

Water Quality and Health Risk Assessment of Surface Water, Groundwater, and Sediments along Kali River

Monu Kumar^{1,2}, Anita¹, Mahiya Kulsoom¹, Aneet Kumar Yadav¹, Kamla Pat Raw¹, Sreekanth Bojjagani^{3,4}, Narendra Kumar^{1*}

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ABSTRACT

The current study assesses the physicochemical properties and heavy metal concentrations (Cd, Ni, As, Cr, Pb, Cu, Mn, Zn, Fe) in groundwater, surface water, and sediment across 15 sites along the Kali River in the Saharanpur, Muzaffarnagar, and Meerut districts of Uttar Pradesh. The results show average pH values of 7.7 in groundwater and 7.2 in surface water, with electrical conductivity measured at 670.87 μScm^{-1} and 1143 μScm^{-1} , and TDS values of 469.61 mgL^{-1} and 800.43 mgL^{-1} , respectively. Various cations and anions were present in the water, such as (Ca^{2+} , Mg^{2+} , Na^{+} , K^{+} , HCO_3^{-} , Cl^{-} , SO_4^{2-} , NO_3^{-} , etc. Indices such as Na%, SAR, MH, and PI indicate that the water is suitable for irrigation with some treatment. Sediment analysis reveals a pH of 7.2, conductivity of 16,701 μScm^{-1} , TOC of 2.37%, and TOM of 4.09%. Heavy metal concentrations in groundwater and sediment follow the order: $\text{Cd} < \text{Ni} < \text{As} < \text{Cr} < \text{Pb} < \text{Cu} < \text{Mn} < \text{Zn} < \text{Fe}$, while in surface water, the order is $\text{Cd} < \text{As} < \text{Ni} < \text{Cr} < \text{Pb} < \text{Zn} < \text{Cu} < \text{Mn} < \text{Fe}$. Some metal levels exceed drinking water standards at certain sites (G1, G2, G8, G12, and S5 to S10). PCA identifies three factors explaining 99.13% of the variance, indicating natural and human metal contamination sources. Risk and heavy metal pollution indices highlight elevated risks at specific sites, posing serious threats not only to crop safety and human health through irrigation but also to broader ecological systems. This underscores the urgent need for site-specific remediation to ensure the sustainability of agricultural practices and to prevent bioaccumulation in the food chain.

Keywords: Heavy metals; Risk assessment; Surface water; Sediment; Groundwater; Kali River.

Highlight

- A comprehensive analysis of physicochemical parameters and heavy metal concentrations was conducted for groundwater, surface water, and sediments of the Kali River at 15 sampling locations.
- Principal Component Analysis (PCA) and Pearson Correlation Analysis revealed strong correlations among heavy metals, suggesting anthropogenic sources such as industrial effluents and domestic discharge.
- Heavy Metal Pollution Index (HPI) and Pollution Load Index (PLI) values confirmed critical pollution levels in surface water and widespread metal contamination in sediments.
- Ecological Risk Index (ERI) results showed a very high potential risk from heavy metal exposure in most sediment samples, requiring urgent environmental management.

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INTRODUCTION

Water, a fundamental element found in aquifers and on the Earth's surface, is essential to human existence, socioeconomic development, and ecological balance (Balamurugan *et al.*, 2020). However, rapid environmental changes are leading to a global decline in groundwater quality and quantity, largely due to development activities (Burri *et al.*, 2019). Aquifers and surface water bodies contain about two-thirds of the planet's accessible freshwater, with a significant amount used for agricultural purposes (Aliyu *et al.*, 2019). Groundwater is connected to surface water resources, such as lakes, rivers, wetlands, reservoirs, and estuaries, around the world. The water exchange between surface and subterranean sources demonstrates this relationship, with changes or pollution in one domain frequently affecting the other (Zhu *et al.*, 2019; Khan and Khan, 2019). Compared to other water sources, surface waters are especially vulnerable to metal contamination since they are essential components of the hydrosphere (Gokmen, 2015). This vulnerability underscores the urgent need to mitigate the detrimental impacts of metal contamination on surface water bodies. Meanwhile, heavy metal retention in these environments is determined by the physicochemical characteristics of the sediment and water,

¹Department of Environmental Science, School of Earth and Environmental Sciences, Babasaheb Bhimrao Ambedkar University, Lucknow 226025, India

²Integrated Environmental Monitoring Studio (IEMS), Tamil Nadu Pollution Control Board, Chennai-600032, India

³Environmental Monitoring Division, Environmental Toxicology Group, CSIR- Indian Institute of Toxicology Research, Vishvavyas Bhawan-31, Mahatma Gandhi Marg, Lucknow 226001, India

⁴Academy of Scientific and Innovative Research (AcSIR), Ghaziabad 201002, India

***Corresponding author:** Narendra Kumar, Department of Environmental Science, School of Earth and Environmental Sciences, Babasaheb Bhimrao Ambedkar University, Lucknow 226025, India, Email: narendrakumar_lko@yahoo.co.in

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including pH, conductivity, total organic matter, and total organic carbon. These factors influence the mobility, solubility, adsorption, desorption, and toxicity of metals (Iyama *et al.*, 2016). Therefore, it is crucial to study heavy metals in any medium or space about the physicochemical characteristics of that environment. However, the dangerous levels of heavy metals in river water and sediment are increasing in India due to rapid industrialization and urbanization (Fu *et al.*, 2013). Heavy metals (HMs) are persistent and harmful pollutants in the environment, characterized by their non-biodegradable nature. As a result, residual heavy metals pose a dual threat to both human health and environmental stability (Vahidipour *et al.*, 2022). Pan *et al.*, (2023) noted that surface runoff infiltration, mining activities, industrial and municipal wastewater discharge, and atmospheric deposition are the primary sources of heavy metal pollution in water bodies. Most HMs tend to transition from the aqueous phase to the solid phase, eventually settling in sediments. Miranda *et al.*, (2021) emphasized that heavy metals, due to their low solubility in incoming water, increase their occurrence in nature, thereby damaging water quality. Numerous studies on the Kali River have documented a persistent decline in water quality, believed to result from the growing accumulation of industrial and municipal waste in the surrounding area (Dwivedi and Yadav 2024; Ogola *et al.*, 2024). Several studies have highlighted severe contamination by heavy metals and organic pollutants due to rapid urbanization and industrial discharge (Rani *et al.*, 2020; Singh *et al.*, 2019). Kumar and Yadav (2018) have reported deteriorating water quality affecting both ecological integrity and human health in the region.

This research aims to characterize the current status of physicochemical parameters and HM contamination in the Kali River's sediment and water, as well as in groundwater near the river basins, and to compare them. Sodium percentage (%Na), Sodium Adsorption Ratio (SAR), Magnesium Hazards (MH), Permeability Index (PI), ecological risk index (ERI), Heavy Metal Pollution Index (HPI), and Pollution Load Index (PLI) were calculated and used for analysis. The harmful effects of HMs on human health were also assessed. This unique study evaluates both the physicochemical parameters and heavy metal content of river water, sediment, and groundwater in the basin areas using indices related to water quality, highlighting the urgent need to preserve the Kali River's water.

MATERIALS AND METHODS

Area of investigation

The Kali River is a well-known tributary of the Hindon River, extending across the Saharanpur, Muzaffarnagar, and Meerut districts of India. It originates from the Doon Valley and merges at the village of Pittholakar, Meerut, U.P., covering a catchment area of 750 km². The coordinates of the Kali River, where samples were taken, are approximately 29°12'47"N to 29°43'59"N and 77°31'37"E to 77°42'4"E, with the region experiencing an average annual precipitation of 1000 mm (Mishra *et al.*, 2015a). Agricultural activities dominate the riverbanks, with limited forest cover. During the monsoon season, the river experiences a substantial increase in flow, reaching levels approximately 10–12 times higher than during the dry season, often resulting in

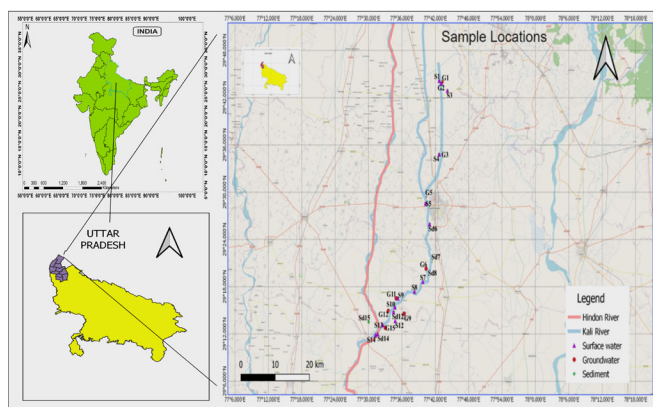


Fig. 1: GIS-based sampling locations and study area

flooding along various sections of its course (Singh *et al.*, 2020). The primary sources of pollution for the Kali River are municipal and industrial waste. The effluents introduced into the river trigger biological processes, leading to a rapid deterioration in water quality within the area. The study map is depicted in Figure 1.

