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Integrated Multivariate and Spatial Assessment of Heavy Metal Contamination and Associated Health Risks in Indo-Gangetic Alluvial Aquifer: A Case Study from the Gorakhpur District, India

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Abstract : Groundwater quality assessment is critical for sustaining safe drinking water supplies, particularly in vulnerable alluvial aquifers such as those of the Indo-Gangetic Basin. This study evaluates the concentration and distribution of eight heavy metals — Zinc (Zn), Chromium (Cr), Iron (Fe), Copper (Cu), Manganese (Mn), Arsenic (As), Lead (Pb), and Uranium (U) — alongside pH and Electrical Conductivity (EC) in groundwater samples collected from 32 locations across Gorakhpur District, Uttar Pradesh. Groundwater samples were collected and analysed following standard protocols.

Samples were collected and analysed following APHA and WHO protocols. Descriptive statistics indicated that 68.8% of the samples exceeded WHO limits for iron, while manganese and arsenic exceeded safe levels in 6 and 1 samples, respectively. Spearman's rank correlation analysis supported strong positive associations among Fe, Mn, and EC, suggesting a shared mobilization mechanism. Multivariate analysis through Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA) identified geogenic reductive processes as dominant contributors to Fe and Mn enrichment. while GIS-based spatial mapping highlighted distinct contamination hotspots in the central and northern parts of the district.

Human health risk assessment showed Hazard Index (HI) >1 in 9 locations for adults, primarily due to iron and manganese exposure. Carcinogenic Risk (CR) assessment flagged elevated lifetime cancer risks ($>10^{-4}$) at 16 locations due to arsenic, lead and uranium. These findings highlight localized but significant non-carcinogenic and carcinogenic risks, emphasizing the need for targeted mitigation, periodic monitoring, and community health surveillance. This integrative framework combining hydro-chemical assessment, multivariate statistics, spatial analysis, and health risk assessment provides a robust basis for sustainable groundwater management in vulnerable alluvial settings.

Keywords : Groundwater Quality, Heavy Metal Contamination, Multivariate Statistical Analysis, PCA, Health Risk Assessment

I. INTRODUCTION

Groundwater serves as an essential resource for drinking, irrigation, and industrial use, particularly in densely populated and agriculturally intensive regions such as the Indo-Gangetic Basin (Shah, 2009; MacDonald et al., 2016). This basin, underlain by extensive Quaternary alluvial deposits, forms one of the most prolific aquifer systems globally, supplying water to nearly a billion people across northern India, Bangladesh, Nepal, and Pakistan (World Bank, 2010; Mukherjee, 2018). The aquifers are primarily composed of unconsolidated sands, silts, and clays deposited by major river systems during the Himalayan orogeny process, creating high-yielding but increasingly vulnerable groundwater reserves (Valdiya, 2010; CGWB, 2022). Over the past few decades, rising demand due to population growth, agricultural intensification, and urban expansion has led to excessive abstraction and deterioration in groundwater quality (Scanlon et al., 2019; CGWB, 2024).

Heavy metal contamination in groundwater has emerged as a significant public health concern in many regions of the Indo-Gangetic Plain. Elements such as arsenic (As), iron (Fe), uranium (U), manganese (Mn), lead (Pb), chromium (Cr), copper (Cu), and zinc (Zn) are frequently reported at concentrations exceeding national and international safety guidelines (Saha et al., 2011; Singh et al., 2013; Tchounwou et al., 2012). While some trace metals are essential micronutrients, chronic exposure to elevated levels can lead to severe health effects, including neurological disorders, organ toxicity, and cancer (WHO, 2011; USEPA, 2015). These contaminants may originate from natural geogenic sources such as mineral weathering and sediment dissolution, or from anthropogenic activities including fertilizer application, industrial discharge, and leaching from landfills (Chakraborti et al., 2010; Kumar et al., 2021).

The Indo-Gangetic Basin is particularly vulnerable due to widespread arsenic contamination in shallow aquifers, especially in parts of India (Bihar, Uttar Pradesh, West Bengal States) and Bangladesh, where concentrations often exceed 50 µg/L — far above the WHO limit of 10 µg/L (Shrestha et al., 2016; Chakraborti et al., 2010). Uranium has also been increasingly reported in groundwater in regions such as Punjab, Haryana, Rajasthan, and Gujarat States of India, posing nephrotoxic and radiological hazards (Saini et al., 2017; Singh et al., 2009). Iron and manganese, while not typically classified as primary toxicants, can cause cumulative health impacts when present at high levels and are often associated with reducing environments in alluvial aquifers (Smedley & Kinniburgh, 2002; CGWB, 2022).

Effective groundwater quality assessment must go beyond elemental concentration measurements to include analysis of underlying geochemical processes. Multivariate statistical techniques such as Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA) have proven effective in identifying potential contaminant sources, hydrochemical facies, and spatial patterns of contamination (Vega et al., 1998; Helena et al., 2000). PCA reduces data complexity by extracting orthogonal components that explain variance and suggest dominant processes, while HCA clusters samples with similar water quality characteristics, revealing regional coherence (Liu et al., 2003; Simeonov et al., 2003).

This study investigates the groundwater quality of the Indo-Gangetic alluvial aquifer, focusing on eight heavy metals (As, Cr, Cu, Fe, Pb, Mn, U, Zn) along with pH and electrical conductivity (EC). Using descriptive statistics, PCA, and HCA, the study aims to identify key geochemical processes and contamination signatures. Additionally, a human health risk assessment based on United States Environmental Protection Agency (USEPA) methodology was conducted to calculate Hazard Quotients (HQs), Hazard Indices (HIs), and Carcinogenic Risks (CRs) for different demographic groups (USEPA, 2004; Wu et al., 2009; Li et al., 2014). The findings provide essential insights for policymakers, planners, and researchers working toward sustainable groundwater management in vulnerable regions of the Indo-Gangetic Basin

II. STUDY AREA

Gorakhpur District (Fig. 1), located in the northeastern part of Uttar Pradesh, lies within the Indo-Gangetic alluvial plains and spans an area of approximately 3,483 km² between latitudes 26°46′ to 27°05′ N and longitudes 83°16′ to 83°37′ E (Census of India, 2011; CGWB, 2020). The district is traversed by a dense fluvial network dominated by the Rapti and Ghaghra rivers, which significantly influence local geomorphology, aquifer recharge, and groundwater dynamics (Kumar et al., 2019; CGWB, 2022).

The region is geologically underlain by Quaternary alluvium comprising varying proportions of sand, silt, clay, and sandy clay, along with kankar and gravel deposits (Valdiya, 2010; CGWB, 2022). These deposits are stratigraphically classified into older alluvium, forming elevated terraces, and younger alluvium, confined to active floodplains (Srivastava et al., 1994; Saha et al., 2011). Groundwater occurs under both unconfined and confined conditions within fine to coarse-grained sand horizons and serves as the primary source of drinking water across the district (CGWB, 2018).

As per the 2011 Census, Gorakhpur district had a population of over 4.4 million, with a decadal growth rate of 17.81% Census of India, 2011). Based on projections, the population is estimated to have exceeded 5 million by 2024 (United Nations, 2022). With the entire drinking water supply in the district reliant on groundwater, the population remains highly vulnerable to issues related to groundwater quality. Studies have reported iron, manganese, and fluoride concentrations above permissible limits in the region, driven by both natural geochemical processes and anthropogenic inputs (Joshi & Gupta, 2018; Rai et al, 2018). Recharge is mainly governed by monsoonal rainfall, river infiltration, and agricultural return flow (Scanlon et al., 2006; CGWB, 2022).

