sediment of Ganga River

Code	Fe	Mn	Cr	Zn	Pb	Ni	Cu	Cd	PLI
July 2021									
L1	0.83	0.61	0.51	0.90	1.25	0.89	0.63	0.81	0.78
L2	0.82	0.69	1.62	1.01	1.10	0.88	0.95	1.33	1.02
L3	0.64	0.47	0.69	0.76	1.03	0.85	0.53	1.28	0.74
L4	0.98	0.83	1.06	0.87	1.28	0.85	0.53	1.34	0.93
L5	0.88	0.72	1	1.38	1.20	0.92	1.06	1.21	1.03
L6	1.27	0.86	1.37	1.47	1.32	1.08	1.90	1.38	1.30
L7	1.23	0.59	1.54	1.50	1.38	1.13	1.69	1.15	1.22
L8	0.84	0.45	0.62	0.93	1.06	0.95	0.74	1.05	0.80
L9	0.73	0.44	0.56	0.79	1.03	0.86	0.63	0.64	0.69
L10	0.72	0.58	0.92	0.71	1.10	0.91	0.42	0.78	0.74
Avg	0.89	0.62	0.99	1.03	1.17	0.93	0.91	1.10	0.93
July 2022									
L1	0.84	0.71	1.58	0.92	0.93	0.70	0.58	0.77	0.84
L2	0.84	0.80	1.55	0.83	0.96	0.67	0.55	0.69	0.82
L3	0.86	0.84	1.68	0.78	0.90	0.65	0.49	0.70	0.81
L4	1.00	0.96	1.75	0.90	0.82	0.68	0.48	0.63	0.84
L5	0.90	0.84	1.66	0.97	0.81	0.70	0.60	0.65	0.85
L6	0.96	0.82	1.68	0.94	0.91	0.69	0.64	0.62	0.86
L7	0.91	0.68	1.52	0.97	1.04	0.73	0.62	0.60	0.84
L8	0.85	0.65	1.39	0.95	0.93	0.72	0.59	0.63	0.81
L9	0.75	0.67	1.32	0.81	0.90	0.66	0.58	0.64	0.77
L10	0.74	0.67	1.28	0.73	0.83	0.63	0.52	0.61	0.72
Avg	0.86	0.76	1.54	0.88	0.90	0.68	0.56	0.65	0.82

In 2021, PLI for all sites ranged between 0.69 & 1.30. Highest value was observed for Nawabganj site L6 followed by L7, L5, L2, L4, L8, L1, L3 & L9. Sites L6, L7, L5 & L2 are contaminated by heavy metals (PLI > 1) indicating the downstream urban influences whereas suspended sediment at sites S1, S3, S4, S8, S9 & S10 in the Ganga River are not metal-contaminated (PLI < 1). Average CF values for all 8 metals ranged

between 0.62 to 1.17 following the increasing order: Mn (0.62) < Fe (0.89) < Cu (0.91) < Ni (0.93) < Cr (0.99) < Zn (1.03) < Cd (1.10) < Pb (1.17). CF values for Mn showed low contamination (CF < 1) at all sites whereas CF values for Pb showed moderate contamination (1< CF < 3) at all locations. Based on the values of CF, it can be stated that sites L6 & L7 are moderately contaminated by all metals except Mn.

In 2022, PLI values at all sites stayed below 1 which indicate all sites are overall uncontaminated. Values of CF for Cr metal lies between 1 & 3 at all sites which indicates moderate contamination by Cr metal. At site L4, the value of CF for Fe metal is 1 and at site L7, CF value for Pb metal is 1.04 which indicate moderate contamination of these sites by these metals. CF value for other metals is below 1 at all sites which shows low contamination by all other metals.

4.3.4 Classification of source of metals

Figures 4.19 and 4.20 present the percentage contributions of anthropogenic and lithogenic sources to heavy metal concentrations in suspended sediments collected in July 2021 and July 2022. The data reveal notable trends in metal contamination caused by human activities across the studied sampling locations.

Findings from July 2021

In 2021, anthropogenic sources contributed to Zn, Pb, and Ni concentrations at all sampled locations. Cadmium (Cd) showed anthropogenic inputs only at upstream sites, with no such contributions recorded at the last three locations. Chromium (Cr) and copper (Cu) displayed significant anthropogenic inputs at midstream locations, while manganese (Mn) had minor contributions at the same sites. Anthropogenic iron (Fe) contributions were recorded at all locations except L3.

Nawabganj Ghaat (L6) stood out as the only site where anthropogenic contributions were observed for all metals, highlighting its susceptibility to human-induced contamination. Lead (Pb) displayed the highest anthropogenic contribution, ranging from 69% to 77%, making it the most affected metal. Zinc (Zn) also exhibited substantial anthropogenic inputs, varying between 29% and 66%. Nickel (Ni) saw contributions from anthropogenic sources accounting for 21% to 40% of its total concentration.

Anthropogenic influences were notably dominant over lithogenic sources at midstream locations such as L2, L4, L5, L6, and L7. These findings point to the significant impact of human activities, including industrial discharge, agricultural runoff, and urban effluents, particularly in the midstream sections of the studied stretch.

Findings from July 2022

In 2022, anthropogenic inputs remained prominent for metals such as Fe, Cr, Zn, and Pb, which showed strong contributions at all sampled locations. Mn exhibited anthropogenic input at midstream sites (L2–L6) but showed no contributions at other locations. There was no anthropogenic input recorded for Cu or Cd at any site in 2022.

Nickel (Ni) exhibited a minimal anthropogenic contribution of less than 8%, limited to a few locations (L1, L5, L6, L7, and L8). Lead (Pb) again recorded the highest anthropogenic contribution, ranging from 61.38% to 70.16%. Zinc (Zn) followed closely, with contributions between 31.33% and 48.51%, reaffirming its association with anthropogenic sources.

Comparative Analysis

The comparison of 2021 and 2022 data indicates a consistent pattern of anthropogenic influence, with Pb and Zn emerging as the most impacted metals in both years. While some metals like Cu and Cd showed declining contributions from anthropogenic sources in 2022, others such as Fe and Cr remained consistently influenced by human activities.