Description of Sampling Sites

Fifteen sites were designated for sampling along the Kali River's course, encompassing groundwater, surface water, and sediment sources (Table 1). In November 2020, samples were collected from the Saharanpur, Muzaffarnagar, and Meerut districts, extending to the confluence point of the Kali River with the Hindon River.

Sampling and sample preparation

Thirty water samples were collected, including 15 surface water and 15 groundwater samples obtained from the river and near the riverbank (Table 1). The samples were carefully stored in clean, opaque polyethylene bottles, filtered through 0.45 mm syringe filters, and acidified with 65% nitric acid until the pH dropped below 2 to prevent precipitation before analysis. Water samples were preserved at 4°C in thermal containers and sent to the laboratory for investigation within 24 hours (Khan and Khan, 2019). Further, fifteen sediment samples were gathered from riverbeds within surface water (Table 1). The collection of sediment samples was carried out using a stainless-steel scoop, and they were subsequently stored in polyethylene bags. Before heavy metal (HM) analysis, the sediment samples were naturally dried at 28°C±2 and passed through a 2 mm mesh sieve.

PHYSICOCHEMICAL ANALYSIS

Physicochemical Analysis of Groundwater and Surface Water

The Orion Versastar Pro meter, also referred to as the Advanced Electrochemistry Meter, was used to measure the physicochemical parameters for groundwater and surface water analysis. These parameters included pH, electrical conductivity, total dissolved solids, and fluoride. The titrimetric method was used to quantify bicarbonate, chloride (Argentometric method), total hardness, calcium, and magnesium using the

Table 1: Monitoring Location with Geological Coordinates

Groundwater				Surface Water and Sediment				
Sample	Latitude	Longitude	Location	Sample	Sample	Latitude	Longitude	Location
G1W	29°43'59"	77°43'12"	Salahpur	S1	Sd1	29°44'9"	77°42'43"	Divaheri
G2	29°43'50"	77°43'3"	Salahpur	S2	Sd2	29°43'50"	77°43'3"	Salahpur
G3	29°34'47"	77°43'06"	Chandpur	S3	Sd3	29°42'53"	77°44'11"	Chandpur
G4	29°34'47"	77°43'06"	Chapar	S4	Sd4	29°34'49"	77°42'42"	Chhapar marg
G5	29°29'25"	77°40'12"	Mimlana	S5	Sd5	29°28'34"	77°40'15"	Sahbudinpur
G6	29°20'17"	77°40'21"	Mansoorpur	S6	Sd6	29°25'57"	77°40'58"	Muzaffarnagar
G7	29°17'26"	77°38'01"	Dable	S7	Sd7	29°18'38"	77°39'46"	Morkuka
G8	29°17'26"	77°38'02"	Dable	S8	Sd8	29°17'23"	77°38'15"	Dabal village
G9	29°14'34"	77°36'24"	Rajpur	S9	Sd9	29°16'32"	77°35'17"	Kalashnagar
G10	29°14'34"	77°36'24"	Rajpur	S10	Sd10	29°15'23"	77°34'45"	Rajpur momin
G11	29°16'31"	77°34'58"	Rajpur	S11	Sd11	29°14'48"	77°34'30"	Husainabad
G12	29°14'55"	77°33'31"	husanbad	S12	Sd12	29°13'40"	77°34'48"	Nahali jungle
G13	29°14'56"	77°33'33"	husanbad	S13	Sd13	29°13'9"	77°32'34"	Pithlokhar
G14	29°12'46"	77°33'2"	Pithlokhar	S14	Sd14	29°11'51"	77°31'15"	Pithlokhar
G15	29°12'47"	77°33'1"	Pithlokhar	S15	Sd15	29°12'01"	77°31'37"	Pithlokhar

EDTA method. Sodium and potassium were measured with a flame photometer, while phosphate, nitrate, and sulphate were measured with a spectrophotometer (APHA, 1998; Nayar et.al.,2020; Moursy et.al.,2022). Quality control and method validation were conducted throughout the process using the multi-element standard solution VI (Merk, Germany).

Physicochemical Analysis of Sediment Samples

The pH, electrical conductivity (EC), and fluoride content of the sediment samples were measured using an Orion Versastar Pro meter by combining sediment samples and deionized water in a 1:1 (w/v) ratio (Simeon *et al.*, 2019). Air-dried soil samples (10 g) were weighed into a 100 ml beaker, and 50 ml of deionized water was added for anion extraction. The samples were stirred for 15 minutes and filtered through filter paper into a vial. Total nitrogen (TN), total phosphorus (TP), and total sulphur (S) were determined by measuring the absorbance value using a UV-Vis spectrophotometer. For cations, the soil samples were extracted for exchangeable Ca, K, Mg, and Na. Air-dried soil samples (2.5 g) were weighed into 50 ml test tubes, and 25 ml of 1 M NH₄Cl was added. The samples were shaken for 30 minutes. After centrifugation, the supernatant was filtered through filter paper into a volumetric flask. Sodium and potassium were analyzed using a flame photometer, and calcium and magnesium were analyzed using the EDTA method (Iordache *et al.*, 2020). The Walkley and Black (1934) method, slightly modified by Marcus and Edori (2017), was used to assess total organic carbon (TOC). The formula for calculating total organic matter was TOC x 1.729. The formula to determine easily oxidizable organic carbon (EOOC%) was followed according to the Walkley-Black method (1934).

Heavy Metal

Inductively Coupled Plasma Mass Spectrometry (ICP-MS), specifically the model ICAPRQ (RQ01013) was used to quantify heavy metals in Kali River water following post-digestion at the Indian Institute of Toxicology Research (IITR) in Lucknow, Uttar Pradesh (Sibal et. al., 2018).

HM Pollution Index (HPI)

The water quality of the Kali River is deteriorated by different heavy metal concentrations, which are measured through the Heavy Metal Pollution Index (HPI), a metric used for grading water quality. This index (ranging between 0 and 1) provides insights into water quality conditions, where a value below 0 signifies uncontaminated water, and a value exceeding 1 indicates severe contamination. By computing this index, one can measure the overall water quality and assess its suitability for consumption (Prasad and Mondal, 2008; Matta *et al.*, 2018).

The calculation process involves

- Determination of the weightage (We) for each parameter.
- Calculate the individual quality rating or subindices (Qe) for each HM.
- Aggregation of subindices (Qe) to derive the overall index.

The *i*th parameter weight is calculated by the formula (1)

$$We = \frac{K}{\sum Si} \dots \dots \dots (1)$$

Where,

We= unit weight

Si = the recommended standard for an *i*th parameter (*i*=1-9),

k = the proportionality constant.

The single quality of HM conc. rating is calculated by following equation (2)

$$Q_i = \sum i = 1n \left[\frac{Me - Ie}{Se - Ie} \right] \times 100 \dots \dots \dots (2)$$

Where, Q_e = the subindex of an ith parameter

Me = the monitored value of the ith parameter in $\mu\text{g/l}$

Se = the standard or permissible limit for the ith parameter

Ie = the ideal value of the ith parameter

the heavy metal pollution index is then calculated by following equation (3)

$$HPI = \frac{\sum i = 1n [Q_e - W_e]}{\sum i = 1n [W_e]} \dots \dots \dots (3)$$

Where Q_e = Sub-Index of the ith parameter

w_e = The unit weight for an ith parameter

n = The number of parameters considered.

However, the CPI (critical pollution index) value is 100 (Shankar, 2019).

Specimen calculation and classification of HPI were done based on Ustaoglu *et al.*, 2020 and Shankar *et al.*, 2019.

Sediment Pollution Load Index (PLI)

Concentration factors (CF) determine the pollutant load index (PLI). The CF calculation is conducted by dividing each metal's conc. with their background value. The n-root of the n-CFs acquired for each metal at a specific site is used to calculate PLI (Soares *et al.*, 1999; Rabee *et al.*, 2011). In 1980, Tomlinson *et al* investigated the calculation of PLI for the first time as follows

W

$$CF = \frac{C_m}{C_b}$$

Where, C_m = Metal conc.

C_b = Background value of metal

Now,

$$PLI = \sqrt[n]{Cf1 \times Cf2 \times Cf3 \times \dots \times Cfn} \dots \dots \dots (4)$$

Where, CF= Contamination factor

N = Metals Number

C = Conc. of heavy metal in the sediment sample

f = Background value of that metal

PLI values more than one indicate contamination, whereas values less than one indicate no pollution (Harikumar *et al.*, 2009). The world average concentration of these metals (Cu-45 $\mu\text{g/gm}$, Ni-68 $\mu\text{g/gm}$, Mn-900 $\mu\text{g/gm}$, Pb-20 $\mu\text{g/gm}$, and Cd-0.3 $\mu\text{g/gm}$) were used as background value (Turekian *et al.*, 1961; Mishra *et al.*, 2018).