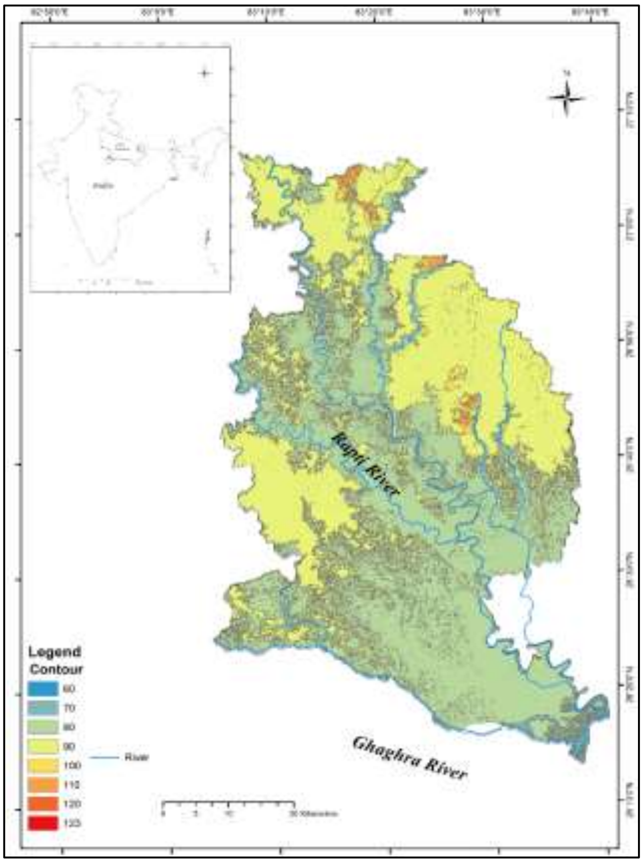

Figure 1: Study Area Map

III. METHODOLOGY

3.1 Sample Collection, Preservation and Analysis

Groundwater samples were collected from drinking water sources from 32 systematically selected locations (Fig. 2), in pre-monsoon season of 2023, to capture spatial variability across the study area. Sampling was performed using pre-cleaned, high-density polypropylene bottles (1 L) in accordance with standard protocols to minimize contamination risks (APHA, 2017; WHO, 2011). Prior to sampling, each handpump was purged for 2–5 minutes to remove stagnant water and ensure retrieval of representative aquifer water (USEPA, 2004; BIS, 2012).

Immediately after collection, samples were filtered using sterile 0.45 µm membrane filters to separate dissolved and particulate fractions, following internationally accepted guidelines (ISO, 2014; APHA, 2017). For trace metal analysis, samples were preserved by acidifying with 2% ultrapure nitric acid (HNO_3) to lower the pH below 2.0, thereby stabilizing dissolved metal species and preventing adsorption losses (USEPA, 1996; WHO, 2017; Hem, 1985).

On-site measurements of pH and electrical conductivity (EC) were conducted using calibrated portable meters (CGWB, 2022; BIS, 2012). Instruments were regularly calibrated using certified standards to ensure data quality (ISO, 2014; USEPA, 2004). All samples were labelled, stored in ice-cooled containers, and transported to the laboratory for further analysis (CGWB, 2022; APHA, 2017). Concentrations of eight heavy metals, namely Zinc (Zn), Chromium (Cr), Iron (Fe), Copper (Cu), Manganese (Mn), Arsenic (As), Lead (Pb), and Uranium (U), were quantitatively determined in each groundwater sample using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) in accordance with standard analytical procedures (APHA, 2017; WHO, 2011). Prior to analysis, all instruments were calibrated using certified multi-element standard solutions, and appropriate quality control measures, including blanks, duplicates, and spiked samples, were incorporated to ensure analytical precision and accuracy (APHA, 2017; BIS, 2012).

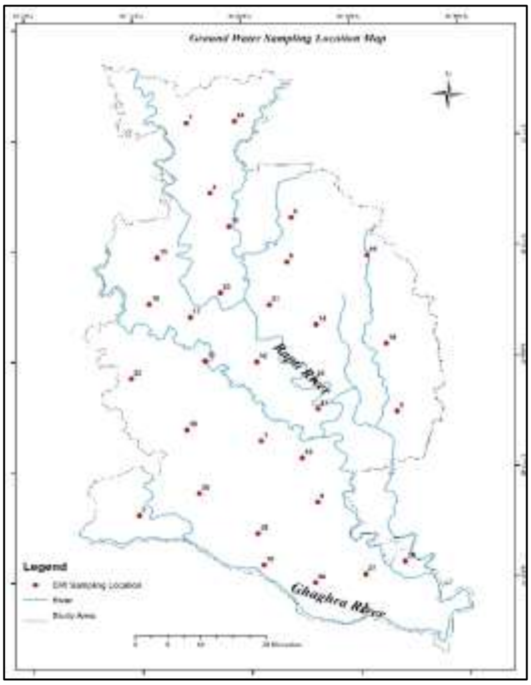

Figure 2: Ground water sampling location map

3.2 Data Analysis

The groundwater quality dataset comprising concentrations of eight heavy metals (Zn, Cr, Fe, Cu, Mn, As, Pb, U), along with pH and Electrical Conductivity (EC), was subjected to systematic statistical and multivariate analyses to understand underlying patterns, source factors, spatial trends, and associated health risks.

Descriptive statistical parameters, including minimum, maximum, mean, median, and standard deviation, were computed for each water quality indicator to characterize their variability and central tendency across the study area (APHA, 2017; WHO, 2011). These statistical descriptors provided a foundational understanding of the spread and skewness in parameter concentrations. Box plots for each parameter were created.

Spearman's rank correlation analysis was employed to explore non-parametric relationships among the chemical parameters. Spearman's correlation is particularly suited for environmental datasets that may not satisfy normality assumptions (Zhang., 2012a; Liu et al., 2003). The computed correlation matrix helped identify statistically significant positive or negative associations between trace metals and physio-chemical parameters, thus supporting the identification of common sources and mobilization pathways.

Geographic Information System (GIS)-based spatial distribution analysis was undertaken to visualize the areal variation of key groundwater quality parameters. Inverse Distance Weighting (IDW) interpolation was applied in ArcGIS-10.6.1 software to generate thematic maps illustrating the concentration distribution across the study area (Tabios and Salas 1985; Mueller et al. 2004). Spatial mapping allowed identification of hotspots, spatial anomalies, and regions requiring priority attention.

Principal Component Analysis (PCA) was employed to reduce the dimensionality of the groundwater dataset and to identify the dominant factors influencing groundwater quality, following established methodologies for environmental data analysis (Helena et al., 2000). Before conducting PCA, the raw data were standardized using Z-score transformation to eliminate the influence of differing measurement units and magnitudes, which is critical to ensuring unbiased factor extraction (Liu et al., 2003; Shrestha & Kazama, 2007). The analysis was performed on a correlation matrix constructed from the standardized dataset, encompassing eight heavy metals and two physicochemical parameters (pH and EC). The number of significant components were determined based on eigenvalues (Kaiser criterion), scree plot inspection, and cumulative variance considerations (Helena et al., 2000; Vega et al., 1998). Varimax rotation was applied to the extracted components to improve the interpretability of loadings and to more clearly associate parameters with specific hydrochemical processes (Zhou et al., 2007). The resulting component loadings were interpreted to infer potential sources and controlling mechanisms for the observed groundwater chemistry, such as geogenic weathering, redox conditions, or anthropogenic influences.