Midstream locations, particularly L2, L4, L5, L6, and L7, continued to exhibit higher anthropogenic contributions compared to upstream and downstream sites. This reflects the concentration of human activities, including industrial operations and agricultural practices, in these areas.

The analysis underscores the significant impact of anthropogenic sources on heavy metal contamination, particularly for Pb, Zn, and Ni. The midstream locations, with their higher human activity levels, are especially vulnerable. Efforts to mitigate pollution should prioritize reducing anthropogenic inputs through stricter industrial regulations, improved wastewater treatment, and sustainable agricultural practices.

Figure 4.19 ▣Anthropogenic and ▣ Lithogenic content in suspended sediment of Ganga River during July 2021

4.3.5 Correlation analysis among metals in suspended sediment

The observed metal concentrations in suspended sediment which are mentioned in Table 4.6 are used to identify correlation among metals in suspended sediment of Ganga River using the correlation matrix as mentioned in Table 4.11. In 2021, it showed a perfect correlation between Cu and Zn ($r = 0.93$; $p < 0.01$) and between Cu and Ni ($r = 0.9$; $p < 0.01$) suggesting that they have similar geochemical nature or their input from a similar source. Similarly, Fe, Zn, Pb, Cu, and Ni had a substantial correlation. Also, we noticed weak correlations between Ni and Mn ($r = 0.24$; $p < 0.01$) and between Ni and Cd ($r = 0.26$; $p < 0.01$) indicating their characteristics and source of contamination are different. Cd is weakly correlated with all the metals indicating its own geochemical behaviour.

In, 2022 The correlation matrix showed a perfect correlation between Zn-Ni, Cr-Mn & Cr-Fe suggesting that they have similar geochemical nature or their input from a similar source. Similarly, Fe-Mn, Fe-Zn, Fe-Ni, Cu-Zn, Cu-Ni, Pb-Ni showed strong correlation. Other metals were either weakly correlated or had negative correlation.

Table 4.11 Correlation (r) matrix of heavy metals in suspended sediment of Ganga River

July, 2021								
	Fe	**Mn**	**Cr**	**Zn**	**Pb**	**Ni**	**Cu**	**Cd**
Fe	1	0.62	0.65	0.85	0.88	0.86	0.89	0.45
Mn	0.62	1	0.59	0.5	0.67	0.24	0.45	0.61
Cr	0.65	0.59	1	0.64	0.52	0.57	0.68	0.64
Zn	0.85	0.5	0.64	1	0.74	0.82	0.93	0.49
Pb	0.88	0.67	0.52	0.74	1	0.68	0.68	0.37
Ni	0.86	0.24	0.57	0.82	0.68	1	0.9	0.26
Cu	0.89	0.45	0.68	0.93	0.68	0.9	1	0.46
Cd	0.45	0.61	0.64	0.49	0.37	0.26	0.46	1
July, 2022								
	Fe	**Mn**	**Cr**	**Zn**	**Pb**	**Ni**	**Cu**	**Cd**
Fe	1	0.71	0.85	0.67	0.01	0.54	0.1	-0.08
Mn	0.71	1	0.86	0.07	-0.47	-0.13	-0.44	0.11
Cr	0.85	0.86	1	0.41	-0.14	0.25	-0.12	0.31
Zn	0.67	0.07	0.41	1	0.28	0.94	0.68	-0.05
Pb	0.01	-0.47	-0.14	0.28	1	0.52	0.45	0.05
Ni	0.54	-0.13	0.25	0.94	0.52	1	0.65	0
Cu	0.1	-0.44	-0.12	0.68	0.45	0.65	1	-0.19
Cd	-0.08	0.11	0.31	-0.05	0.05	0	-0.19	1

Chapter 5
CONCLUSIONS AND RECOMMENDATIONS

5.1 Introduction

The current study assessed the sediment quality (both riverbed and suspended sediment) of the Ganga River by examining heavy metal contamination, conducting risk assessments, characterizing the sources of heavy metals, and exploring correlations among different heavy metals. A total of 10 sampling locations were chosen along a 225 km stretch of the Ganga River, spanning from Kanpur to Prayagraj in Uttar Pradesh, India. Riverbed sediment samples were gathered in the pre-monsoon season in April 2019 and April 2021, while suspended sediment samples were collected during the peak monsoon season in July 2021 and April 2022. In this investigation, conclusions have been drawn, and potential directions for future research that could enhance and supplement the findings presented in this thesis are explored.

5.2 Conclusions

The main aim to this study was to examine the heavy metals pollution in the sediment of Ganga River. Based on this study following conclusions are drawn:

1. Fe is the most abundant metal in both riverbed sediment and suspended sediment of Ganga River and Cd is in scarce.

2. The concentrations of Cu increased drastically in riverbed sediment collected in 2021 which can be attributed due to more adsorption of Cd metal in riverbed sediment during covid-19 when the concentrations of other metals were low.

3. In 2021, concentrations of all metals in riverbed sediment collected from the sampling sites showed less variations which shows uniform distribution of metals along the sampling sites in 2021 whereas in 2019, metal concentrations showed huge variations which indicate non uniform accumulation of metals in the riverbed sediment in 2019.

4. Based on the values of sediment quality indices, it can be concluded that riverbed sediment had moderate contamination of Pb and Cd metal.

5. The PLI for riverbed sediment indicated that Manikpur was the most polluted site (PLI = 0.964) in 2019 and was very close to degradation level (PLI > 1) but the values of PLI values in 2021 remained well below 1 for all sites and indicate only baseline levels of pollution in the riverbed sediment of the selected stretch of Ganga River.

6. The values of Ac and Lc for riverbed sediment indicate the input of Cd and Pb metal in the selected stretch from anthropogenic sources such as pesticides and fertilizers, tanneries, paint, welding and electroplating industries.