Ecological Risk Index (ERI)

Water Risk Index (RI)

The risk index calculation has been based on Adimalla and Wang

(2018); Taiwo *et al.*, (2019). In this investigation, equations 5 and 6 were used to determine the ERI (=RI) of the water samples.

$$PI = \frac{C_p}{C_b} \dots \dots \dots (5)$$

$$RI = Tr \times PI \dots \dots \dots (6)$$

Where, RI = The potential risk factor of every heavy metal

Tr = Toxic response of each heavy metal

C_p = The present Conc. of heavy metal

C_b = The background value of heavy metal

Several researchers highlighted the background value of heavy metals as As = 10, Cd = 30, Fe, Cr, Zn, and Mn = 1, and Co, Cu, Ni, and Pb = 5 are the heavy metals' hazardous response factors (Bhutiani *et al.*, 2017; Adimalla and wang 2018; Taiwo *et al.*, 2019).

Sediment Risk Index

Ecological risk index (RI) was proposed by Hakanson in 1980 and considers various factors, Heavy metal (HM) synergetic effects, toxicology, background concentration of HMs, and HM pollution sensitivity towards the environment (Han *et al.*, 2018). the risk of an individual metal E^i and the comprehensive RI of sampling sites were calculated as follows (Hakanson, 1980)

$$RI = \sum E_r^i = \sum T_r^i C_f^i \dots \dots \dots (7)$$

$$E_r^i = T_r^i C_f^i \dots \dots \dots (8)$$

$$C_f^i = C_o^i / C_n^i \dots \dots \dots (9)$$

Where C_f^i = the single contamination

C_o^i = the concentration in sediments,

C_n^i = the background concentration of element i

T_r^i = the biological toxic factor for a given heavy metal like (Hg=40, Cd=30, As=10, Cu=Pb=Ni=5, Cr=2, Mn = Zn=1)

There are four classification levels of the ecological risk index based on Vahidipour *et al.*, (2022).

Statistical Analysis

Statistical analysis was conducted using Excel and Past4.0 software to compute correlation, mean, maximum, and minimum values and perform Principal Component Analysis (PCA). Pearson's correlation analysis, a fundamental statistical technique, was employed to determine the degree of interdependence among variables and assess their associations' strength (Mishra *et al.*, 2018). The correlation analysis of heavy metals (HMs) found in water samples from various sampling sites along the Kali River was determined using Pearson's correlation, with a significance level of $P < 0.05$.

PCA is a multivariate statistical approach used to reduce data dimensionality, aiming to extract essential information from the dataset (Akoto *et al.*, 2019). This method helps identify significant parameters that collectively explain the variability within the entire dataset. Principal Components (PCs) are linear combinations of all variables, which are mutually independent. PCA is particularly advantageous as it eliminates the need to analyze each factor individually; typically, two or three PCs are sufficient to explain at least 70-80% of the data variation (Zou *et al.*, 2006; Mishra *et al.*, 2018).

RESULTS AND DISCUSSION

Physical Parameters: Groundwater, Surface water, and Sediment Samples

The fundamental characteristics of water are revealed by its physicochemical qualities, which also shed light on its suitability for industrial, agricultural, and domestic use. In the current investigation, the pH ranged from 7.3-8.2, 6.7-7.7, and 7.6-8.5, while EC values ranged from 387-1326, 550-840, and 688-2186 μScm^{-1} in groundwater (GW), surface water (SW), and sediment (Sd) samples, respectively. These variations in EC and TDS may directly influence the solubility and mobility of heavy metals such as Fe, Cr, and Mn (see Fig. 2a-c), which showed elevated concentrations at sites with higher conductivity, particularly G2, S6, and Sd12 for iron. This suggests a correlation between physicochemical parameters and heavy metal bioavailability. The results for TDS and TH showed that the average values are within the permissible limits; however, a few sampling sites have values exceeding the allowable limit in both GW and SW, as mentioned in Tables 2, 3, and 4. Meanwhile, %Na, SAR, MH, and PI were calculated for GW and SW to assess water quality for irrigation purposes after some modifications. High MH (80.43 mg/L) in GW and poor PI in SW (avg. 1.82 mg/L) may indicate an unsuitability for irrigation, which aligns with high Na% and SAR values. These elevated ionic concentrations can influence metal desorption from sediments into water columns, thus contributing to observed heavy metal enrichment. In sediment samples, the Easily Oxidizable Organic Carbon (EOOC) ranged from 0.15-1.65%, TOC from 0.39-1.95%, and OM from 0.57-28.91%. The average TOC value is above the detection limit. Organic carbon is typically found in sediment at locations where river flow is weak or currents are low, as well as in effluents from sources high in carbon (Edori and Kpee, 2016). Within this river, the carbon might have originated from sources such as illicit refining within and around the coastline. The amount of organic carbon present corresponds to the type and size of the sediment particles (Edori and Marcus, 2019). The organic matter in this river most likely came from natural sources, including plant decomposition and dead crustaceans, which are common in the area. Total organic matter is a metric that provides details about the composition and properties of the particles, as well as their ability to contain complex molecules (Edori and Kpee, 2016). The results of the physicochemical analysis of GW, SW, and sediment from the Kali River indicate that certain treatments and awareness programs are needed to minimize waste discharge into the river.

Concentration of Heavy Metals (HMs) in Groundwater, Surface Water, and Sediments

In this study, the concentrations of HMs in water and sediments are presented in Figures 2a, 2b, and 2c. The results indicate that the maximum concentrations of chromium were found in groundwater, surface water, and sediments at the G12 station (1.69 mg l^{-1}), S8 station (0.48 mg l^{-1}), and Sd 12 (279.95 mg l^{-1}), respectively. Only four groundwater stations (G3, G4, G10, and G11) were within the permissible limit, while in surface water, only two stations (S1 and S2) were within the limits.

All sediment stations showed very high concentrations of chromium (Fig.2c), which is mutagenic and carcinogenic to living organisms and causes several diseases in humans (Kumar and Dwivedi, 2020). For health reasons, the permissible amount of chromium (Cr^{+6}) in drinking water is 0.05 mg l^{-1} (Moffat et. al., 2018). Chromium enters aquatic ecosystems through surface runoff or aerial deposition, interacts with particulate matter, and settles in bed sediment. The highest concentration of nickel was found at stations G1 and G13 (0.14 mg l^{-1} and 0.10 mg l^{-1}) in groundwater; the remaining samples were within the standard limits prescribed by WHO (0.07 mg l^{-1}). Higher concentrations of nickel in surface water and sediments were found at S-5 (0.3 mg l^{-1}) and Sd 12 (96.55 mg kg^{-1}); all sediment stations had values exceeding the standard limit. Nickel can cause numerous health issues, including contact dermatitis, lung fibrosis, asthma, cardiovascular disease, and respiratory tract cancer (Kumar and Dwivedi, 2020). The primary pathway for nickel-induced damage in the respiratory tract, lungs, and immune system is inhalation exposure in work environments (Genchi et al., 2020). However, as drinking water and/or food may contain nickel contaminants, the majority of human exposure concerns oral intake through food and water (Sinicropi et al., 2012). However, the highest concentration of manganese in groundwater was found at G1 (2.09 mg l^{-1}), while the highest concentrations in surface water and sediments were at S8 (7.52 mg l^{-1}) and Sd2 (1313 mg l^{-1}), respectively. The gastrointestinal and respiratory systems absorb manganese most efficiently, and it can cross the blood-brain barrier, accumulating in brain regions such as the basal ganglia, where it exerts neurotoxic effects (Soares et al., 2020). Manganese buildup in these regions is linked to several neurodegenerative conditions, including Parkinson's disease (Kumar and Dwivedi, 2020). Meanwhile, the highest concentration of iron in groundwater was found at G2 (13.28 mg l^{-1}), while the highest concentrations in surface water and sediments were at S6 (18.67 mg l^{-1}) and Sd12 (58448 mg l^{-1}), respectively. Iron deficiency is the most prevalent dietary deficiency worldwide and a major contributor to anemia. Insufficient iron intake causes the body to produce inadequate haemoglobin, reducing the blood's ability to carry oxygen. Hemochromatosis, a disorder characterized by excessive iron absorption and buildup in the body, results in iron overload (Puntarulo, 2005). The maximum amount of zinc in groundwater, surface water, and sediments was found at G10 (6.55 mg l^{-1}), S8 (5.83 mg l^{-1}), and Sd13 (4476.83 mg kg^{-1}), respectively. As we know, zinc is a vital nutrient necessary for all life; excessive levels of zinc in soil can cause phytotoxicity, inhibiting root formation, turning leaves yellow, and stunting plant growth. Excessive zinc uptake can also disrupt ion uptake balance, leading to nutritional imbalances and reduced plant health (Zonta et al., 2019). The maximum copper (in conc.) was found at G1 (0.77 mg l^{-1}), S8 (32.72 mg l^{-1}), and Sd2 (587.49 mg kg^{-1}), in groundwater, surface water, and sediments respectively. Although copper deficiencies are rare in plants, high copper concentrations can be hazardous and cause phytotoxicity. Overconsumption of copper in humans can be harmful, especially with prolonged exposure or genetic abnormalities affecting copper metabolism (Kumar and Dwivedi, 2020). The highest concentrations of arsenic in groundwater, surface water, and sediments were found at

