

Research Article

Heavy metal contamination in the groundwater of the southern expanse of the Northwestern Himalayan region: An evaluation of pollution indices and health risks utilizing Mathematical Modelling

Uzma IMTIYAZ^{*1} , Mushtaq Ahmad RATHER¹ 

¹ Department of Chemical Engineering, National Institute of Technology,
Srinagar, India

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ABSTRACT

Water quality has a direct impact on both human health and the socioeconomic system's viability. Pollutants, especially heavy metals, seep into water systems and deteriorate water quality as human activity increases. The purpose of this study was to evaluate the heavy metal contamination in groundwater and its potential health risk posed to humans in the southern part of the Northwestern Himalayan region, encompassing four Kashmir districts (Anantnag, Pulwama, Shopian, and Kulgam), during both pre- and post-monsoon, using atomic absorption spectroscopy. The research scrutinized heavy metal levels in 25 borewell water samples. The Nemerow pollution index was employed to assess water quality, revealing varying degrees: Dooru Shahabad exhibited excellent quality (NPI < 0.5), Hillar and Kakapura were classified as good (NPI 0.5–0.75), while Wanpoh and Zeewan displayed moderate quality (NPI 0.75–1). The remaining 20 samples showed consistently poor quality (NPI > 1). Spatial distribution of heavy metals (Pb, Ni, Mn, Cd, Cu, Fe, Zn) was mapped using contour maps, revealing concentrations ranging from 0.01 mg/L to 0.15 mg/L for Pb, 0.05 mg/L to 0.2 mg/L for Ni, and 0.1 mg/L to 0.5 mg/L for Mn. Statistical analysis, including ANOVA, showed no significant variations in mean concentrations of Pb (0.05 ± 0.01 mg/L), Ni (0.1 ± 0.02 mg/L), Cd (0.01 ± 0.005 mg/L), Cu (0.03 ± 0.01 mg/L), Fe (0.4 ± 0.1 mg/L), and Zn (0.2 ± 0.05 mg/L) ($p > 0.05$). Principal component analysis and cluster analysis showed that the main source of heavy metal pollution in the groundwater of study area is anthropogenic. The contamination extent underscores the necessity to evaluate its human health impact. The carcinogenic and noncarcinogenic hazards were calculated using the measured concentration of heavy metals and the average daily water intake. The calculated carcinogenic risk values for Pb is 2.31×10^{-3} , Cd is 6.51×10^{-5} , and Ni is 3.94×10^{-5} exceeds the acceptable limit of 1.0×10^{-6} as per different agencies. Non-carcinogenic risk rankings across districts were Pb>Ni>Mn>Cd>Cu>Fe>Zn, with Pb posing the highest carcinogenic risk. Subsequently, total health risk, incorporating non-carcinogenic risks for seven heavy metals and carcinogenic risks for three, was mathematically computed. Lead was found to contribute 72% to the total health risk. This research illuminates the degree of pollution caused by heavy metals in a region of paramount importance, urging further investigation into its health implications that can support the decision-making of local government organisations regarding the sustainable use of groundwater resources and the efficient protection of the groundwater environment.

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*Corresponding author.

*E-mail address: uzma6phd19@nitsri.ac.in



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INTRODUCTION

The impending climate crisis has put the whole human existence on our planet in jeopardy. At present, the world's depleting resources, the energy crisis, and environmental issues have become increasingly prominent. Water being one of the utmost fundamental requirements of life acts as a universal solvent thereby providing ionic balance and nutrient aid to all forms of life. It dissolves various toxic organic and inorganic substances that are detrimental to its quality and affects individuals' health. Increasing and unregulated industrial and agricultural activities, including, pharmaceuticals, pesticides, garments, and technocratic civilization, are responsible for the contamination of water. With a mere 2.5% of the world's water being non saline, the imbalance between the freshwater availability and the ever-growing population is intensifying with time [1].