7. Correlation matrix of riverbed sediment indicate that Pb-Mn and Fe-Cr had good correlation both in 2019 & 2021 suggesting that they have similar geochemical behavior or input from the same source. Though other metals also showed positive correlation with each other in the riverbed sediment collected in April, 2019 but in 2021, except Pb-Mn, other metals showed less or negative correlation indicating that they have different geochemical behavior.

8. Except Mn & Cr, average concentrations of all other metals in the suspended sediment reduced in samples collected in 2022 as compared to that in suspended sediment collected in 2021 which indicate fresh deposition of Mn & Cr metal from the upstream areas.

9. In 2022, metals concentrations in suspended sediment had less variations along the sampling sites which shows uniform distribution of metals in 2022 whereas in 2021, metal concentrations had large variations which shows non uniformity in the concentrations of metals along the sampling locations.

10. Bases on the values of sediment quality indices it can be concluded that suspended sediment had moderate contamination by Cr metal.

11. PLI value for Nawabganj, Manikpur, Unchahar, Maharajpur was beyond 1 in 2021 indicating that these sites were contaminated but in 2022 the PLI values showed sharp reduction and all sites showed pollution at baseline levels only in 2022.

12. From the values of Anthropogenic content, it was noticed that more than 50 % of Pb concentrations in suspended sediment collected in 2022 were seen to be coming from anthropogenic sources whereas Fe, Cr & Zn also had significant anthropogenic inputs at all sites which shows the strong anthropogenic input

of these metals from upstream areas whereas little spikes in Anthropogenic content were seen for Mn & Ni metal at some mid locations which can be attributed due to local inputs.

13. The pollution indices used for determining the quality of sediment revealed that riverbed sediment are moderately contaminated by Cd and Pb metal in 2019 which significantly reduced in 2021 but showed moderate contamination by Cd in 2021. Whereas, suspended sediment were moderately contaminated by Cu and Cr metal in 2021 which significantly reduced in 2022 but still showed moderate contamination by Cr in 2022.

14. The reduction in concentrations of most metals in 2022 may have resulted due to reduction in disposal of untreated industrial effluent into Ganga River because of Covid-19 lockdown in the country.

5.3 Some Preventive Measures

Though various remediation technologies are available like electroosmosis, phytoremediation, soil washing etc but following measures should be adopted to prevent further degradation of Ganga River

1. Industrial units should ensure proper treatment of toxic effluent wastewater before disposing into the Ganga River.

2. Government agencies like CPCB and SPCB must ensure strict compliance with environmental standards of municipal and industrial effluents to save the Ganga River from further depletion by these metals.

5.4 Future Recommendations

The subsequent investigations are recommended for further exploration in order to advance this field of study:

1. The present study was conducted on a 225 km stretch of Ganga River; it can be extended further for critical locations on the entire stretch of Ganga River.

2. Study of the seasonal variations in the heavy metals' concentrations in sediment of Ganga River can be conducted which could not be conducted due to various restrictions during the covid-19.

3. The effect of various physiochemical characteristics (moisture content, electrical conductivity, sodium, potassium, calcium, total phosphate, available phosphate, total kjeldahl nitrogen, total organic carbon) of sediment on the concentrations of heavy metals can also be identified in the further studies.

4. The present study can be extended to the various tributaries of Ganga River and other rivers in India.

5. The study of adsorption level and precipitation levels of heavy metals.

List of Publications

International Journals

1. Mohit Aggarwal, S. Anbukumar, and T. Vijaya Kumar. **"Heavy metals concentrations and risk assessment in the sediment of Ganga River between Kanpur and Prayagraj, UP, India."** *Sādhanā* 47, no. 4 (2022): 195. https://doi.org/10.1007/s12046-022-01972-6

2. Mohit Aggarwal, S. Anbukumar, and T. Vijaya Kumar. **"Analysis and pollution assessment of heavy metals in suspended sediment of the middle stretch of river Ganga between Kanpur to Prayagraj, UP, India."** *Sādhanā* 48, no. 4 (2023): 1-13. https://doi.org/10.1007/s12046-023-02325-7

3. Mohit Aggarwal, S. Anbukumar, and T. Vijaya Kumar. **"Measurement of Heavy Metals Content in Suspended Sediment of Ganges River Using Atomic Absorption Spectrometry."** *MAPAN* (2024):1-18. https://doi.org/10.1007/s12647-024-00771-0

4. Mohit Aggarwal, S. Anbukumar, and T. Vijaya Kumar**. "Investigation of pollution by toxic Metals in the bed sediments of Ganga River along Kanpur to Prayagraj city of Uttar Pradesh, India"** *Under Review after Revision* in ***Iranian Journal of Science and Technology, Transactions of Civil Engineering,*** *Aug, 2024*

5. Mohit Aggarwal, S. Anbukumar, and T. Vijaya Kumar. **"Assessment of pollution risks posed by trace elements in the riverbed sediment of the Ganges River in Eastern Uttar Pradesh, India"** *Under Review* in ***Water Supply,*** *September, 2024*

6. Mohit Aggarwal, S. Anbukumar, and T. Vijaya Kumar. **"The relationship between pH, organic matter and heavy metal concentrations in surface sediment of Ganga River, India"** *Under Review* in ***Water Environment Research,*** *October, 2024*

7. Mohit Aggarwal, S. Anbukumar, and T. Vijaya Kumar. **"Assessment and Insights into Heavy Metal Contamination in Sediments of the Ganga River: Sources, Trends, and Ecological Implications"** *Under Submission Stage in **Water Resources Management**, December, 2024.*

International Conference

1. Mohit Aggarwal, S. Anbukumar, and T. Vijaya Kumar. (2023) **"Enrichment of heavy metals in suspended sediment particles of Ganga River",** presented in 4th International Conference on Computational & Experimental Methods in Mechanical Engineering (ICCEMME-2023), February 09-11, 2023, Greater Noida, India.

2. Mohit Aggarwal, S. Anbukumar, and T. Vijaya Kumar. (2023) **"Abundance of Heavy Metals Concentration in Sediment of Ganga River using Atomic Absorption Spectrometer"**, presented in 4th International Conference on Computational & Experimental Methods in Mechanical Engineering (ICCEMME-2023), February 09-11, 2023, Greater Noida, India.