Hierarchical Cluster Analysis (HCA) was applied to group groundwater sample locations and parameters based on their chemical similarity and underlying hydrogeochemical characteristics, as recommended for spatial classification and source identification in environmental datasets (Helena et al., 2000; Reghunath et al., 2002; Simeonov et al., 2003). The clustering was performed using an agglomerative approach with Ward's linkage method, which minimizes the variance within clusters during the merging process, and euclidean distance was selected as the dissimilarity metric due to its suitability for continuous environmental datasets (Helena et al., 2000; Vega et al., 1998). A dendrogram was constructed to visually represent the hierarchical structure of relationships among all groundwater sampling sites and measured water quality parameters, a method widely employed in hydrogeological and environmental studies to uncover grouping patterns and chemical affinities (Cloutier et al., 2008; Fabbrocino et al., 2019). The optimal number of clusters was initially inferred by examining significant vertical breaks in the dendrogram and further validated using the Elbow Method, which plots the within-cluster sum of squares (inertia) against the number of clusters to identify a point of diminishing returns (Ketchen & Shook, 1996). This method allowed the segmentation of the dataset into chemically coherent groups, facilitating interpretation of hydrochemical facies and spatial risk zones.

In addition, human health risk assessment was performed by estimating the Hazard Quotient (HQ), is a dimensionless metric used to evaluate non-carcinogenic health risks associated with exposure to a single contaminant (USEPA, 1989). It is defined as the ratio of the estimated exposure dose (ADD) to a reference dose (RfD), where HQ > 1 indicates a potential health risk (USEPA, 1989; Wu et al., 2009). When multiple contaminants are present, their cumulative impact is assessed using the Hazard Index (HI), which is the sum of individual HQs. HQ and HI values were calculated separately for male and female, using group-specific exposure assumptions for ingestion rate, body weight, exposure duration, and averaging time (ICMR-NIN,2020). An HI exceeding unity suggests potential additive or synergistic health effects, especially among sensitive populations such as children or the elderly (USEPA, 2004; Li et al., 2014).

The Average Daily Dose (ADD) for each metal through oral ingestion pathway was calculated by equation 1.

$$ADD = (C * IR * ED)/\,(BW * AT) \quad (1)$$

where:

C = Concentration of contaminant in water (mg/L)
IR = Ingestion Rate (L/day)
EF = Exposure Frequency (days/year)
ED = Exposure Duration (years)
BW = Body Weight (kg)
AT = Averaging Time (days)

Hazard Quotient (HQ) for individual metals was computed by dividing the ADD by respective Reference Dose (RfD) values as per equation 2.

The HQ is calculated as:

$$HQ = ADD/RfD \quad (2)$$

Where:

ADD is expressed in mg/kg/day.

RfD is reference dose by United States Environmental Protection Agency (USEPA).

the Hazard Index (HI) was calculated as the sum of HQs (equation 3) to evaluate the cumulative non-carcinogenic risk (USEPA, 1989; USEPA, 2004; WHO, 2017).

$$HI = \sum HQ \quad (3)$$

HI values exceeding unity were considered indicative of potential health hazards, especially for sensitive sub-populations.

Carcinogenic risk assessment was carried out to estimate the potential lifetime cancer risk associated with oral ingestion of groundwater contaminated with trace elements. The analysis followed the guidelines provided by the United States Environmental Protection Agency (USEPA, 2005). The carcinogenic risk (CR) for each metal was calculated using the equation 4:

$$CR = LADD * SF \quad (4)$$

where LADD is the Lifetime Average Daily Dose (mg/kg/day), and SF is the carcinogenic slope factor (mg/kg/day^{-1}), representing the incremental risk per unit of chemical intake. The LADD was calculated using the standard formula (equation 5):

$$LADD = (C * IR * EF * ED)/\,(BW * AT) \quad (5)$$

Here, C is the concentration of the contaminant (mg/L), IR is the daily ingestion rate (L/day), EF is the exposure frequency (days/year), ED is the exposure duration (years), BW is the body weight (kg), and AT is the averaging time (days), which for carcinogenic effects equals lifetime exposure (ED × 365). Carcinogenic slope factors (SFs) were obtained from authoritative toxicological databases and peer-reviewed literature. The slope factor for arsenic was taken as 1.5 mg/kg/day^{-1}, based on long-standing documentation of its carcinogenicity by the United States Environmental Protection Agency (USEPA, 1998; USEPA, 2005). For uranium, a slope factor of 0.0005 mg/kg/day^{-1} was adopted from World Health Organization (WHO) guidance and supporting literature on uranium's chemical toxicity and radiological behavior in groundwater (WHO, 2011; Saini et al., 2017). Although lead is classified as a probable human carcinogen, the USEPA has not established an official oral slope factor. Therefore, a literature-derived estimate of 0.0085 mg/kg/day^{-1} was used, consistent with values applied in previous environmental health risk studies (Widyantoro, 2021). Carcinogenic risk (CR) values were calculated separately for males and females. In line with USEPA guidelines, CR values exceeding 1×10^{-4} were considered indicative of unacceptable lifetime cancer risk, CR values 10^{-6} < to ≤ 10^{-4} were considered acceptable risk while CR values ≤ 10^{-6} were considered as negligible risk (USEPA, 2005).

All statistical analyses were conducted using Microsoft Excel (Office 365) and open-source platforms such as R and Python (Pandas, NumPy, Scikit-learn libraries). GIS-based spatial interpolations and mapping were completed using ArcGIS 10.6.1 software, ensuring methodological robustness and reproducibility throughout the data analysis workflow.

IV. RESULTS AND DISCUSSION

General Statistical Analysis

Groundwater quality analysis across 32 sampled locations in Gorakhpur District reflects an overall favourable compliance with World Health Organization (WHO) drinking water standards for most assessed parameters as indicated by the table-1. Chromium (Cr) and Copper (Cu) were undetectable across all groundwater samples, suggesting negligible industrial or geogenic inputs for these metals in the study area (APHA, 2017; ISO, 2014). Box plots (Fig. 3) were employed to statistically evaluate the distribution of groundwater quality parameters, including pH, electrical conductivity (EC), and concentrations of key heavy metals. The pH values ranged from approximately 7.55 to 8.23, with a median of 7.95, indicating slightly alkaline (WHO, 2017) groundwater conditions typical of alluvial aquifers (Smedley & Kinniburgh, 2002). The distribution was relatively symmetric and displayed no significant outliers, suggesting consistent pH behaviour across the study area. Electrical conductivity (EC) exhibited a broader range, from 328 to over 1000 µS/cm, with a median value near 523 µS/cm. The positively skewed distribution of EC implies elevated ionic concentrations at certain locations, likely due to localized mineral dissolution, anthropogenic influence, or both (Freeze & Cherry, 1979)

Table 1: Statistical summary of the results.n=32 (values are in µg/L, except for pH and EC)

GW Quality Parameter	Min	Max	Average	Median	Standard Deviation	WHO Standard	Number of Samples above WHO limit
pH	7.54	8.21	7.93	7.95	0.165	6.5 – 8.5	0
EC (µS/cm)	328	1030	582	523	189	1500	0
Cr	0	0	0	0	0	50	0
Fe	0	5172	1159	927	1192	300	22
Mn	0	208	64	64	55	100	6
Cu	0	0	0	0	0	2000	0
Zn	0	1515	392	192	482	3000	0
As	0	22	2.31	1.15	4.15	10	1
Pb	0	2.06	0.50	0	0.78	10	0
U	0	12.35	1.85	0	3.09	30	0

Box plots for trace metals were plotted on a logarithmic scale to accommodate the wide concentration range. Iron (Fe) displayed the highest variability, with values ranging from below 100 µg/L to over 5000 µg/L, and multiple outliers. The median Fe concentration exceeded the WHO permissible limit (300 µg/L). Notably, 22 out of 32 samples exceeded the WHO permissible limit of 0.30 mg/L, indicating widespread iron enrichment likely sourced from natural leaching of iron-rich alluvial deposits under fluctuating redox conditions (Smedley & Kinniburgh, 2002; CGWB, 2022).