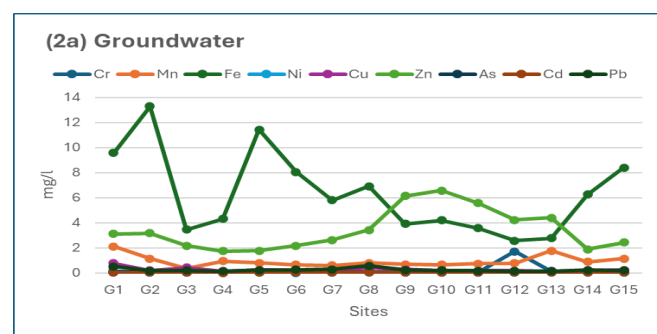


Fig.2.(a): Heavy metal concentration in groundwater,

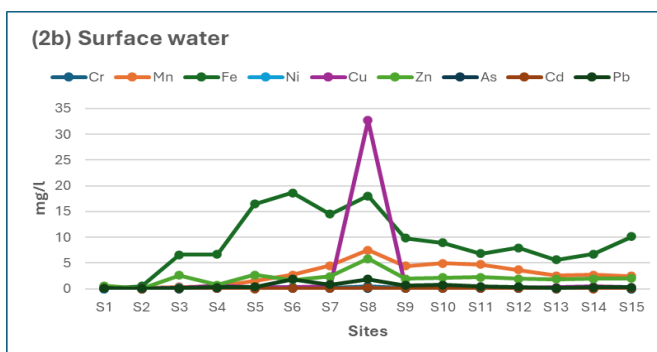


Fig.2.(b): Heavy metal concentration in Surface water,

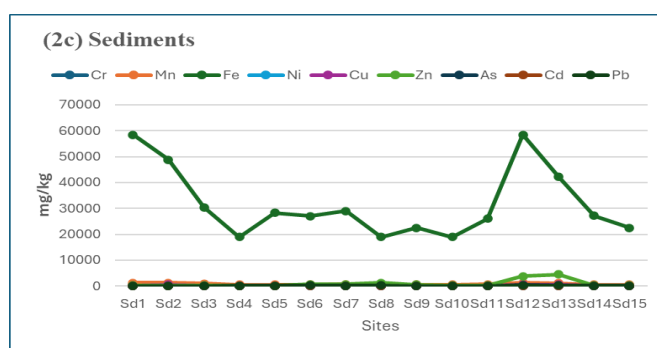


Fig.2.(a): Heavy metal concentration in Sediments

G8 (0.06 mg l^{-1}), S5 (0.08 mg l^{-1}), and Sd12 (49.13 mg kg^{-1}), respectively. Inorganic arsenic is highly toxic and can cause cancer with prolonged exposure through food and WWd water. It is the most significant chemical contaminant in drinking water worldwide and a known carcinogen (Prakash and Verma, 2021). However, the cadmium conc. was maximum found at G8 (0.05 mg l^{-1}), S8 (0.08 mg l^{-1}), and Sd 6 (34.62 mg kg^{-1}) in groundwater, surface water, and sediments respectively. Cadmium is a toxic metal that causes various health issues in humans. Its bioavailability, bio accessibility, and accumulation in soil-plant systems contribute to its transmission to various trophic levels. Bioaccumulation of cadmium in the human body causes oxidative stress, leading to various illnesses (Suhani *et al.*, 2021). But the lead conc. was higher at G8 (0.55 mg l^{-1}), S8 (1.84 mg l^{-1}), and Sd 12 ($378.25 \text{ mg kg}^{-1}$), in groundwater, surface water, and sediments were found respectively. Lead poisoning is one of the most hazardous forms of metal toxicity. It induces oxidative stress by disrupting the cellular membrane through lipid peroxidation, leading to severe health issues, including

haemolytic anemia and organ damage. Lead can also affect neurotransmitter levels and cause fatalities (Debnath *et al.*, 2019). Meanwhile, in this study, HM concentrations were higher in sediments compared to groundwater and surface water, as they have lower solubility in surface water and are easily absorbed by sediments. In aquatic ecosystems, sediments serve as significant reservoirs for HMs (Sojka and Jaskula 2022). Fluvial processes that continuously occur with the course of rivers cause heavy metals to accumulate in river sediments. Several processes—physical, chemical, hydrological, and hydraulic—control the concentration and distribution of heavy metals in river sediments (Bednarova *et al.*, 2013). However, the increased concentrations of some heavy metals at a few locations, namely chromium at G12, S8, Sd132, nickel at G1, G13, S5, Sd12, manganese at G1, S8, Sd2, iron at G2, S6, and copper at G1, S8, Sd2 indicate localised contamination caused by human activity. These locations show regional differences in pollution levels in addition to exceeding WHO drinking water standards. A closer look shows that in the districts of Saharanpur and Muzaffarnagar, the electroplating, dyeing, sugar milling, and metal processing sectors are among the known industrial clusters that are either downstream or adjacent to G1, S5, S8, and G12. For example, chromium levels in G12 (groundwater) and S8 (surface water) are startlingly high, most likely because of untreated outflow from metal-finishing or tanneries. Furthermore, a distinct upstream-downstream gradient is shown by the distribution of metal concentrations, with downstream locations exhibiting cumulative increases in pollutants, especially Ni and Cu, which reflect the combined effects of several pollution sources along the river's path. For instance, Ni contamination is already present in G1 and G13 in upstream and midstream areas, suggesting early pollution entry points that may have been caused by smaller industrial outlets or agricultural runoff. Since industrial proximity, hydrological flow direction, and ineffective effluent management appear to be closely linked to the spatial variance in pollution levels, so stricter regulatory enforcement and site-specific remediation methods are necessary.

Finding the Sources of Heavy Metal Contamination

Understanding the distribution of heavy metals can provide insights into their sources. Pearson's Correlation Analysis and Principal Component Analysis (PCA) were employed to investigate the relationships and sources of the heavy metals (Chai *et al.*, 2017; Jiang *et al.*, 2019)

All parameters measured in mg/l except pH, EC ($\mu\text{S/cm}$), and Bold value show the maximum amount among all sampling stations.

All parameters measured in mg/l except pH, EC ($\mu\text{S/cm}$), and P, S, & N measured in mg/kg . The bold value shows the maximum amount among all sampling stations.

All parameters measured in mg/l except pH, EC ($\mu\text{S/cm}$), and P, S, & N measured in mg/kg . The bold value shows the maximum amount among all sampling stations.

CORRELATION ANALYSIS

The findings indicated that the heavy metals (HMs) assessed in this study along the Kali River showed significant differences ($P < 0.05$, two-tailed) in surface water, groundwater near river basins,

Table 2: Physico-chemical characteristics of Groundwater samples collected along the Kali River as the mean of three replicates (i.e., n=3) $\pm$ SD).