References

[1]   Abadin, H., Ashizawa, A., Llados, F., & Stevens, Y. W. (2007). Toxicological profile for lead.

[2]   Abadin, H., Fay, M., Ingerman, L., Tencza, B., Yu, D., & Wilbur, S. B. (2012). Toxicological profile for chromium. Agency for toxic substances and disease registry. *Public Heal Serv US Dep. Heal Hum. Serv. US.*

[3]   Ahdy, H. H., & Khaled, A. (2009). Heavy metals contamination in sediments of the western part of Egyptian Mediterranean Sea. *Australian Journal of Basic and Applied Sciences*, *3*(4), 3330-3336.

[4]   Akan, J. C., Abdulrahman, F. I., Sodipo, O. A., Ochanya, A. E., & Askira, Y. K. (2010). Heavy metals in sediments from river Ngada, Maiduguri Metropolis, Borno state, Nigeria. *Journal of Environmental Chemistry and Ecotoxicology*, *2*(9), 131-140.

[5]   Ambedkar, G., & Muniyan, M. (2012). Analysis of heavy metals in water, sediments and selected freshwater fish collected from Gadilam River, Tamilnadu, India. *Int J Toxicol Appl Pharmacol*, *2*(2), 25-30.

[6]   Ansari, A. A., Singh, I. B., & Tobschall, H. J. (2000). Importance of geomorphology and sedimentation processes for metal dispersion in sediments and soils of the Ganga Plain: identification of geochemical domains. *Chemical Geology*, *162*(3-4), 245-266.

[7]   Ansari, A. A., Singh, I. B., & Tobschall, H. J. (1999). Status of anthropogenically induced metal pollution in the Kanpur-Unnao industrial region of the Ganga Plain, India. *Environmental Geology*, *38*, 25-33.

[8]   Avantika, P., Ramteke, P. W., & Verma, O. P. (2013). Evaluation of heavy metals loading of rivers Ganga and Yamuna IN. *International Journal of Pharma and Bio Sciences*, *4*(3).

[9]   Bayuo, J., Rwiza, M., & Mtei, K. (2022). A comprehensive review on the decontamination of lead (II) from water and wastewater by low-cost biosorbents. *RSC advances*, *12*(18), 11233-11254.

[10]   Beg, K. R., & Ali, S. (2008). Chemical contaminants and toxicity of Ganga river sediment from up and down stream area at Kanpur. *American Journal of Environmental Sciences*, *4*(4), 362.

[11]   Bhatnagar, M. K., Singh, R., Gupta, S., & Bhatnagar, P. (2013). Study of tannery effluents and its effects on sediments of river Ganga in special reference to heavy metals at Jajmau, Kanpur, India. *Journal of Environmental Research and Development*, *8*(1), 56-59.

[12]   Bhattacharya, A. K., Mandal, S. N., & Das, S. K. (2008). Heavy metals accumulation in water, sediment and tissues of different edible fishes in upper stretch of Gangetic West Bengal. *Trends in Applied Science Research*, *3*(1), 61-68.

[13]   Brown, S. L., Chaney, R. L., Angle, J. S., & Baker, A. J. M. (1994). *Phytoremediation potential of Thlaspi caerulescens and bladder campion for zinc-and cadmium-contaminated soil* (Vol. 23, No. 6, pp. 1151-1157). American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America.

[14]   Buccolieri, A., Buccolieri, G., Cardellicchio, N., Dell'Atti, A., Di Leo, A., & Maci, A. (2006). Heavy metals in marine sediments of Taranto Gulf (Ionian Sea, southern Italy). *Marine chemistry*, *99*(1-4), 227-235.

[15]   Cavet, J. S., Borrelly, G. P., & Robinson, N. J. (2003). Zn, Cu and Co in cyanobacteria: selective control of metal availability. *FEMS Microbiology Reviews*, *27*(2-3), 165-181.

[16]   Chakravarty, M., & Patgiri, A. D. (2009). Metal pollution assessment in sediments of the Dikrong River, NE India. *Journal of Human Ecology*, *27*(1), 63-67.

[17]   Chen, C. W., Kao, C. M., Chen, C. F., & Dong, C. D. (2007). Distribution and accumulation of heavy metals in the sediments of Kaohsiung Harbor, Taiwan. *Chemosphere*, *66*(8), 1431-1440.

[18]   Chen, J. P., Wang, L. K., Wang, M. H. S., Hung, Y. T., & Shammas, N. K. (2016). *Remediation of heavy metals in the environment*. CRC press.

[19] Copaja, S. V., Molina, X., & Tessada, R. (2014). Determination of heavy metals in Choapa river sediments using BCR sequential extraction procedure. *Journal of the Chilean Chemical Society*, *59*(1), 2353-2358.

[20] Davutluoglu, O. I., Seckin, G., Ersu, C. B., Yilmaz, T., & Sari, B. (2011). Assessment of metal pollution in water and surface sediments of the Seyhan River, Turkey, using different indexes. *CLEAN–Soil, Air, Water*, *39*(2), 185-194.

[21] Delorme, T. A., Gagliardi, J. V., Angle, J. S., & Chaney, R. L. (2001). Influence of the zinc hyperaccumulator Thlaspi caerulescens J. & C. Presl. and the nonmetal accumulator Trifolium pratense L. on soil microbial populations. *Canadian journal of microbiology*, *47*(8), 773-776.

[22] Demirak, A., Yilmaz, F., Tuna, A. L., & Ozdemir, N. (2006). Heavy metals in water, sediment and tissues of Leuciscus cephalus from a stream in southwestern Turkey. *Chemosphere*, *63*(9), 1451-1458.

[23] Dhanakumar S, Mani S, Murthy RC, Veeramani M, Mohanraj R (2011) Heavy metals and their fractionation profile in surface sediments of upper reaches in the Cauvery. Int J Geol Earth Environ Sci 1:38–47

[24] Dorsey, A., & Ingerman, L. (2004). Toxicological profile for copper.