Elevated iron levels not only affect aesthetic water quality but are increasingly recognized for potential adverse health impacts when consumed in high concentrations over prolonged periods (WHO, 2011; USEPA, 2015). Manganese (Mn) concentrations mostly fell below 300 µg/L, with a median value close to the WHO threshold of 100 µg/L. six samples exceeded the guideline, suggesting localized mobilization under reducing aquifer conditions (Hem, 1985; Stumm & Morgan, 1996). Manganese contamination, though less commonly discussed compared to iron and arsenic, has been associated with neurological and cognitive effects, particularly in sensitive populations (WHO, 2017; ATSDR, 2012).

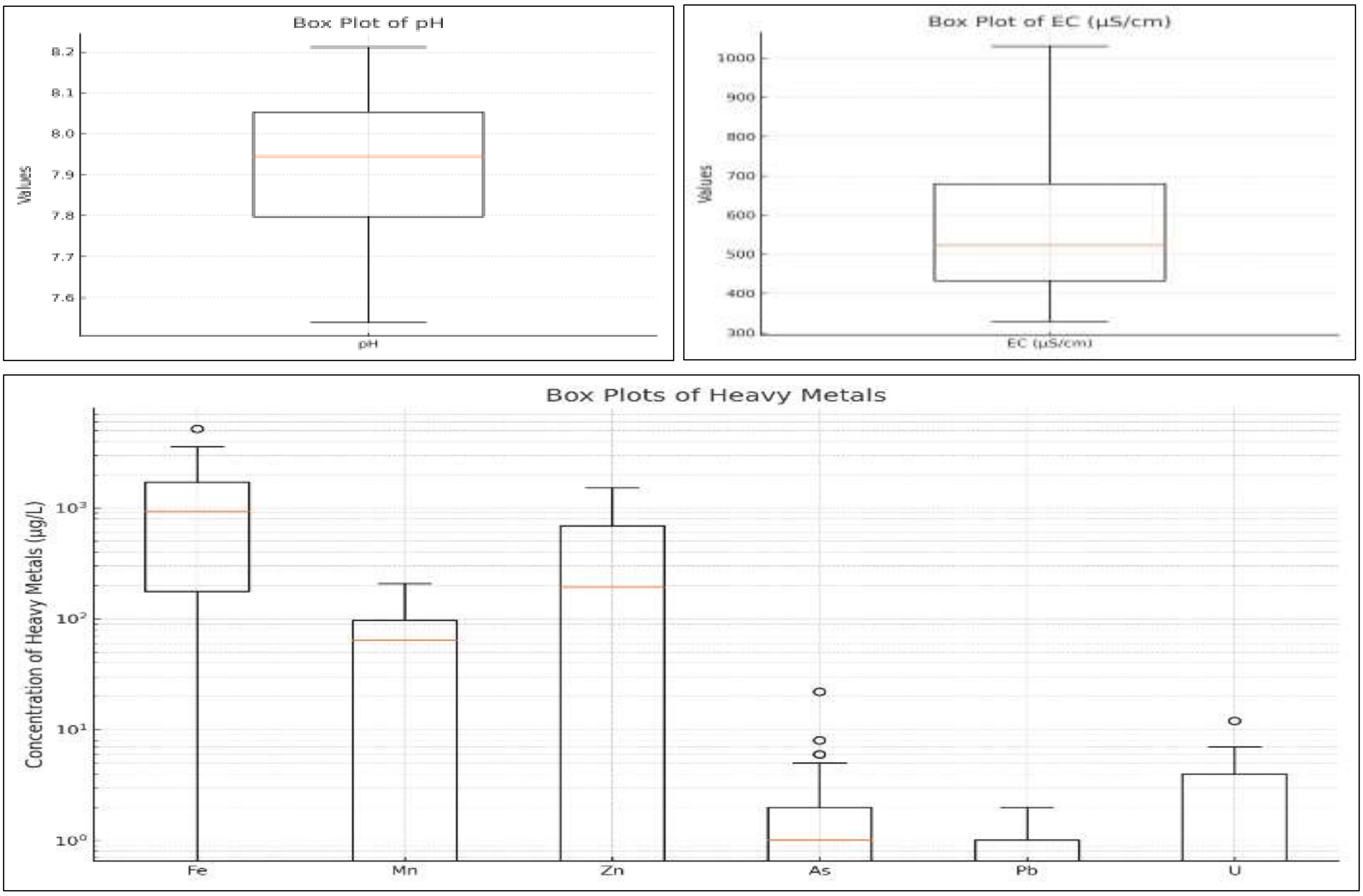

Figure 3: Box Plots of Assessd ground water qaulity parameters.