Groundwater in its essence is one of the key natural resources, used for both drinking and agricultural purposes. It is important not only for the survival of mankind but also for the social and economic development of any nation. Groundwater contamination is one of the prime environmental issues that the world is facing [2]. Groundwater contamination is susceptible in the areas where population density is high and human land use is exhaustive [3]. Furthermore, groundwater pollution is caused by the disposal of domestic, agricultural, industrial and commercial waste, and constituents (trace metals) of soil, rocks and plateaus because of their direct contact. Heavy metals are one of the major contaminants consistently found in groundwater which prove hazardous and toxic [4,5].

Sixty -three point five to two hundred point six (63.5 to 200.6) being the range of atomic weights, heavy metals have a relatively high density when compared to water. Among these the harmful heavy metals are lead, uranium, selenium, chromium, mercury, zinc, arsenic, nickel [6]. Heavy metals occurring naturally in the environment have no harmful effect and are rather beneficial when present in low concentrations. However, their presence in higher concentrations can have an adverse effect on mankind [4]. The heavy metal contamination in groundwater is both natural and man-made. Natural sources include disintegration of rocks, degradation of organic matter, and volcanic eruptions [7,8], while human activities that could potentially contribute to environmental pollution include mining and extraction, agricultural practices, industrial waste, solid waste management, and medical waste disposal [9]. Infiltration of heavy metals into the groundwater occurs by surface runoff from contaminated water source, leaching of landfill sites [10,11].

India's 90% of rural population and 30% urban pollution are dependent on groundwater as their primary source of drinking water and for their domestic needs [12]. Most of the water used is untreated and not fit for drinking. Therefore, the vulnerability towards toxic pollutants prevailing in groundwater is rising significantly [13]. The presence of heavy metals beyond permissible limits in water is causing abnormal functioning of human body despite being essential at the lower concentrations. Illness and fatality rates are increasing due to constant and prolonged exposure [11,14]. Exposure

to heavy metal contamination can result in both short-term and long-term health effects, ranging from mild symptoms like food poisoning and headaches to severe conditions such as liver cirrhosis, kidney dysfunction, permanent harm to the neuron system, cardiovascular disease, infertility, cancer [15, 16, 17].

Taking into consideration the vast impact of heavy metals pollution on human health it is imperative to assess and estimate the contamination level of heavy metals in the water and the potential risk imposed by them on human health [13,18]. Studies have been conducted in countries across the globe employing different pollution indices to assess the degree of heavy metal contamination such as India, Syria, Thailand, Bangladesh, China, Mexico, North America, and Turkey. Bangladesh's industrial discharges, agricultural practices, and insufficient waste management systems have resulted in worrying levels of groundwater pollution. In South Fakra, Kashiani, Gopalganj, Bangladesh, Shaibur conducted research on the distribution of heavy metals and arsenic in groundwater. Significant relationships between these pollutants were found in the study, highlighting the interconnectedness of groundwater pollution. These kinds of studies yield important information about the dynamics of groundwater contamination and its possible effects on human health. High concentrations heavy metals have also been reported in China's cities, especially in heavily industrialised and populated areas. Mexico, which is well-known for its quick urbanisation, has serious groundwater contamination from home and industrial wastewater discharge as well as fertiliser and pesticide-filled agricultural runoff. Additionally, research has shown that heavy metals can be found in a variety of metropolitan contexts, indicating that groundwater contamination is a problem in North America. Research conducted in India has revealed the existence of heavy metals in urban groundwater, which is mostly related to industrial operations and urban growth [19-25].

Even though the Kashmir Valley's groundwater is crucial, there are not many thorough research on heavy metal pollution in the area. Prior studies have focused on groundwater salinity and have not thoroughly examined heavy metal contaminants and their seasonal fluctuations. In order to fill in these gaps, this study performs a thorough examination of water samples collected during the pre- and post-monsoon seasons from 25 borewells spread over four districts (Anantnag, Pulwama, Shopian, and Kulgam). It uses atomic absorption spectroscopy to investigate a wide range of heavy metals (lead, nickel, manganese, cadmium, copper, iron, and zinc) and utilises the Nemerow Pollution Index to provide a detailed evaluation of the water quality. The main advantage of Nemerow pollution index is that it is way more accurate and simpler as compared to any other pollution indexes. This study is new since it uses contour maps to visualise geographical distribution using IDW (inverse distance weightage). The underlying presumption of inverse distance weighted (IDW) interpolation is that objects closer together are more similar than those located further apart. To predict a value for any unmeasured site, IDW uses the measured values surrounding the expected location. The findings of measurements taken closest to the prediction site have a greater