[25] Faroon, O., Ashizawa, A., Wright, S., Tucker, P., Jenkins, K., Ingerman, L., & Rudisill, C. (2013). Toxicological profile for cadmium.

[26] Feng, H., Han, X., Zhang, W., & Yu, L. (2004). A preliminary study of heavy metal contamination in Yangtze River intertidal zone due to urbanization. *Marine pollution bulletin*, *49*(11-12), 910-915.

[27] Franco-Uría, A., López-Mateo, C., Roca, E., & Fernández-Marcos, M. L. (2009). Source identification of heavy metals in pastureland by multivariate analysis in NW Spain. *Journal of hazardous materials*, *165*(1-3), 1008-1015.

[28] Fu, J., Hu, X., Tao, X., Yu, H., & Zhang, X. (2013). Risk and toxicity assessments of heavy metals in sediments and fishes from the Yangtze River and Taihu Lake, China. *Chemosphere*, *93*(9), 1887-1895.

[29] Fu, J., Zhao, C., Luo, Y., Liu, C., Kyzas, G. Z., Luo, Y., ... & Zhu, H. (2014). Heavy metals in surface sediments of the Jialu River, China: their relations to environmental factors. *Journal of hazardous materials*, *270*, 102-109.

[30] Fujita, M., Ide, Y., Sato, D., Kench, P. S., Kuwahara, Y., Yokoki, H., & Kayanne, H. (2014). Heavy metal contamination of coastal lagoon sediments: Fongafale Islet, Funafuti Atoll, Tuvalu. *Chemosphere*, *95*, 628-634.

[31] Ghrefat, H. A., Abu-Rukah, Y., & Rosen, M. A. (2011). Application of geoaccumulation index and enrichment factor for assessing metal contamination in the sediments of Kafrain Dam, Jordan. *Environmental monitoring and assessment*, *178*, 95-109.

[32] Gupta, A., Rai, D. K., Pandey, R. S., & Sharma, B. (2009). Analysis of some heavy metals in the riverine water, sediments and fish from river Ganges at Allahabad. *Environmental monitoring and assessment*, *157*, 449-458.

[33] Hammer, D., & Keller, C. (2003). Phytoextraction of Cd and Zn with Thlaspi caerulescens in field trials. *Soil Use and Management*, *19*(2), 144-149.

[34] Kar, D., Sur, P., Mandai, S. K., Saha, T., & Kole, R. K. (2008). Assessment of heavy metal pollution in surface water. *International Journal of Environmental Science & Technology*, *5*, 119-124.

[35] Knight, B., Zhao, F. J., McGrath, S. P., & Shen, Z. G. (1997). Zinc and cadmium uptake by the hyperaccumulator Thlaspi caerulescens in contaminated soils and its effects on the concentration and chemical speciation of metals in soil solution. *Plant and soil*, *197*, 71-78.

[36] Goswami, D. N., & Sanjay, S. S. (2014). Determination of heavy metals, viz. cadmium, copper, lead and zinc in the different matrices of the Ganges River from Rishikesh to Allahabad through differential pulse anodic striping voltametry. *International Journal of Advanced Research in Chemical Science*, *1*(5), 7-11.

[37] Gupta, A., Rai, D. K., Pandey, R. S., & Sharma, B. (2009). Analysis of some heavy metals in the riverine water, sediments and fish from river Ganges at Allahabad. *Environmental monitoring and assessment*, *157*, 449-458.

[38] Hakanson, L. (1980). An ecological risk index for aquatic pollution control. A sedimentological approach. *Water research*, *14*(8), 975-1001.

[39] Issa, B. R., Arimoro, F. O., Ibrahim, M., Birma, G. J., & Fadairo, E. A. (2011). Assessment of sediment contamination by heavy metals in River Orogodo (Agbor, Delta State, Nigeria). *Current World Environment*, *6*(1), 29.

[40] Iqbal, J., & Shah, M. H. (2014). Occurrence, risk assessment, and source apportionment of heavy metals in surface sediments from Khanpur Lake, Pakistan. *Journal of Analytical Science and Technology*, *5*, 1-12.

[41] Jain, C. K., (2002), A hydrochemical study of a mountainous watershed: The Ganga, India, Water Research, 36: 1262-1274.

[42] Jain, C. K. (2004). Metal fractionation study on bed sediments of River Yamuna, India. *Water research*, *38*(3), 569-578.

[43] Kansal, A., Siddiqui, N. A., & Gautam, A. (2011). Assessment of heavy metals and their interrelationships with some physicochemical parameters in eco-efficient rivers of Himalayan region. *International Journal of Environmental Sciences*, *2*(2), 440-450.

[44] Katiyar, S. (2011). Impact of tannery effluent with special reference to seasonal variation on physico-chemical characteristics of river water at Kanpur (UP), India. *J Environ Anal Toxicol*, *1*(117), 4.

[45] Kayser, A., Wenger, K., Keller, A., Attinger, W., Felix, H.R., Gupta, S.K. and Schulin, R. (2000). Enhancement of phytoextraction of Zn, Cd, and Cu from calcareous soil: The use of NTA and sulfur amendments. *Environmental Science & Technology*, 34: 1778-1783.94

[46] Khwaja A.R., Singh R. & Tandon S.N., (2001), Monitoring of Ganga water and sediments vis-à-vistannery pollution at Kanpur (India), A case study, Environ. Moni Assess, 68 (1): 19-35.

[47] Kumar, A., Mishra, A. K., & Shukla, D. N. (2014). Seasonal heavy metal concentration variation in the river Ganga at Allahabad. *Kalash Sci*, *2*.

[48] Kumar, A., Jaiswal, D., & Watal, G. (2009). Studies on chemical composition and energy transformation in river Ganga at Kanpur and Varanasi due to environmental degradation. *J. Environ. Biol*, *30*, 445-450.

[49] Kumar, D., Malik, D. S., Kumar, N., Gupta, N., & Gupta, V. (2020). Spatial changes in water and heavy metal contamination in water and sediment of river Ganga in the river belt Haridwar to Kanpur. *Environmental geochemistry and health*, *42*, 2059-2079.