Sample	pH	EC	TDS	TH	Mg++	Ca++	K+	Na+	HCO ₃ ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ⁻²	PO ₄ ⁻³	%Na	SAR	MH	PI
G1	7.8 $\pm$ 0.5	447 $\pm$ 23	312.9 $\pm$ 23.5	360 $\pm$ 41	26.4 $\pm$ 28	28 $\pm$ 8	12 $\pm$ 3	44 $\pm$ 31	286 $\pm$ 26	16.99 $\pm$ 12	468.5 $\pm$ 31	377.5 $\pm$ 9	4.56 $\pm$ 6	38.15	0.50	61.11	73.98
G2	8.1 $\pm$ 0.6	428 $\pm$ 17	299.6 $\pm$ 42.1	440 $\pm$ 33	43.2 $\pm$ 31	16 $\pm$ 4	10 $\pm$ 5	85 $\pm$ 23	274 $\pm$ 31	1.99 $\pm$ 0.78	11.5 $\pm$ 13	77.5 $\pm$ 9	7.63 $\pm$ 7	47.32	0.88	81.82	71.83
G3	7.4 $\pm$ 0.4	702 $\pm$ 45	491.4 $\pm$ 62	800 $\pm$ 19	88.8 $\pm$ 26	12 $\pm$ 8	14 $\pm$ 4	38 $\pm$ 27	408.7 $\pm$ 33	2.99 $\pm$ 1.4	213 $\pm$ 12	215 $\pm$ 14	14.98 $\pm$ 5	20.09	0.29	92.50	43.93
G4	7.8 $\pm$ 0.3	387 $\pm$ 28	270.9 $\pm$ 23.6	280 $\pm$ 23	24 $\pm$ 11	16 $\pm$ 9	9 $\pm$ 7	37 $\pm$ 18	244 $\pm$ 19	101.96 $\pm$ 21	56 $\pm$ 28	240 $\pm$ 13	4.64 $\pm$ 9	39.65	0.48	71.43	81.85
G5	7.3 $\pm$ 1.2	691 $\pm$ 36	483.7 $\pm$ 41.1	640 $\pm$ 37	62.4 $\pm$ 15	24 $\pm$ 3	14 $\pm$ 11	79 $\pm$ 10	439.2 $\pm$ 28	4.99 $\pm$ 23	887.5 $\pm$ 15	502.5 $\pm$ 11	10.63 $\pm$ 4.8	37.22	0.68	81.25	62.21
G6	8 $\pm$ 0.4	759 $\pm$ 43	531.3 $\pm$ 38.2	640 $\pm$ 45	62.4 $\pm$ 9	24 $\pm$ 6	16 $\pm$ 8	52 $\pm$ 9.1	506.3 $\pm$ 11	41.98 $\pm$ 31	1182.5 $\pm$ 17	1380 $\pm$ 17	2.02 $\pm$ 3.9	29.45	0.45	81.25	59.37
G7	7.9 $\pm$ 0.6	428 $\pm$ 31	299.6 $\pm$ 26	440 $\pm$ 78	42.24 $\pm$ 21	17.6 $\pm$ 11.2	12 $\pm$ 9	91 $\pm$ 31	317.2 $\pm$ 23	5.99 $\pm$ 4	532 $\pm$ 9 $\pm$ 39	190 $\pm$ 18	9.66 $\pm$ 7.3	49.22	0.94	80.00	74.63
G8	8.2 $\pm$ 0.9	489 $\pm$ 21	342.3 $\pm$ 43.3	160 $\pm$ 20	13.44 $\pm$ 9	9.6 $\pm$ 9.3	10 $\pm$ 17	128 $\pm$ 37	298.9 $\pm$ 25	4.99 $\pm$ 8	123.5 $\pm$ 31	267.5 $\pm$ 17	3.59 $\pm$ 11	78.44	2.20	70.00	108.56
G9	7.9 $\pm$ 0.2	560 $\pm$ 65	392 $\pm$ 28.1	240 $\pm$ 35	21.6 $\pm$ 10	12 $\pm$ 2.8	14 $\pm$ 9	74 $\pm$ 12	378.2 $\pm$ 19	2.99 $\pm$ 5	272.5 $\pm$ 24	40 $\pm$ 15	14.45 $\pm$ 21	59.84	1.04	75.00	101.60
G10	8 $\pm$ 0.3	523 $\pm$ 48	366.1 $\pm$ 44.2	440 $\pm$ 45	40.32 $\pm$ 29	20.8 $\pm$ 7	13 $\pm$ 8	80 $\pm$ 32	603.9 $\pm$ 16	11.99 $\pm$ 7	22.55 $\pm$ 19	82.5 $\pm$ 13	3.67 $\pm$ 3	46.42	0.83	76.36	84.09
G11	7.8 $\pm$ 0.7	498 $\pm$ 51	348.6 $\pm$ 37.13	480 $\pm$ 61	50.4 $\pm$ 38	12 $\pm$ 11	12 $\pm$ 9	62 $\pm$ 29	305 $\pm$ 12	3.99 $\pm$ 5	156 $\pm$ 9	105 $\pm$ 15	5.41 $\pm$ 3	38.49	0.62	87.50	65.79
G12	7.2 $\pm$ 0.8	1326 $\pm$ 73	928.2 $\pm$ 19.3	800 $\pm$ 17	81.6 $\pm$ 16	24 $\pm$ 9	19 $\pm$ 9.5	147 $\pm$ 18	628.3 $\pm$ 21	51.98 $\pm$ 19	77.5 $\pm$ 8	530 $\pm$ 11	2.17 $\pm$ 5	46.23	1.13	85.00	66.71
G13	8.1 $\pm$ 0.9	1186 $\pm$ 33	830.2 $\pm$ 61.9	1760 $\pm$ 49	189.12 $\pm$ 25	36.8 $\pm$ 16	9 $\pm$ 11	138 $\pm$ 9	457.5 $\pm$ 42	101.96 $\pm$ 16	1182.5 $\pm$ 12	3577.5 $\pm$ 31	0.67 $\pm$ 1	26.15	0.72	89.55	37.03
G14	7.6 $\pm$ 0.2	869 $\pm$ 19	608.3 $\pm$ 33.2	640 $\pm$ 53	64.8 $\pm$ 18	20 $\pm$ 12	17 $\pm$ 8.3	103 $\pm$ 13	427 $\pm$ 30	46.98 $\pm$ 23	47.5 $\pm$ 11	222.5 $\pm$ 21	3.07 $\pm$ 1	43.43	0.89	84.38	65.49
G15	7.3 $\pm$ 1.2	770 $\pm$ 28	539 $\pm$ 13	560 $\pm$ 39	60 $\pm$ 23	12 $\pm$ 5	18 $\pm$ 7.8	107 $\pm$ 21	433.1 $\pm$ 19	56.98 $\pm$ 11	408 $\pm$ 24	140 $\pm$ 10	4.71 $\pm$ 1.6	47.73	0.98	89.29	71.37
Average Value	7.76	670.87	469.61	578.67	58.04	18.98	13.26	84.33	400.49	30.58	376.04	529.83	6.12	43.19	0.84	80.43	71.23

Table 3: Physico-chemical characteristics of surface water samples collected along the Kali River as the mean of three replicates (i.e., n=3) $\pm$ SD).

sample	pH	EC	TDS	TH	Mg++	Ca++	K+	Na+	Cl-	F-	HCO ₃ ⁻	NO ₃ ⁻	SO ₄ ²⁻	PO ₄ ³⁻	%Na	SAR	MH	PI
S1	7.5 $\pm$ 0.7	550 $\pm$ 50	385 $\pm$ 39	480 $\pm$ 50	38.4 $\pm$ 4	32 $\pm$ 3	12 $\pm$ 2	67 $\pm$ 7	11.99 $\pm$ 2	0.98 $\pm$ 0.06	237.9 $\pm$ 25	37.87 $\pm$ 5	25.62 $\pm$ 3	2 $\pm$ 0.02	44.85	11.29	54.55	2.908
S2	7.6 $\pm$ 0.7	586 $\pm$ 52	410.2 $\pm$ 43	480 $\pm$ 53	48 $\pm$ 5	16 $\pm$ 1.5	14 $\pm$ 2	72 $\pm$ 8	6.99 $\pm$ 0.7	0.26 $\pm$ 0.01	372.1 $\pm$ 40	1.25 $\pm$ 0.02	23.25 $\pm$ 4	1.08 $\pm$ 0.01	48.00	12.73	75.00	2.488
S3	7.5 $\pm$ 0.7	569 $\pm$ 45	398.3 $\pm$ 42	480 $\pm$ 52	24 $\pm$ 3	56 $\pm$ 6	15 $\pm$ 2	70 $\pm$ 8	5.99 $\pm$ 0.6	0.25 $\pm$ 0.03	396.5 $\pm$ 45	2.17 $\pm$ 1.5	14.55 $\pm$ 3	0.29 $\pm$ 0.02	42.42	11.07	30.00	2.131
S4	7.5 $\pm$ 0.6	645 $\pm$ 55	451.5 $\pm$ 40	680 $\pm$ 70	60.96 $\pm$ 6	34.4 $\pm$ 4	20 $\pm$ 3	74 $\pm$ 6	38.98 $\pm$ 4	0.19 $\pm$ 0.01	366 $\pm$ 41	19.77 $\pm$ 3	27.75 $\pm$ 4	0.34 $\pm$ 0.03	39.08	10.72	63.93	2.043
S5	7.7 $\pm$ 0.8	676 $\pm$ 60	473.2 $\pm$ 45	720 $\pm$ 75	69.6 $\pm$ 7	28 $\pm$ 3	21 $\pm$ 3	76 $\pm$ 9	19.99 $\pm$ 2	0.1 $\pm$ 0.01	463.6 $\pm$ 49	6.12 $\pm$ 0.07	31.37 $\pm$ 5	1.25 $\pm$ 0.03	39.05	10.88	71.31	1.814
S6	7 $\pm$ 0.5	852 $\pm$ 70	596.4 $\pm$ 65	800 $\pm$ 85	81.6 $\pm$ 9	24 $\pm$ 3	34 $\pm$ 4	78 $\pm$ 9	26.99 $\pm$ 3	0.27 $\pm$ 0.02	610 $\pm$ 63	10.15 $\pm$ 2	33.12 $\pm$ 4	2.86 $\pm$ 0.3	35.85	10.73	77.27	1.451
S7	7.3 $\pm$ 0.6	1225 $\pm$ 111	857.5 $\pm$ 90	560 $\pm$ 60	56.64 $\pm$ 58	17.6 $\pm$ 3	50 $\pm$ 6	143 $\pm$ 16	31.99 $\pm$ 43	0.22 $\pm$ 0.03	524.6 $\pm$ 55	0.25 $\pm$ 0.03	55.87 $\pm$ 61	0.87 $\pm$ 0.09	53.51	23.47	76.29	2.336
S8	7 $\pm$ 0.5	1485 $\pm$ 132	1039.5 $\pm$ 103	424 $\pm$ 45	33.12 $\pm$ 4	29.6 $\pm$ 3	58 $\pm$ 6	162 $\pm$ 17	169.94 $\pm$ 18	0.4 $\pm$ 0.03	701.5 $\pm$ 81	23.72 $\pm$ 3	100.88 $\pm$ 2	3.28 $\pm$ 0.4	57.30	28.93	52.81	2.163
S9	7.2 $\pm$ 0.6	1196 $\pm$ 110	837.2 $\pm$ 80	600 $\pm$ 62	52.8 $\pm$ 5	32 $\pm$ 4	53 $\pm$ 4	150 $\pm$ 17	31.99 $\pm$ 5	0.43 $\pm$ 0.02	640.5 $\pm$ 69	13.02 $\pm$ 15	87.62 $\pm$ 9	4.75 $\pm$ 0.05	52.12	23.04	62.26	2.059
S10	6.7 $\pm$ 0.7	1840 $\pm$ 160	1288 $\pm$ 130	1000 $\pm$ 98	86.4 $\pm$ 9	56 $\pm$ 6	142 $\pm$ 15	147 $\pm$ 15	111.96 $\pm$ 12	0.36 $\pm$ 0.04	1006.5 $\pm$ 105	99.37 $\pm$ 11	192.5 $\pm$ 22	1.17 $\pm$ 0.02	34.08	17.42	60.67	1.074
S11	7 $\pm$ 0.5	1781 $\pm$ 165	1246.7 $\pm$ 120	1040 $\pm$ 99	96 $\pm$ 8	48 $\pm$ 5	146 $\pm$ 13	141 $\pm$ 15	41.98 $\pm$ 5	0.23 $\pm$ 0.03	915 $\pm$ 95	82.07 $\pm$ 10	179.38 $\pm$ 23	2.75 $\pm$ 0.3	32.71	16.62	66.67	1.082
S12	6.9 $\pm$ 0.7	1731 $\pm$ 160	1211.7 $\pm$ 115	1320 $\pm$ 105	38.4 $\pm$ 4	200 $\pm$ 21	149 $\pm$ 161	83 $\pm$ 9	16.99 $\pm$ 3	0.21 $\pm$ 0.01	610 $\pm$ 65	40.2 $\pm$ 5	185.63 $\pm$ 24	2.79 $\pm$ 0.3	17.64	7.60	16.11	0.714
S13	6.8 $\pm$ 0.5	1525 $\pm$ 135	1067.5 $\pm$ 109	920 $\pm$ 95	81.6 $\pm$ 9	48 $\pm$ 5	98 $\pm$ 0	142 $\pm$ 15	236.92 $\pm$ 25	0.35 $\pm$ 0.02	628.3 $\pm$ 69	82.47 $\pm$ 9	381.13 $\pm$ 42	1.32 $\pm$ 0.1	38.42	17.64	62.96	1.533
S14	7.5 $\pm$ 0.7	1276 $\pm$ 116	893.2 $\pm$ 90	840 $\pm$ 86	80.16 $\pm$ 9	34.4 $\pm$ 5	62 $\pm$ 7	141 $\pm$ 17	201.93 $\pm$ 20	0.25 $\pm$ 0.01	1000.4 $\pm$ 110	108.13 $\pm$ 11	67.87 $\pm$ 8	2.37 $\pm$ 0.3	44.40	18.63	69.97	1.404
S15	6.8 $\pm$ 0.6	1215 $\pm$ 115	850.5 $\pm$ 75	560 $\pm$ 62	55.68 $\pm$ 6	19.2 $\pm$ 2	51 $\pm$ 4	139 $\pm$ 15	114.96 $\pm$ 10	0.27 $\pm$ 0.01	555.1 $\pm$ 61	1.5 $\pm$ 0.2	49.37 $\pm$ 5	2.83 $\pm$ 0.3	52.48	22.72	74.36	2.227
Average Value	7.2	1143	800.43	726.93	60.22	45.01	61.66	112.33	71.30	0.31	601.87	35.20	97.06	1.99	42.13	16.23	60.94	1.82