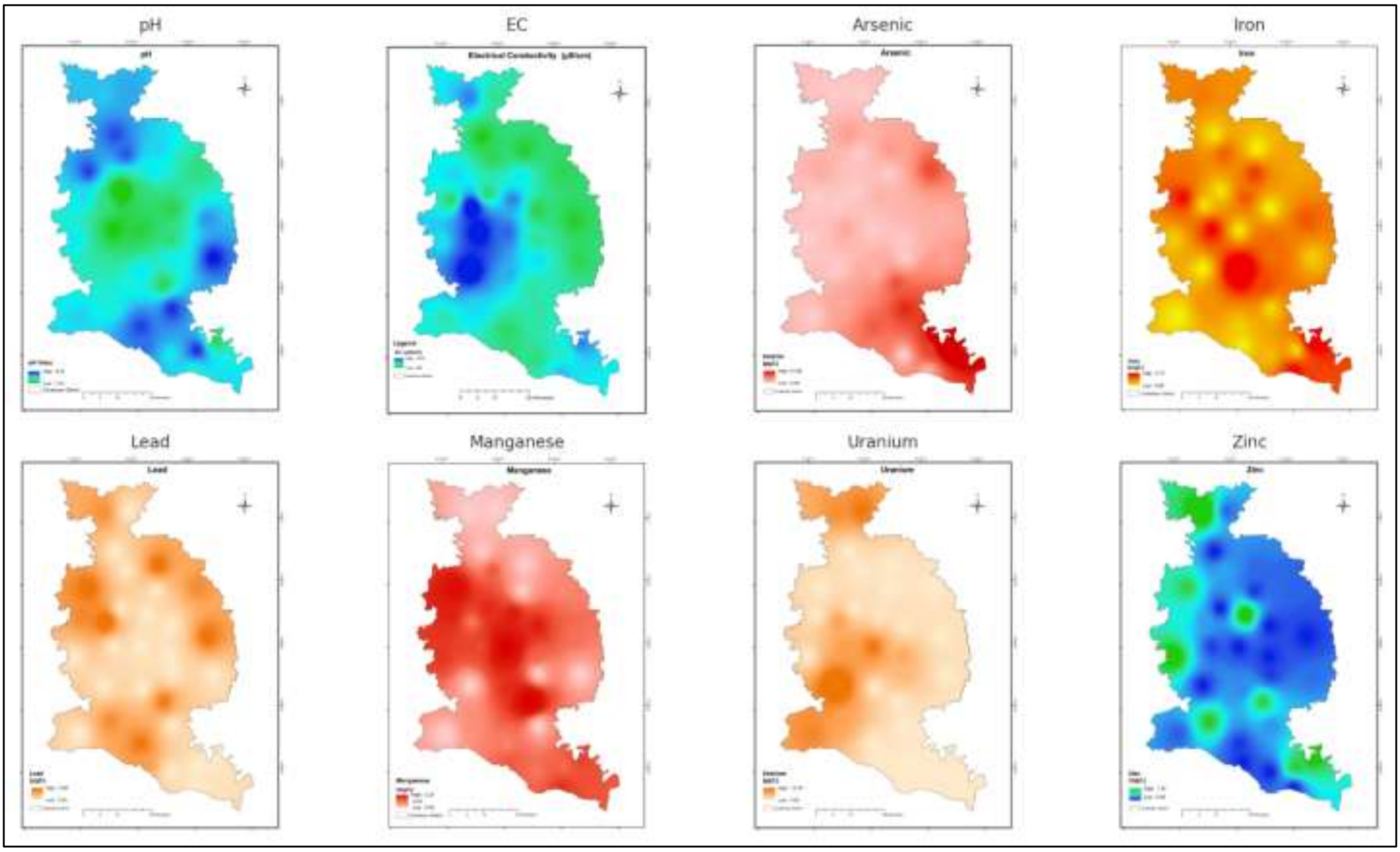

Figure 4: Spatial distribution of ground water quality parameters.

Zinc (Zn) showed a wide spread, although all values remained within the acceptable range of 3000 µg/L. Arsenic (As) was detected at low concentrations, with a maximum recorded value of 0.02 mg/L. Only one sample exceeded the WHO guideline of 0.01 mg/L, indicating sporadic arsenic contamination. Such isolated exceedances are consistent with known patterns of arsenic mobilization in

Indo-Gangetic floodplains, influenced by reductive dissolution of iron oxyhydroxides (Chakraborti et al., 2010; Shrestha et al., 2016). Lead (Pb) concentrations remained uniformly low with no outliers, suggesting negligible contamination risk. Uranium (U) concentrations were also largely below the WHO guideline of 30 µg/L, with a few mild outliers; the median value was close to 1–2 µg/L, implying limited radiotoxicological risk under existing conditions (WHO, 2011; Saini et al., 2020; Singh et al., 2020).

Spatial Analysis

The spatial distribution (Fig.4) of groundwater quality parameters across Gorakhpur District reveals considerable heterogeneity, reflecting both natural and anthropogenic influences. pH values were uniformly within the WHO permissible range (6.5–8.5), indicating mildly alkaline conditions characteristic of alluvial aquifers (WHO, 2011; CGWB, 2022). Elevated electrical conductivity (EC) in central and southern regions points to mineral dissolution and agricultural runoff. Iron (Fe) and manganese (Mn) showed significant enrichment in central and southern areas, likely mobilized under reducing aquifer conditions (Smedley & Kinniburgh, 2002). Arsenic (As) was concentrated in the southeastern parts, consistent with patterns observed in other Ganges floodplain areas (Chakraborti et al., 2010; Shrestha et al., 2016). Uranium (U) hotspots in the southwest suggest possible geogenic mobilization under alkaline, oxidizing environments (Saini et al., 2020). Zinc (Zn) and lead (Pb) were generally low, with some localized elevations possibly linked to anthropogenic inputs (Singh et al., 2013). Overall, the maps highlight potential contamination hotspots, particularly for As, Fe, Mn, and U, and underscore the need for targeted monitoring and mitigation strategies.

Spearman correlation

The spearman correlation coefficient matrix (ρ-values) revealed several statistically meaningful associations. A moderate negative correlation was observed between pH and Mn (ρ = -0.45), suggesting that manganese concentrations tend to be higher in lower pH conditions. This aligns with known

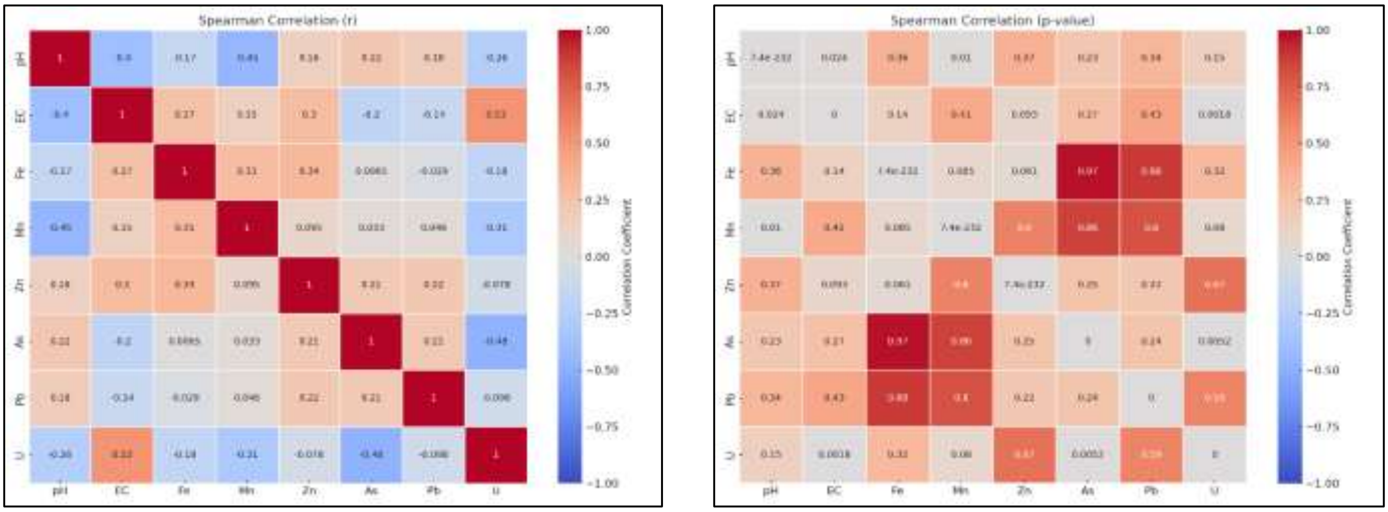

Figure 5: Spearman correlation r-value and p-value matrix.

geochemical behaviour of Mn, which becomes more soluble under reducing and low-pH conditions (Smedley & Kinniburgh, 2002). Electrical conductivity (EC) exhibited a positive correlation with uranium (ρ = 0.53), implying that locations with higher ionic strength may also show increased uranium concentrations, potentially due to mineral dissolution or anthropogenic leaching (Saini et al., 2017). Similarly, EC showed weak to moderate correlations with Zn (ρ = 0.30) and Fe (ρ = 0.27), suggesting common sources such as geogenic weathering or input from domestic and agricultural activities (Scanlon et al., 2019).

Inter-metal correlations, such as between Fe and Mn (ρ = 0.31) and Fe and Zn (ρ = 0.34), indicate a potential for co-mobilization from aquifer materials, possibly under shared redox or depositional conditions (Saha et al., 2011). The weak negative correlation between As and U (ρ = -0.48) suggests distinct geochemical pathways for their mobilization, with arsenic often released under reducing conditions and uranium under oxidizing conditions (Smedley & Kinniburgh, 2002). The accompanying p-value matrix affirms the significance of many of these correlations. Statistically significant associations ($p < 0.05$) were observed for pairs such as EC–U ($p = 0.0018$) and pH–Mn ($p = 0.01$), reinforcing their hydrochemical relevance. The Spearman correlation analysis provides evidence of both geogenic and anthropogenic influences on groundwater chemistry, helping to distinguish between parameters affected by natural mineral dissolution and those potentially influenced by human activities. This approach enhances the understanding of contaminant transport mechanisms and aids in prioritizing elements of concern for health and environmental monitoring (Liu et al., 2003; Vega et al., 1998).