[50] Kumar, M., Balwant, K., & Padhy, P. K. (2012). Characterisation of metals in water and sediments of Subarnarekha River along the projects' sites in lower

basin, India. *Universal Journal of Environmental Research and Technology*, *2*(5), 402-410.

[51]   Kumar, M., Kumar, P., Ramanathan, A. L., Bhattacharya, P., Thunvik, R., Singh, U. K., Tsujimura, M., & Sracek, O. (2010). Arsenic enrichment in groundwater in the middle Gangetic Plain of Ghazipur District in Uttar Pradesh, India. *Journal of Geochemical Exploration*, *105*(3), 83-94.

[52]   Kumar, M., Gupta, N., Ratn, A., Awasthi, Y., Prasad, R., Trivedi, A., & Trivedi, S. P. (2020). Biomonitoring of heavy metals in river ganga water, sediments, plant, and fishes of different trophic levels. *Biological trace element research*, *193*, 536-547.

[53]   Kumar, R. N., Solanki, R., & Kumar, J. N. (2013). Seasonal variation in heavy metal contamination in water and sediments of river Sabarmati and Kharicut canal at Ahmedabad, Gujarat. *Environmental monitoring and assessment*, *185*, 359-368.

[54]   Leena, S., Choudhary, S. K., & Singh, P. K. (2012). Status of heavy metal concentration in water and sediment of River Ganga at selected sites in the Middle Ganga Plain. *Int. J. Res. Chem. Environ*, *2*(4), 236-243.

[55]   Liaghati, T., Preda, M., & Cox, M. (2004). Heavy metal distribution and controlling factors within coastal plain sediments, Bells Creek catchment, southeast Queensland, Australia. *Environment International*, *29*(7), 935-948.

[56]   Ma, X., Zuo, H., Tian, M., Zhang, L., Meng, J., Zhou, X., ... & Liu, Y. (2016). Assessment of heavy metals contamination in sediments from three adjacent regions of the Yellow River using metal chemical fractions and multivariate analysis techniques. *Chemosphere*, *144*, 264-272.

[57]   MacDonald, D. D., Ingersoll, C. G., & Berger, T. A. (2000). Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *Archives of environmental contamination and toxicology*, *39*, 20-31.

[58]   Martin, J. M., & Meybeck, M. (1979). Elemental mass-balance of material carried by major world rivers. *Marine chemistry*, *7*(3), 173-206.

[59] Mishra, A. (2010). Assessment of water quality using principal component analysis: a case study of the river Ganges. *Journal of Water Chemistry and Technology*, *32*, 227-234.

[60] Muller, G. (1969). Index of geoaccumulation in sediments of the Rhine River. *Geojournal*, *2*, 108-118.

[61] Naushad, S. S., Lall, A. M., & Charan, A. A. (2014). Determination of heavy metals in water of Ganga and Yamuna river basin in Allahabad. *Asian Journal of Environmental Science*, *9*(2), 106-108.

[62] Okonkwo, F O; ejike (2011) Simulation of heavy metal contamination of fresh water bodies: toxic effects in the catfish and its amelioration with co-contamination with glyphosate J. Appl. Sci. Environ. Manage. *June*, 2011 Vol. 15 (2) 341 – 345

[63] Osakwe J O, Adowei P, Jnr MH (2014) Evaluation of heavy metal species in bottom sediments from Imo River system, Southeastern Nigeria. Res J Chem Sci 4(6):23–30.

[64] Padmapriya G. and Murugesan A.G. (2012)Phytoremediation of various heavy metals (Cu, Pb and Hg) from aqueous solution using water hyacinth and its toxicity on plants.

[65] Pandey J, Singh AV, Singh A, Singh R (2013) Impact of changing atmospheric deposition chemistry on nitrogen and phosphorous loading to Ganga River. Bull Environ Contam Toxicol 91:184–190.

[66] Pandey, J., Shubhashish, K., Pandey, R., Kanethe, E., & Kironchi, G. (2010). Heavy metal contamination of Ganga river at Varanasi in relation to atmospheric deposition. *Tropical ecology*, *51*(2), 365-373.

[67] Pandey, J., Shubhashish, K., & Pandey, R. (2009). Metal contamination of Ganga River (India) as influenced by atmospheric deposition. *Bulletin of environmental contamination and toxicology*, *83*, 204-209.

[68] Pandey, M., Tripathi, S., Pandey, A. K., & Tripathi, B. D. (2014). Risk assessment of metal species in sediments of the river Ganga. *Catena*, *122*, 140-149.

[69]   Park, J., & Presley, B. J. (1997). Trace metal contamination of sediments and organisms from the Swan Lake area of Galveston Bay. *Environmental Pollution*, *98*(2), 209-221.

[70]   Paul, D., & Sinha, S. N. (2013). Assessment of various heavy metals in surface water of polluted sites in the lower stretch of river Ganga, West Bengal: a study for ecological impact. *Discovery Nature*, *6*(14), 8-13.

[71]   Pehlivan, E., Özkan, A. M., Dinç, S., & Parlayici, Ş. (2009). Adsorption of Cu2+ and Pb2+ ion on dolomite powder. *Journal of Hazardous Materials*, *167*(1-3), 1044-1049.

[72]   Purushothaman, P., & Chakrapani, G. J. (2007). Heavy metals fractionation in Ganga River sediments, India. *Environmental monitoring and assessment*, *132*, 475-489.

[73]   Qadir, A., & Malik, R. N. (2011). Heavy metals in eight edible fish species from two polluted tributaries (Aik and Palkhu) of the River Chenab, Pakistan. *Biological trace element research*, *143*, 1524-1540.

[74]   Rai, P. K., Mishra, A., & Tripathi, B. D. (2010). Heavy metal and microbial pollution of the River Ganga: A case study of water quality at Varanasi. *Aquatic Ecosystem Health & Management*, *13*(4), 352-361.