and sediment. A Pearson correlation matrix was generated, as shown in Table 5 (a, b, and c). In groundwater, high correlations (above 0.5) were observed between Fe and Mn, Cu and Ni, Cu and Pb, Cd and As, Pb and As, and Cd and Pb (Table 5a). In surface water, strong correlations (above 0.5) were observed between Mn and Cr, Fe and Cr, Fe and Mn, Ni and Fe, Cu and Cr, Cu and Mn, Zn and Cr, Zn and Mn, Zn and Fe, Zn and Cu, As and Cr, As and Fe, As and Ni, Cd and Cr, Cd and Mn, Cd and Fe, Cd and Cu, Cd and Zn, Pb and Cr, Pb and Mn, Pb and Fe, Pb and Cu, Pb and Zn, Pb and As, Pb and Cd (Table 5b). In sediments, a strong correlation (above 0.5) was observed among all parameters except Zn and Mn, Zn and Fe, Cd and Mn, Cd and Fe, Cd and As, Pb and Mn, Pb and Fe, which showed a weak correlation (Table 5c).

PCA

Groundwater

Principal component analysis (PCA) was conducted for groundwater, surface water, and sediment samples using PAST (4.0) open-source software. Only components with an eigenvalue greater than 1 were retained. Due to the significant differences between the units or variables, the correlation matrix was used. A varimax rotation was also carried out to address the issue of variables loading on multiple axes. The PCA results revealed two principal components (PCs) in groundwater with a cumulative variance of 99.35% and eigenvalues greater than 1 (Table 6a). The first principal component (PC1) accounted for approximately 88.64% of the total variance, with positive loadings for iron and zinc and negative loadings for chromium, manganese, nickel, copper, arsenic, cadmium, and lead. The negative loadings of dangerous metals imply inputs from industrial effluents or leaching from contaminated soils, whereas Fe and Zn may come from natural geological strata. PC2 accounted for about 10.70% of the total variance, with positive loadings for zinc only and strong negative loadings for Fe, Ni, Cu, As, Cd, and Pb. These indicate localized industrial discharge or corrosion from infrastructure, where selective metal mobilization may take place. It is dominated by Zn (positive) and has substantial negative loadings for Fe and heavy metals (Mansor *et al.*, 2024).

Surface Water

The PCA results showed three PCs with eigenvalues greater than 1 and a cumulative variance of 99.70% (Table 6b (i)). The first principal component (PC1) accounted for about 67.35% of the total variance, with positive loadings for Mn, Fe, and Cu, which is probably due to a combination of fertilizer and agrochemical contributions as well as natural weathering and soil runoff. However, negative loadings for Cr, Ni, Zn, As, Cd, and Pb. PC2 accounted for about 30.59% of the total variance, with positive loadings for Cr, Mn, Fe, Ni, Zn, As, Cd, and Pb, and a negative loading for Cu only. These indicate a significant anthropogenic influence, especially from wastewater inputs, urban runoff, or industrial discharges. PC3 accounted for about 1.58% of the total variance, with positive loadings for Mn and Zn and strong negative loadings for Cr, Fe, Ni, Cu, As, Cd, and Pb. These localized changes may be related to the use of agrochemicals or natural fluctuations in the metal content of catchment soils.

Table 4: Physico-chemical characteristics of sediment samples collected along the Kali River as the mean of three replicates (i.e., n=3) $\pm$ SD).