Principal Component Analysis (PCA)

Principal Component Analysis (PCA) revealed that initial 3 PC's represent 62.74% of total variance present in the data set (Table 2). Loding factors (Fig 6) for these PC's were plotted. Dominant PC for each ground water quality was assessed and presented in Table 3. It clearly indicates that initial 3 PC's are cumulatively dominant at 26 locations.

Table 2: PCA results

Principal Component	Eigenvalue	Variance (%)	Cumulative Variance (%)
PC1	2.068	25.038	25.04
PC2	1.942	23.518	48.56
PC3	1.171	14.186	62.74
PC4	1.120	13.561	76.30
PC5	0.748	9.059	85.36
PC6	0.624	7.556	92.92
PC7	0.358	4.333	97.25
PC8	0.227	2.751	100

Table 3: Dominant PC analysis result.

Principal Component 1 (PC1)

Dominant PC	No of Samples	Sample/Location Numbers									
PC1	10	4	5	6	10	11	12	13	21	26	29
PC2	7	3	18	19	24	30	31	32			
PC3	9	2	7	14	15	17	20	23	25	28	
PC4	1	9									
PC5	2	1	8								
PC6	3	16	22	27							

PC1 shows strong positive loadings for EC (0.469), Fe (0.424), Mn (0.442), and Zn (0.360), and a strong negative loading for pH (–0.458). This component likely represents a geogenic mineralization process under near-neutral pH, wherein higher EC and elevated Fe–Mn concentrations are linked to reductive dissolution of Fe-Mn oxyhydroxides, mobilizing these metals into groundwater (Smedley & Kinniburgh, 2002; Singh et al., 2020). The moderate positive association with Zn may also suggest influence from both natural mineral leaching and possible anthropogenic inputs.

Principal Component 2 (PC2)

PC2 has a strong positive loading for U (0.641) and moderate for EC (0.411), and strong negative loadings for As (–0.386) and Zn (–0.272). This component may capture contrasting mobilization pathways of U and As in the aquifer. While U tends to mobilize under oxidizing and alkaline conditions, As mobilization is favoured under reducing environments (Saini et al., 2017; Smedley & Kinniburgh, 2002). Hence, PC2 may reflect redox-sensitive processes influencing groundwater chemistry.

Principal Component 3 (PC3)

PC3 is heavily dominated by Pb (0.634) and Zn (0.508), indicating a potential anthropogenic signature, possibly due to industrial effluents or surface runoff contamination. The relatively low loadings from geogenic indicators support the interpretation of external contamination sources.

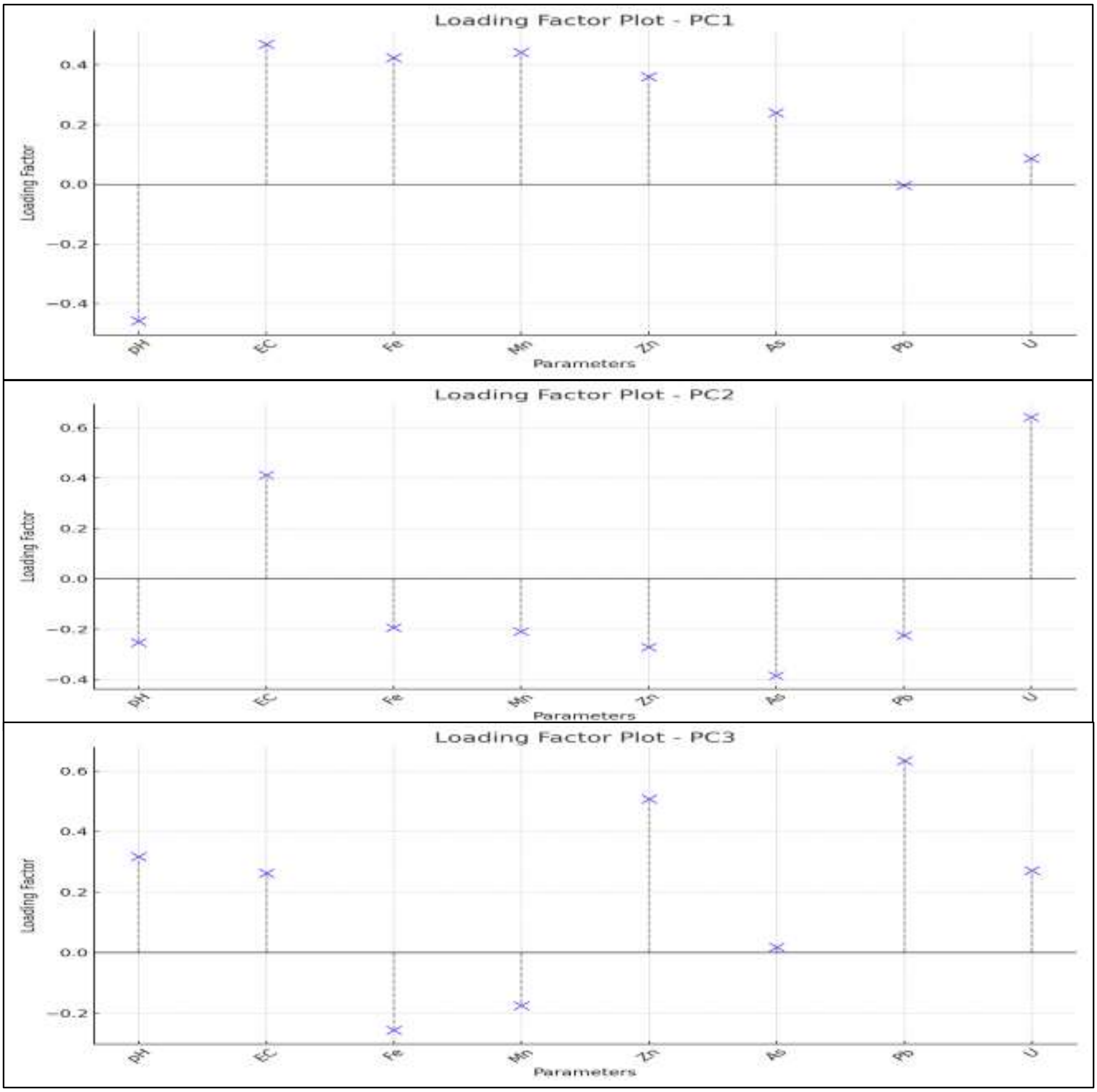

Figure 6: Loading factors for PC1, PC2 and PC3.

Hierarchical Cluster Analysis (HCA)

To identify spatially coherent water types and interpret underlying hydrogeochemical processes, the groundwater samples were grouped into three clusters based on Hierarchical Cluster Analysis (HCA). Each cluster exhibited distinct patterns in the concentration levels of physio-chemical and trace metal parameters, as reflected in the boxplots (Fig. 7).