[75]   Ramesh R, Subramanian V, Grieken RV (1990) Heavy metal distribution in sediments of Krishna River basin. Environ Geol Water Sci 15:207–216.

[76]   Reza, R., & Singh, G. (2010). Heavy metal contamination and its indexing approach for river water. *International journal of environmental science & technology*, *7*, 785-792.

[77]   Rzetala MA (2015) Assessment of toxic metal contamination of bottom sediments in water bodies in urban areas. Soil Sediment Contam Int J 24(1):49–63.

[78]   Saha, P. K., & Hossain, M. D. (2011). Assessment of heavy metal contamination and sediment quality in the Buriganga River, Bangladesh. In *Proceeding: 2nd International Conference on Environmental Science and Technology. IPCBEE, Singapore* (Vol. 6, pp. 384-8).

[79]   Salati, S., & Moore, F. (2010). Assessment of heavy metal concentration in the Khoshk River water and sediment, Shiraz, Southwest Iran. *Environmental monitoring and assessment*, *164*, 677-689.

[80]   Sargaonkar, A. P., Gupta, A., & Devotta, S. (2008). Multivariate analysis of groundwater resources in Ganga-Yamuna basin (India). *J. Enviorn. Sci. Engg*, *50*(3), 215.

[81]   Sarkar, S. K., Saha, M., Takada, H., Bhattacharya, A., Mishra, P., & Bhattacharya, B. (2007). Water quality management in the lower stretch of the river Ganges, east coast of India: an approach through environmental education. *Journal of Cleaner Production*, *15*(16), 1559-1567.

[82]   Sauve, S., Dumestre, A., McBride, M., Gillett, J.W., Berthelin, J. and Hendershot, W. selective control of metal availability. *FEMS Microbiology Reviews*, 27: 165-181. *References* 87.

[83]   Sekabira, K., Origa, H. O., Basamba, T. A., Mutumba, G., & Kakudidi, E. (2010). Assessment of heavy metal pollution in the urban stream sediments and its tributaries. *International journal of environmental science & technology*, 7, 435-446.

[84]   Sharma, P., Meher, P. K., & Mishra, K. P. (2012). Distribution of non-radioactive heavy elements in water of river Ganges form Rishikesh to Allahabad: a study on possible health effects. *J Nehru Gram Bharati Univ*, *1*(1), 52-58.

[85]   Sharmin, S., Zakir, H. M., & Shikazono, N. (2010). Fractionation profile and mobility pattern of trace metals in sediments of Nomi River, Tokyo, Japan. *Journal of Soil Science and Environmental Management*, *1*(1), 001-014.

[86]   Shen, Z. G., Zhao, F. J., & McGrath, S. P. (1997). Uptake and transport of zinc in the hyperaccumulator Thlaspi caerulescens and the non-hyperaccumulator Thlaspi ochroleucum. *Plant, Cell & Environment*, *20*(7), 898-906.

[87]   Shukla, U. K. (2009). Sedimentation model of gravel-dominated alluvial piedmont fan, Ganga Plain, India. *International Journal of Earth Sciences*, *98*, 443-459.

[88]   Shukla, U. K., & Singh, I. B. (2004). Signatures of palaeofloods in sandbar-levee deposits, Ganga Plain, India. *Geological Society of India*, *64*(4), 455-460.

[89]   Shukla, U. K., Singh, I. B., Sharma, M., & Sharma, S. (2001). A model of alluvial megafan sedimentation: Ganga Megafan. *Sedimentary Geology*, *144*(3-4), 243-262.

[90]   Shukla, U. K., & Janardhana Raju, N. (2008). Migration of the Ganga river and its implication on hydro-geological potential of Varanasi area, UP, India. *Journal of earth system science*, *117*, 489-498.

[91]   Singh, H., Yadav, S., Singh, B. K., Dubey, B., Tripathi, K., Srivastava, V., & Shukla, D. N. (2013). Assessment of geochemical environment from study of river sediments in the middle stretch of River Ganga at Ghazipur, Buxar and Ballia area. *Proceedings of the National Academy of Sciences, India Section B: Biological Sciences*, *83*, 371-384.

[92]   Singh, I. B. (1996). Geological evolution of Ganga Plain—an overview. *Journal of the Palaeontological Society of India*, *41*, 99-137.

[93]   Singh, I. B., Srivastava, P., Sharma, S., Sharma, M., Singh, D. S., Rajagopalan, G., & Shukla, U. K. (1999). Upland interfluve (Doab) deposition: alternative model to muddy overbank deposits. *Facies*, *40*, 197-210.

[94]   Singh, K. P., Malik, A., Sinha, S., Singh, V. K., & Murthy, R. C. (2005). Estimation of source of heavy metal contamination in sediments of Gomti River (India) using principal component analysis. *Water, air, and soil pollution*, *166*, 321-341.

[95]   Singh, M., Müller, G., & Singh, I. B. (2002). Heavy metals in freshly deposited stream sediments of rivers associated with urbanisation of the Ganga Plain, India. *Water, Air, and Soil Pollution*, *141*, 35-54.

[96]   Singh, M., Müller, G., & Singh, I. B. (2003). Geogenic distribution and baseline concentration of heavy metals in sediments of the Ganges River, India. *Journal of Geochemical Exploration*, *80*(1), 1-17.

[97]   Smilde, K. W., Van Luit, B., & Van Driel, W. (1992). The extraction by soil and absorption by plants of applied zinc and cadmium. *Plant and soil*, *143*, 233-238.

[98] Subramanian, V., Van't Dack, L., & Van Grieken, R. (1985). Chemical composition of river sediments from the Indian sub-continent. *Chemical Geology*, *48*(1-4), 271-279.

[99] Sundaray, S. K., Nayak, B. B., Kanungo, T. K., & Bhatta, D. (2012). Dynamics and quantification of dissolved heavy metals in the Mahanadi river estuarine system, India. *Environmental monitoring and assessment*, *184*, 1157-1179.