Sample	pH	EC	Na+	K+	F-	EOOC%	TOC%	OM%	Ca++	Mg++	P	S	N
Sd1	8.5 $\pm$ 0.7	728 $\pm$ 18	584 $\pm$ 51	32 $\pm$ 8	0.5 $\pm$.22	0.6 $\pm$.3	0.78 $\pm$.45	2.313 $\pm$.95	462.62 $\pm$ 50	648 $\pm$ 25	0.15 $\pm$.12	19 $\pm$ 4	8 $\pm$ 1.3
Sd2	7.8 $\pm$ 1	1745 $\pm$ 47	592 $\pm$ 35	32 $\pm$ 6	0.37 $\pm$.31	0.3 $\pm$.35	0.39 $\pm$.21	1.157 $\pm$ 1.2	231.3 $\pm$ 17	72 $\pm$ 10	0.24 $\pm$.17	10 $\pm$ 3	6 $\pm$.9
Sd3	8.3 $\pm$ 2.1	724 $\pm$ 41	576 $\pm$ 28	40 $\pm$ 8	0.32 $\pm$.21	1.35 $\pm$.41	1.755 $\pm$ 1.2	5.204 $\pm$ 1.8	1040.88 $\pm$ 51	216 $\pm$ 16	0.25 $\pm$.10	11. $\pm$ 1.6	10.5 $\pm$ 2
Sd4	8.5 $\pm$ 1.0	755 $\pm$ 37	600 $\pm$ 22	16 $\pm$ 9	0.46 $\pm$.15	0.3 $\pm$.34	0.39 $\pm$.18	1.157 $\pm$.98	231.3 $\pm$ 25	1440 $\pm$ 28	0.43 $\pm$.11	28 $\pm$ 2	50 $\pm$ 10
Sd5	8.3 $\pm$ 1.4	688 $\pm$ 38	576 $\pm$ 19	32 $\pm$ 7.1	0.3 $\pm$.18	0.3 $\pm$.17	0.39	1.565 $\pm$.74	313 $\pm$ 16	288 $\pm$ 13	0.25 $\pm$.21	160 $\pm$ 3	36.6 $\pm$ 6
Sd6	8.1 $\pm$ 2.6	912 $\pm$ 31	600 $\pm$ 51	72 $\pm$ 3.8	1.5 $\pm$.29	1.5 $\pm$.15	1.95 $\pm$ 1.1	5.782 $\pm$ 2.1	1156.4 $\pm$ 36	1584 $\pm$ 52	0.27 $\pm$.21	80 $\pm$ 4	40.5 $\pm$ 9
Sd7	8.2 $\pm$ 2.1	1422 $\pm$ 22	568 $\pm$ 25	48 $\pm$ 5.9	1.5 $\pm$.21	1.5 $\pm$.91	1.95 $\pm$.9	5.780 $\pm$ 1.8	1156 $\pm$ 38	1872 $\pm$ 56	0.25 $\pm$.18	20 $\pm$ 7	15 $\pm$ 3
Sd8	8.1 $\pm$ 1.9	1482 $\pm$ 23	576 $\pm$ 28	8 $\pm$ 6	0.9 $\pm$.17	0.9 $\pm$.88	1.17 $\pm$ 1	3.469 $\pm$ 1.01	693.8 $\pm$ 18	1224 $\pm$ 45	0.31 $\pm$.12	48 $\pm$ 4	45 $\pm$ 12
Sd9	8.4 $\pm$ 1.7	688 $\pm$ 19	576 $\pm$ 10	32 $\pm$ 6.3	0.3 $\pm$.12	0.3 $\pm$.21	0.39 $\pm$.22	1.157 $\pm$.92	231.3 $\pm$ 25	72 $\pm$ 19	0.32 $\pm$.18	75 $\pm$ 8	20 $\pm$ 8
Sd10	7.9 $\pm$ 1.2	2114 $\pm$ 16	656 $\pm$ 23	192 $\pm$ 3.8	0.3 $\pm$.12	0.3 $\pm$.24	0.39 $\pm$.21	1.157 $\pm$.84	231.3 $\pm$ 28	288 $\pm$ 32	0.72 $\pm$.26	65 $\pm$ 8	88 $\pm$ 18
Sd11	8.3 $\pm$ 0.8	550 $\pm$ 29	512 $\pm$ 28	32 $\pm$ 4.8	0.15 $\pm$.11	0.15 $\pm$.08	0.195 $\pm$.09	0.578 $\pm$.32	115.64 $\pm$ 33	144 $\pm$ 18	0.56 $\pm$.31	100 $\pm$ 9	65 $\pm$ 15
Sd12	7.6 $\pm$ 0.5	2186 $\pm$ 19	632 $\pm$ 18	104 $\pm$ 4.7	7.5 $\pm$.83	7.5 $\pm$.98	9.75 $\pm$.39	28.914 $\pm$ 2.8	5782.74 $\pm$ 78	3744 $\pm$ 41	0.34 $\pm$.22	102 $\pm$ 16	70 $\pm$ 12
Sd13	8 $\pm$ 0.3	1879 $\pm$ 28	672 $\pm$ 55	176 $\pm$ 1.9	4.5 $\pm$.6	4.5 $\pm$ 1.0	5.85 $\pm$.43	17.348 $\pm$ 1.8	3469.64 $\pm$ 76	3312 $\pm$ 35	0.37 $\pm$.19	101 $\pm$ 18	58 $\pm$ 8
Sd14	8 $\pm$ 0.5	1345 $\pm$ 34	720 $\pm$ 48	200 $\pm$ 21	0.6 $\pm$.2	0.6 $\pm$.4	0.78 $\pm$.66	2.313 $\pm$ 1.1	462.62 $\pm$ 47	288 $\pm$ 28	0.19 $\pm$.09	95 $\pm$ 9	55 $\pm$ 8
Sd15	7.8 $\pm$ 1	1125 $\pm$ 23	688 $\pm$ 67	176 $\pm$ 18	0.45 $\pm$.7	0.45 $\pm$.42	0.585 $\pm$.34	1.735 $\pm$.87	346.96 $\pm$ 56	72 $\pm$ 21	0.39 $\pm$.21	90 $\pm$ 11	65 $\pm$ 6
Average Value	8.12	1222.86	608.53	84.26	1.31	1.37	1.781	5.30	1061.7	1017.6	0.340	67	42.18

Table 5 (a): Pearson correlation matrix of heavy metals in Groundwater

Groundwater									
	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
Cr	1								
Mn	-0.054	1							
Fe	-0.284	0.262	1						
Ni	-0.122	**0.909	0.052	1					
Cu	-0.132	0.432	0.267	**0.58844	1				
Zn	0.120	-0.029	-0.456	-0.043	-0.091	1			
As	-0.022	0.059	0.342	0.196	0.363	-0.295	1		
Cd	-0.145	-0.087	0.174	0.077	0.345	0.040	**0.52481	1	
Pb	-0.174	0.240	0.300	0.444	**0.73433	-0.118	**0.66196	**0.81905	1

Table 5 (b): Pearson correlation matrix of heavy metals in Surface water

Surface water									
	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
Cr	1								
Mn	**0.79601	1							
Fe	**0.8174	**0.55599	1						
Ni	0.37375	0.000244	**0.52333	1					
Cu	**0.79453	**0.61744	0.43919	0.25085	1				
Zn	**0.87764	**0.74757	**0.68008	0.46117	**0.81772	1			
As	**0.59604	0.3674	**0.7609	**0.57381	0.34578	0.4092	1		
Cd	**0.90284	**0.68013	**0.603	0.22897	**0.92798	**0.80657	0.41637	1	
Pb	**0.87067	**0.64934	**0.78994	0.14056	**0.6263	**0.59623	**0.6172	**0.81721	1

Table 5 (c): Pearson correlation matrix of heavy metals in Sediments.

Sediment									
	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
Cr	1								
Mn	**0.53251	1							
Fe	**6389	**0.92392	1						
Ni	**0.96385	0.61372	0.75007	1					
Cu	** 0.74526	**0.6482	**0.63761	**0.76132	1				
Zn	**0.95715	0.38388	0.46165	**0.88212	**0.72041	1			
As	**0.7456	**0.91862	**0.93048	** 0.8161	**0.8189	**0.63131	1		
Cd	**0.68648	0.10394	0.27717	**0.6903	**0.54754	**0.73321	0.42164	1	
Pb	**0.86561	0.22871	0.39047	**0.8332	**0.66591	**0.89938	**0.5521	**0.91857	1

Sediment

The PCA results showed two PCs with eigenvalues greater than 1 and a cumulative variance of 99.99% (Table 6b (ii)). The first principal component (PC1) accounted for about 99.88% of the total variance, with positive loadings for Fe. PC2 accounted for about 99.99% of the total variance. A major geogenic origin is

suggested by PC1 (99.88%), which is significantly loaded on Fe and most likely results from the natural mineral composition of the riverbed silt.

PC2 accounted for about 99.99% of the total variance, with positive loadings for Cr, Mn, Fe, Ni, Cu, As, Cd, and Pb, and a strong negative loading for Zn only. PC2 demonstrates

Table 6(a): PCA analysis in Groundwater

Eigenvalue	82.5517	9.97311	0.314191	0.248485
% variance	88.642	10.709	0.33737	0.26682
%Cumulativevariance	88.642	99.351	99.68837	99.95519
Component	PC 1	PC 2	PC 3	PC 4
Cr	-4.4961	-0.38617	-0.76009	1.1127
Mn	-1.4911	-0.13178	1.3558	0.52591
Fe	22.2	-3.3039	-0.11581	-0.01808
Ni	-4.841	-0.89757	-0.04093	-0.27375
Cu	-4.0032	-0.76448	0.078838	-0.28372
Zn	6.4503	8.0669	-0.1042	-0.10496
As	-4.8451	-0.9052	-0.17247	-0.30546
Cd	-4.8992	-0.91071	-0.17761	-0.32172
Pb	-4.0744	-0.76713	-0.06356	-0.33095

Table 6 (b): PCA analysis in (i) Surface water (ii) Sediment.

(i) Surface water				(ii) Sediment			
Eigenvalue	184.662	83.6554	4.32615	Eigenvalue	1.94E+09	2.21E+06	2.80E+04
% variance	67.532	30.593	1.5821	% variance	9.99E+01	1.13E-01	1.00E-03
% Cumulativevariance	67.532	98.125	99.7071	%Cumulativevariance	99.88	99.993	99.994
Component	PC 1	PC 2	PC 3	Component	PC 1	PC 2	PC 3
Cr	-8.9704	1.6364	-0.76003	Cr	-15455	472.57	103.61
Mn	2.5021	1.8833	5.3096	Mn	-12665	757.77	-303.79
Fe	30.508	11.304	-1.4182	Fe	1.18E+05	95.186	7.7474
Ni	-9.3357	1.7513	-0.94725	Ni	-15658	638.33	99.258
Cu	12.022	-22.853	-0.52159	Cu	-15034	292.14	-254.8
Zn	-0.88259	1.3385	0.79854	Zn	-11785	-3918.7	-3.7007
As	-9.5218	1.7162	-0.84377	As	-15743	667.7	77.966
Cd	-9.4776	1.603	-0.83256	Cd	-15794	654.72	101.39
Pb	-6.8447	1.62	-0.78477	Pb	-15365	340.27	172.31

anthropogenic contamination, particularly from industrial waste deposition and atmospheric deposition from surrounding factories.