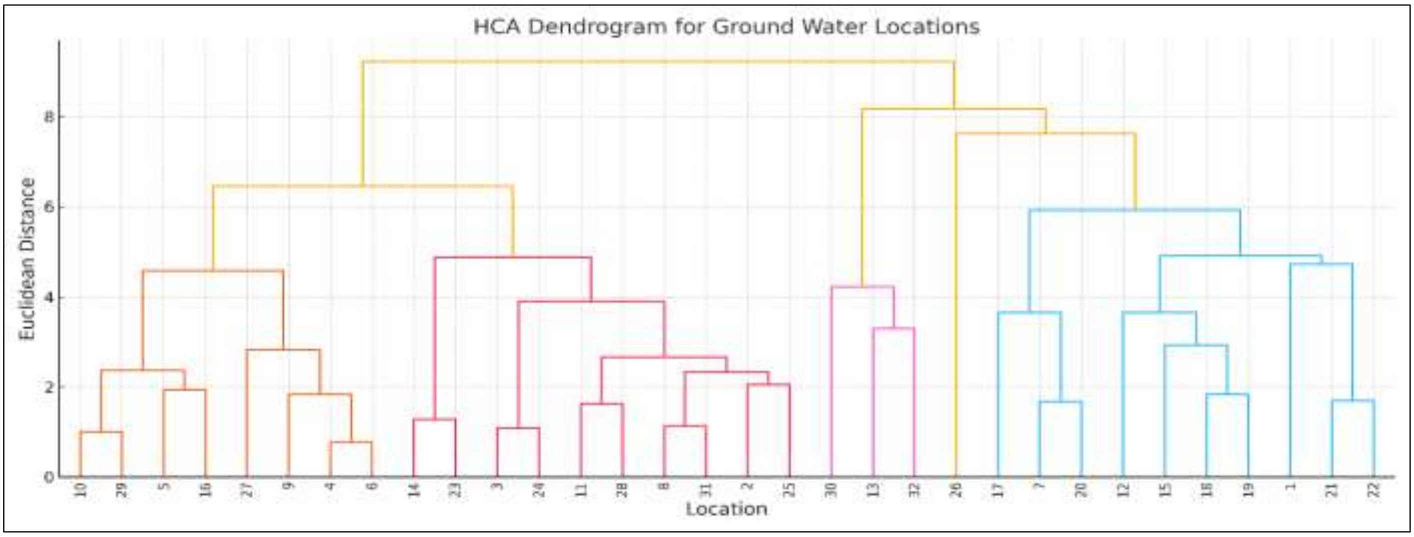

Figure 7: Dendrogram for ground water quality locations.

Hierarchical Cluster Analysis (HCA) categorized the 32 groundwater samples into five distinct clusters based on their hydrochemical signatures. This classification revealed spatial and compositional variability in groundwater quality, aiding in the identification of contamination patterns and hydrogeochemical regimes (Simeonov et al., 2003; Vega et al., 1998).

Cluster 1 (8 samples) was characterized by low to moderate levels of Fe, Mn, and Zn, with generally acceptable EC and pH values. These samples likely reflect natural geochemical conditions with limited anthropogenic influence. Cluster 2 (10 samples) represented the least contaminated group, showing negligible concentrations of all heavy metals and uniformly low EC values, indicating pristine or minimally impacted groundwater quality. Cluster 3 (3 samples), though limited in size, exhibited elevated uranium (U) concentrations, suggesting a localized geogenic enrichment, potentially from alluvial or granitic source rocks—a pattern consistent with observations in other parts of northern India (Saini et al., 2020).

Cluster 4 (10 samples) displayed the highest variability in heavy metal concentrations, particularly Fe, Mn, and Zn, along with elevated EC. These findings point to mixed contamination sources, possibly stemming from leaching of ferromanganese minerals, coupled with domestic or agricultural runoff (Singh et al., 2013). Notably, Cluster 5 (sample 26) emerged as a discrete high-risk cluster, with markedly elevated levels of Fe (3556.8 µg/L), Zn (1236.6 µg/L), and As (22 µg/L), far exceeding WHO guideline values. This sample indicates potential point-source contamination or intensive geochemical mobilization, necessitating urgent mitigation (WHO, 2011; CGWB, 2022).

The box plots with a log-scale axis for trace metals further illustrated skewed distributions, highlighting localized anomalies. The clustering outcomes emphasize the hydrogeochemical heterogeneity across Gorakhpur and underline the necessity of site-specific water quality management strategies (Helena et al., 2000; Liu et al., 2003).

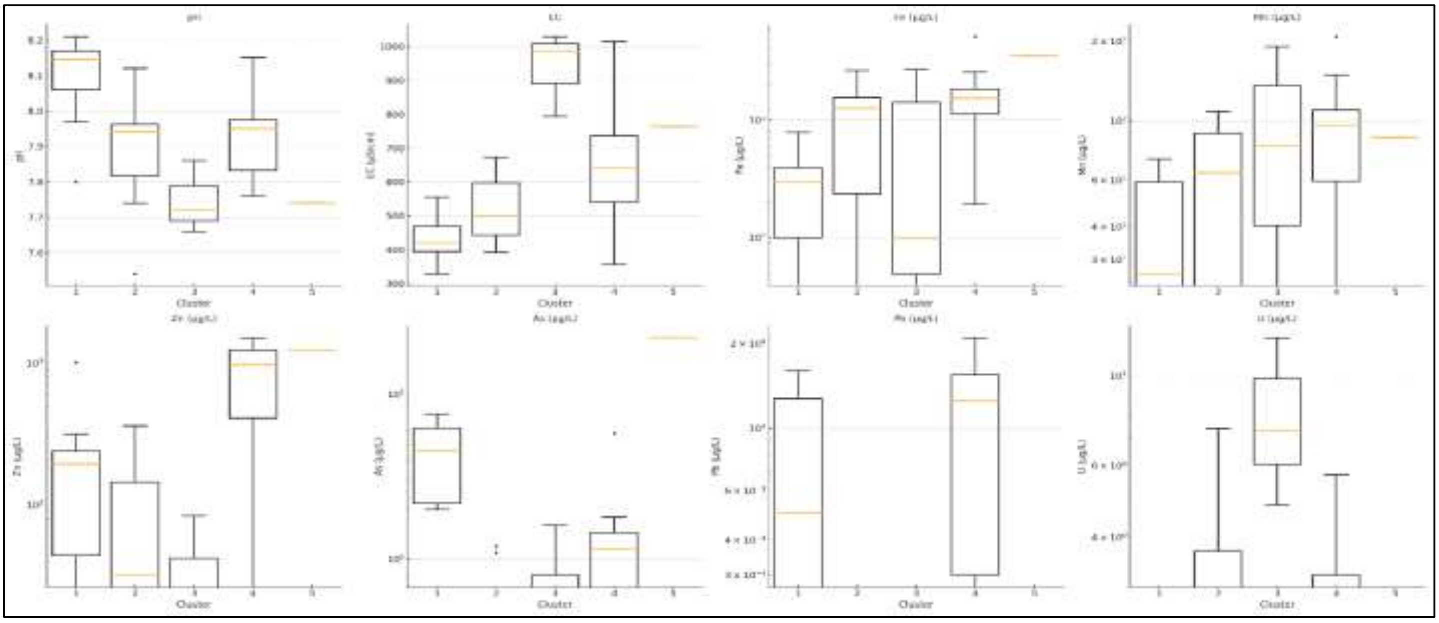

Figure 8: Box plots for ground water quality parameters in each cluster.

Non-Carcinogenic Risk Assessment (HQ and HI)

Human health risk assessment based on the calculation of Hazard Quotient (HQ) and Hazard Index (HI) suggested that the majority of samples posed minimal non-carcinogenic risk. However, in samples where Fe and Mn concentrations exceeded safe thresholds, the calculated HQ values approached or marginally exceeded unity, indicating the need for targeted risk mitigation (USEPA, 1989; Wu et al., 2009).

The non-carcinogenic health risk assessment performed revealed that 9 out of 32 groundwater samples exhibited Hazard Index (HI) values exceeding the threshold, suggesting potential health risks due to chronic exposure to multiple contaminants (USEPA, 1989). The most concerning sample, Site 26, recorded HI values of 4.73 (male) and 4.08 (female), indicating substantial cumulative toxicity, with arsenic (As) identified as the predominant contributor, as supported by HQ values exceeding 1 across both populations (ATSDR, 2007). Samples 9, 12, and 27 also recorded HI values between 1.3 and 1.5, highlighting significant multi-elemental exposure. The elevated HQ values for arsenic align with prior reports that document As as a major groundwater contaminant in the Indo-Gangetic plains and parts of northern India (Shankar et al., 2014).