[100] Suthar, S., Nema, A. K., Chabukdhara, M., & Gupta, S. K. (2009). Assessment of metals in water and sediments of Hindon River, India: impact of industrial and urban discharges. *Journal of Hazardous materials*, *171*(1-3), 1088-1095.

[101] Thareja, S., Choudhury, S., & Trivedi, P. (2011). Assessment of water quality of Ganga River in Kanpur by using principal components analysis. *Advances in Applied Science Research*, *2*(5), 84-91.

[102] Tomlinson, D. L., Wilson, J. G., Harris, C. R., & Jeffrey, D. W. (1980). Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. *Helgoländer meeresuntersuchungen*, *33*, 566-575.

[103] Turekian, K. K., & Wedepohl, K. H. (1961). Distribution of the elements in some major units of the earth's crust. *Geological society of America bulletin*, *72*(2), 175-192.

[104] USEPA, 2001. Methods for Collection, Storage, and Manipulation of Sediments for Chemical and Toxicological Analyses: Technical Manual, EPA/823/B-01/002. Office of Water.

[105] Venkatesha Raju, K., Somashekar, R. K., & Prakash, K. L. (2012). Heavy metal status of sediment in river Cauvery, Karnataka. *Environmental monitoring and assessment*, *184*, 361-373.

[106] Varol, M. (2011). Assessment of heavy metal contamination in sediments of the Tigris River (Turkey) using pollution indices and multivariate statistical techniques. *Journal of hazardous materials*, *195*, 355-364.

[107] Varol, M., & Şen, B. (2012). Assessment of nutrient and heavy metal contamination in surface water and sediments of the upper Tigris River, Turkey. *Catena*, *92*, 1-10.

[108] Viers, J., Dupré, B., & Gaillardet, J. (2009). Chemical composition of suspended sediments in World Rivers: New insights from a new database. *Science of the total Environment*, *407*(2), 853-868.

[109] Voijant Bieby Tangahu, Abdullah Siti Rozaimah Sheikh, Hassan Basri,Mushrifah Idris, Nurina Anuar, and Muhammad Mukhlisin (2011) A Review on HeavyMetals (As, Pb, and Hg) Uptake by Plants through Phytoremediation International Journal of chemical engineering.

[110] Vukovic D, Stankovic S, Vukovic Z, Jankovic K. 2014. Transport and storage of heavy metals in the Sava River Basin in Serbia. J Serb Chem Soc. 79(3):379–387. doi:10.2298/JSC130128085V

[111] Wang, X. C., Feng, H., & Ma, H. Q. (2007). Assessment of metal contamination in surface sediments of Jiaozhou Bay, Qingdao, China. *CLEAN–Soil, Air, Water*, *35*(1), 62-70.

[112] Wang, Y., Yang, Z., Shen, Z., Tang, Z., Niu, J. and Gao, F. (2011). Assessment of heavy metals in sediments from a typical catchment of the Yangtze River, China. Environ Monit Assess172(1-4):407-417.

[113] Wang, Z. M., Chen, L. D., Zhang, H. P., & Sun, R. H. (2014). Multivariate statistical analysis and risk assessment of heavy metals monitored in surface sediment of the Luan River and its tributaries, China. *Human and Ecological Risk Assessment: An International Journal*, *20*(6), 1521-1537.

[114] Wasim Aktar, M., Paramasivam, M., Ganguly, M., Purkait, S., & Sengupta, D. (2010). Assessment and occurrence of various heavy metals in surface water of Ganga river around Kolkata: a study for toxicity and ecological impact. *Environmental monitoring and assessment*, *160*, 207-213.

[115] Wazne, M., & Korfali, S. (2016). Spatial and temporal assessment of metal pollution in the sediments of the Qaraoun reservoir, Lebanon. *Environmental Science and Pollution Research*, *23*, 7603-7614.

[116] Wenning, R. J. (Ed.). (2005). *Use of sediment quality guidelines and related tools for the assessment of contaminated sediments*. SETAC.

[117] Whiting, S. N., de Souza, M. P., & Terry, N. (2001). Rhizosphere bacteria mobilize Zn for hyperaccumulation by Thlaspi caerulescens. *Environmental science & technology*, *35*(15), 3144-3150.

[118] Williams, M., Todd, G. D., Roney, N., Crawford, J., Coles, C., McClure, P. R., Garey, J. D., Zaccaria, K., & Citra, M. (2013). Toxicological profile for manganese.

[119] World Health Organization. (2000). Environment health criteria 221: zinc. *Environmental Health Criteria*, (221).

[120] World Health Organization. (2019). *Preventing disease through healthy environments: exposure to cadmium: a major public health concern* (No. WHO/CED/PHE/EPE/19.4. 3). World Health Organization.

[121] Xiao, R., Bai, J., Huang, L., Zhang, H., Cui, B., & Liu, X. (2013). Distribution and pollution, toxicity and risk assessment of heavy metals in sediments from urban and rural rivers of the Pearl River delta in southern China. *Ecotoxicology*, *22*, 1564-1575.

[122] Zakir, H. M., & Shikazono, N. (2011). Environmental mobility and geochemical partitioning of Fe, Mn, Co, Ni and Mo in sediments of an urban river. *Journal of Environmental chemistry and Ecotoxicology*, *3*(5), 116-126.

[123] Zahra, A., Hashmi, M. Z., Malik, R. N., & Ahmed, Z. (2014). Enrichment and geo-accumulation of heavy metals and risk assessment of sediments of the Kurang Nallah—feeding tributary of the Rawal Lake Reservoir, Pakistan. *Science of the Total Environment*, *470*, 925-933.

[124] Zhang, L., Ye, X., Feng, H., Jing, Y., Ouyang, T., Yu, X., ... & Chen, W. (2007). Heavy metal contamination in western Xiamen Bay sediments and its vicinity, China. *Marine pollution bulletin*, *54*(7), 974-982.

[125] Zhang, Z., Juying, L., Mamat, Z., & QingFu, Y. (2016). Sources identification and pollution evaluation of heavy metals in the surface sediments of Bortala River, Northwest China. *Ecotoxicology and environmental safety*, *126*, 94-101.