In all PCA analysis of groundwater, surface water, and sediments, most of the variance in the first two components was controlled by parameters and pollution sources. Compared to groundwater, surface water, and sediment, the particle size distribution of the sediment is another significant factor influencing the amelioration of heavy metals (Zonta *et al.*, 2019). Heavy metals can be adsorbed by sediment particles through chemical and physical means. The specific surface area of the sediment plays a major role in physical adsorption; sediment with smaller particle size has a larger surface area and stronger adsorption capability. Chemical adsorption is

related to the active ingredients present in sediment particles, and sediment with smaller particle sizes tends to adsorb more active ingredients (Hegedusova *et al.*, 2016; Zonta *et al.*, 2019).

Indexes of Heavy Metal Pollution, HPI and PLI

Out of 15 groundwater samples, 3 were classified as excellent, 4 as good, 3 as poor, 1 as very poor, and 4 as unacceptable. In terms of surface water, the HPI results showed that 3 sample locations were in a good category, 3 were poor, 1 was very poor, and 8 were at unacceptable critical pollution levels (Table 7). On the other hand, Table 8 displays the results of the Pollution Load Index (PLI) for sediment samples. This index provides a quick and easy way to compare different heavy metal pollution levels. $PLI > 1$ indicates the presence of pollution; $PLI < 1$

Table 7: HPI and PLI values of Groundwater (GW), Surface water (SW), and Sediments (Sd)

Sample (GW)	HPI	Level	sample (SW)	HPI	Level	sample (Sd)	PLI	Status
G1	753.70	Unaccepted	S1	914.25	Unaccepted	Sd1	5184.17	Polluted
G2	148.96	Unaccepted	S2	62.87	Poor	Sd2	6053.27	Polluted
G3	90.38	Very Poor	S3	267.17	Unaccepted	Sd3	4191.86	Polluted
G4	24.78	Excellent	S4	161.04	Unaccepted	Sd4	3323.94	Polluted
G5	73.55	Poor	S5	115.02	Unaccepted	Sd5	3689.72	Polluted
G6	68.10	Poor	S6	283.13	Unaccepted	Sd6	9863.29	Polluted
G7	66.62	Poor	S7	190.66	Unaccepted	Sd7	7519.02	Polluted
G8	115.36	Unaccepted	S8	491.65	Unaccepted	Sd8	8279.72	Polluted
G9	39.77	Good	S9	131.3	Unaccepted	Sd9	3501.21	Polluted
G10	28.56	Good	S10	87.78	Very Poor	Sd10	3175.49	Polluted
G11	27.55	Good	S11	52.91	Poor	Sd11	3735.08	Polluted
G12	159.32	Unaccepted	S12	65.60	Poor	Sd12	26263.6	Polluted
G13	16.873	Excellent	S13	27.82	Good	Sd13	23649.4	Polluted
G14	30.0303	Good	S14	30.45	Good	Sd14	4999.64	Polluted
G15	19.5968	Excellent	S15	45.65	Good	Sd15	4671.94	Polluted
Max	753.70		Max	914.25		Max	26263.6	
Min	16.87		Min	27.82		Min	3175.49	
Average	110.88		Average	195.15		Average	7873.42	

Table 8: Risk Index level (a) in groundwater and (b) in surface water

(a)			(b)		
Sample (GW)	RI	Risk Level	Sample (SW)	RI	Risk Level
G1	4069.70	Very high	S1	1347.30	Very high
G2	2612.27	Very high	S2	723.38	Very high
G3	1966.03	Very high	S3	2564.21	Very high
G4	1882.64	Very high	S4	3350.80	Very high
G5	2165.48	Very high	S5	4761.98	Very high
G6	2317.72	Very high	S6	6909.56	Very high
G7	2128.89	Very high	S7	5917.51	Very high
G8	3599.16	Very high	S8	26602	Very high
G9	2305.54	Very high	S9	4888.48	Very high
G10	2215.40	Very high	S10	5479.72	Very high
G11	2025.76	Very high	S11	3515.93	Very high
G12	20259	Very high	S12	2959.21	Very high
G13	2412.38	Very high	S13	2598.88	Very high
G14	2644.95	Very high	S14	3129.41	Very high
G15	2064.57	Very high	S15	2836.95	Very high

indicates the absence of metal pollution. In this study, all sample locations showed PLI values greater than 1, indicating metal pollution for all metals (Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, Pb). Due to biomagnification and toxicity, heavy metals pose a hazard to aquatic life, human health, and the environment, making research on heavy metal concentrations crucial (Han *et al.*, 2018; Vahidipour *et al.*, 2022). According to Rezaei *et al.*, (2019), HPI is a crucial method for evaluating the content of heavy metals in water. The HPI was determined by assigning a score or weight to each selected criterion.

Ecological Risk Index (ERI)

Table 8a shows the initial observations of the RI (potential ecological risk) for heavy metals in groundwater samples before the ERI evaluation. The RI is classified into four risk levels, as described in the literature (Bhutani *et al.*, 2017; Adimalla and Wang, 2018; Taiwo *et al.*, 2019). In this study, the RI results showed a very high potential risk index (> 600) for all samples, concerning the 8 heavy metals mentioned above. In surface water samples, RI results revealed a very high potential risk (> 600) for all studied heavy metals (Table 8a). The RI considers various factors, including heavy metal synergistic effects, toxicology, background concentrations of heavy metals, and environmental sensitivity (Han *et al.*, 2018). In this investigation, RI results concluded that a few sample locations (Sd-1, 2, 9, and 10) showed low potential risk for all metals, 2 samples (Sd-2, Sd-11) showed moderate risk, 3 samples (Sd-4, Sd-14, Sd-15) showed considerable risk, and 5 sample locations (Sd-6, Sd-7, Sd-8, Sd-12, and Sd-13) showed a very high potential risk index.

Assessing the Health Risks Linked to Heavy Metals Exposure in the Kali River

Assessing the health risks (Table 8b) associated with heavy metal exposure in the Kali River involves a comprehensive evaluation of potential hazards to human health from contaminants present in groundwater, surface water, sediment, and aquatic organisms. Metals such as Cr, Ni, and Pb concentrations exceeded permissible limits in GW, SW, and Sd significant non-carcinogenic and carcinogenic risks. Stations G8, S8, and Sd12, which exhibited peak values for Cd, As, and Pb, also corresponded with poor physicochemical quality and high OM content, reinforcing the role of water chemistry and sediment composition in influencing human exposure risks. These contaminants are mostly introduced through anthropogenic activities, with some contribution from natural sources, as explained by the PCA analysis (Table 8). This study found that heavy metals such as Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, and Pb were present in the groundwater, surface water, and sediment of the Kali River. After PCA and correlation analysis, it was observed that strong two-tailed correlations ($P < 0.05$) were found throughout the study, and the PCA results provided cumulative variance for each heavy metal. The risk index (Table 8b) explains the current conditions of the sampling stations along the Kali River, which require urgent attention. Due to increasing industrialization and modernization, large amounts of heavy metals used in various sectors are directly or indirectly discharged into river areas. The HPI and PLI values calculated in this study highlight the need for urgent intervention to reduce the heavy metal

pollution load in the river. Heavy metals pose several health risks when their concentrations exceed permissible limits, including neurotoxicity, carcinogenicity, organ damage, increased risk of hypertension, kidney damage, and reproductive disorders (Kumar and Dwivedi, 2020). HMs can accumulate and biomagnify at each trophic level, leading to severe impacts on all life forms (Huang *et al.*, 2020). Based on these results, researchers should focus on managing heavy metal contamination in the river waters and sediments of the Kali River to prevent further degradation.

CONCLUSION

The current investigation is being carried out to assess heavy metal pollution and physico chemical parameters of Kali River at fifteen sampling points (S1-S15). The investigation found that anthropogenic influence, were mainly from industrial discharge and urban runoff on the Kali River. Most water and sediments parameters indicated notable chemical pollution, with high conductivity in sediment being the only concerning factor presently but, in the future, may become an alarming situation. The average HPI was determined to be higher above the crucial value in GW (110), SW (195), and Sd (7873). Each sampling sites were heavy metals were found to be significantly loaded contributed to a distinct principal component in the PCA of heavy metal data sets. This result suggests that the pollution load in river water is significantly influenced by human and industrial sources. The findings highlight the urgent need for intervention to restore river health. The recommendation include:

- Mandatory treatment of industrial effluents before discharge via advanced Wastewater Treatment Plants, particularly near major industries.
 - Sediment remediation, including dredging of highly contaminated zones (e.g., Sd12 and Sd13) and phytoremediation to reduce bioavailable heavy metals.
 - Buffer zones and green belts along riverbanks to filter runoff and minimize direct pollutant entry.
- Implementing this measure can reduce the current pollution load, safeguard aquatic ecosystems, and protect communities relying on the Kali River for agriculture and livelihoods.

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Availability of data and materials

All data related to this publication are made available in the article.

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