Additionally, samples such as 13, 20, 29, and 30 exhibited HI values greater than 1 for males but remained below the threshold for females, suggesting sex-based variability due to physiological and behavioural exposure factors such as body weight and ingestion rate (USEPA, 2004). In these cases, although individual HQ values for lead (Pb), manganese (Mn), and zinc (Zn) remained below unity, their additive contributions pushed the overall HI beyond the safe limit, reflecting the relevance of cumulative exposure assessment (Solecki et al., 2020). This analysis reinforces the need to evaluate health risks holistically, considering additive and synergistic effects of multiple contaminants. According to USEPA guidelines, locations with HI ≥ 1 require urgent intervention, including alternative water supply provisioning, exposure mitigation, and long-term monitoring (USEPA, 2000).

Carcinogenic Risk Assessment (CR)

A carcinogenic risk (CR) assessment values were calculated for three known carcinogens commonly found in groundwater: arsenic (As), uranium (U), and lead (Pb), using United States Environmental Protection Agency (USEPA) methodology (USEPA, 2005).

Among the 32 samples analyzed: For the male population, CR values ranged from 8.8×10^{-8} to 1.88×10^{-3}, with a mean CR of approximately 2.14×10^{-4}. 16 out of 32 samples (50%) exceeded the high-risk threshold (CR > 10^{-4}). For the female population, CR values ranged from 7.6×10^{-8} to 1.62×10^{-3}, with a mean CR of approximately 1.83×10^{-4}. 13 out of 32 samples (41%) exceeded the high-risk threshold. These findings align with exposure estimates based on lifetime daily intake assumptions, adjusted for body weight and gender-specific ingestion rates as per USEPA exposure factors handbook (USEPA, 2011).

Arsenic (As) emerged as the primary contributor to total CR in most samples, particularly in those classified under the high-risk category. This is consistent with studies from other parts of the Indo-Gangetic Plain where arsenic contamination is geogenically driven (Chakraborti et al., 2010). Uranium (U) and lead (Pb) contributed marginally to the total CR in most samples but were significant in specific samples (e.g., samples 7, 17, and 18) where arsenic was absent.

Samples exceeding the 1×10^{-4} threshold (Fig.7) indicate a probability of one additional cancer case per 10,000 individuals due to lifetime exposure. Such samples require immediate mitigation through alternate water sources or treatment interventions (USEPA, 2005). Samples within the acceptable range still warrant regular monitoring, particularly in densely populated or agriculturally active

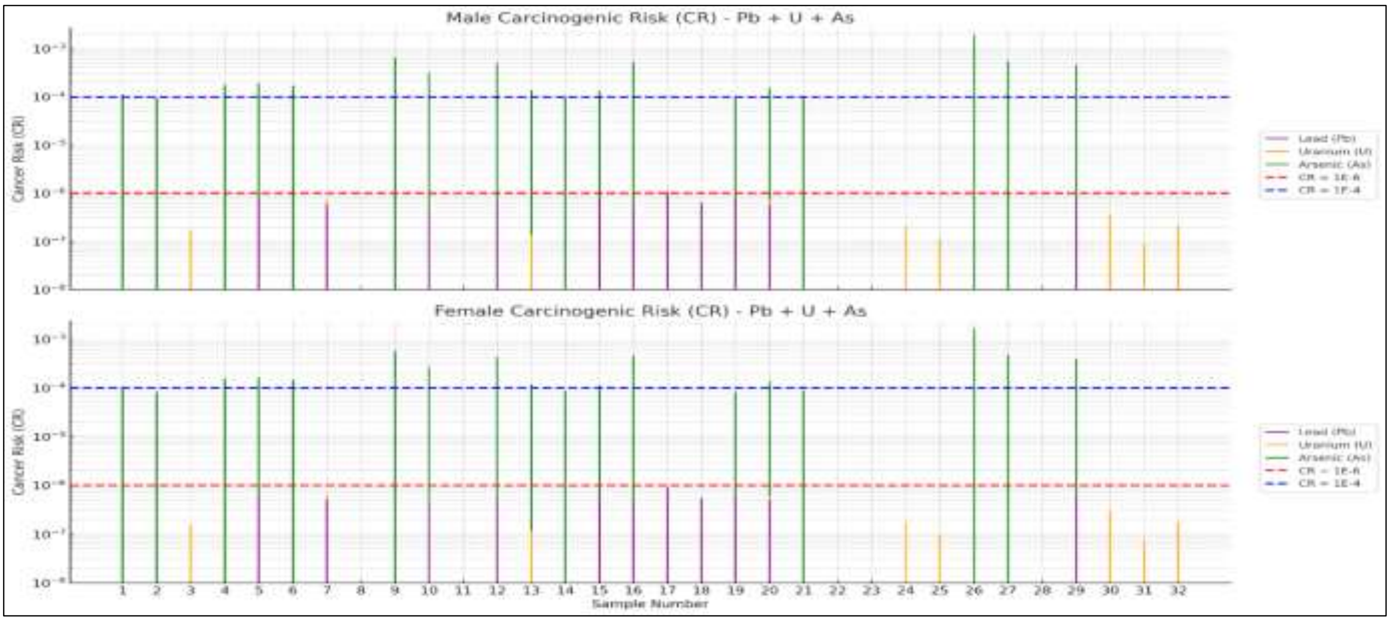

Figure 9: Carcinogenic risk for male and female.

areas. Samples with negligible CR values (e.g., samples 3, 24, 30–32) are considered safe from a carcinogenic risk perspective and may serve as reference locations for regional comparisons.

V. CONCLUSION

The comprehensive assessment of heavy metals in Gorakhpur District's groundwater—through hydrochemical analysis, multivariate statistics, spatial mapping, and health-risk evaluation reveals that most physicochemical parameters comply with WHO (2011) guidelines. However, iron (Fe), manganese (Mn), and arsenic (As) frequently exceed permissible limits, indicating overlapping geogenic and anthropogenic influences on water quality (Smedley & Kinniburgh, 2002; Chakraborti et al., 2010). Principal Component Analysis (PCA) attributes observed variations in groundwater chemistry to processes such as reductive dissolution and redox-controlled mobilization. Hierarchical Cluster Analysis (HCA) further delineates five distinct hydrogeochemical clusters, among which a "high-risk" Cluster 5 emerges as a hotspot requiring immediate attention.

Health-risk assessments highlight that nine out of thirty-two locations present non-carcinogenic hazards (HI > 1), reflecting differences in physiological susceptibility and exposure rates (USEPA, 2004; Wu et al., 2009). Carcinogenic-risk analysis identifies arsenic as the predominant concern, with 16 sites exceeding the 10^{-4} threshold, underscoring potential long-term impacts. To mitigate these risks, a multifaceted strategy is essential. First, high-risk locations identified by HI and spatial analyses should be prioritized for rigorous monitoring. Second, community-scale treatment technologies—such as reverse osmosis and ion-exchange units—must be deployed in areas where Fe, Mn, or As surpass safe limits to guarantee access to potable water. Third, integrating health-risk indices (HQ, HI, and CR) into groundwater quality frameworks will enable more health-focused policy decisions beyond mere concentration thresholds. Finally, population-level awareness campaigns should educate residents about contamination risks and promote safer water-use practices. Close coordination among groundwater authorities, environmental regulators, and public health institutions is vital to implement targeted interventions and to regulate pollution sources, especially agricultural runoff and unregulated industrial discharges.

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