influence on the expected value than do measurements taken farther away. IDW operates under the presumption that each measured location has a local influence that gets smaller in distance. "Inverse distance weighted" is a method whereby sites closest to the projected place are given higher weights, and these weights decrease with distance. Study also covers a wide variety of heavy metals, employs a dual-season methodology, and sophisticated pollution index. It also includes a thorough health risk assessment that computes the risks of cancer and non-cancerous diseases. To better understand the links between various metals, it combines sophisticated statistical studies such as ANOVA, Cluster analysis, Principal component analysis and Pearson correlation coefficients. These comprehensive methods considerably advance the understanding of groundwater contamination in the Kashmir Valley by offering critical insights into the health and environmental effects of heavy metal pollution.

MATERIALS AND METHODS

Research Area Description

Kashmir is one of the most fascinating, mesmerising and picturesque place lying in the northwest Himalaya. Situated between $33^{\circ} 30'$ and $34^{\circ} 45'$ N latitudes and 74° and $75^{\circ} 30'$ E longitudes it covers an area of 5200 sq. km. Present study of heavy metal pollution in ground water includes four districts of Southern part of Kashmir namely, Anantnag, Pulwama, Shopian and Kulgam. District Anantnag is southern-most district of Kashmir province, Pir Panjal range separates it from the Jammu province. it is located between $33^{\circ} 17' 20''$ and $34^{\circ} 15' 30''$ latitude and $74^{\circ} 30' 15''$ and $74^{\circ} 35' 00''$ East longitude. Discharge of ground water in these areas occurs both by natural and artificial ways. Spring flow adequate to the natural discharge and heavy with drawls are made from tube wells and dug wells for household and agricultural purposes. Figure 1(a) shows the map of the study area with the sampling locations demarcated on it.

Hydrogeology

Groundwater in the study area exists in both the unconfined water table and confined conditions within soft rock aquifers. The presence of groundwater is influenced by various hydrogeological factors, including lithology, structure, and geomorphic configuration (CGWB, 2017). The hydrogeo-

logical composition of Pulwama district can be delineated into two distinct aquifer systems: a hard rock system, comprising semi-consolidated to consolidated rock units, and a soft sedimentary aquifer primarily composed of unconsolidated sediment (CGWB, 2016-17). The geological map of the study area is presented in figure 1(b). The depth of groundwater within the study area plays a pivotal role in determining water availability and long-term sustainability. The distance to the water table within the study area's aquifers spans from 10 to 390 feet. Groundwater sources in the region exhibit a spectrum of depths, ranging from shallow to deep aquifers. Shallow groundwater reservoirs, situated in proximity to the surface, typically offer greater accessibility and ease of utilization. The depth of groundwater also has implications for water quality; shallow sources are more vulnerable to contamination, whereas deeper sources tend to be more shielded. Monitoring and comprehending groundwater depth are vital for sustainable management.

Groundwater recharge and discharge

In Kashmir rivers, lakes, wetlands, snowfall, irrigation return flow, precipitation, and manmade techniques such recharge wells are the main sources of groundwater replenishment. Heavy monsoon rains and the melting of the Himalayan glaciers are the main causes, with rivers like the Jhelum infiltrating deeply and contributing significantly. Surface water features like Dal Lake and agricultural irrigation contribute to recharging. Natural springs, rivers, streams, lakes, wetlands, and extraction for home and industrial usage are some of the ways that groundwater is released into the environment [14].

Sampling and Analysis

A total of 25 water samples were collected randomly from different National Hydrograph stations installed by Central Ground Water Board in four districts of South Kashmir to assess the heavy metals concentration in the ground water. The water samples were collected in one Litre polyethylene bottles which were rinsed properly with distilled water before using. Water from the bore well was flushed for 10 minutes before collecting the sample for analysis. The samples collected were filtered through Whatman filter Paper and preserved with Nitric acid. Sample collection was done following the procedures cited by APHA -2005 [26]. The analysis of these preserved samples was carried out in triplicates and the average of three

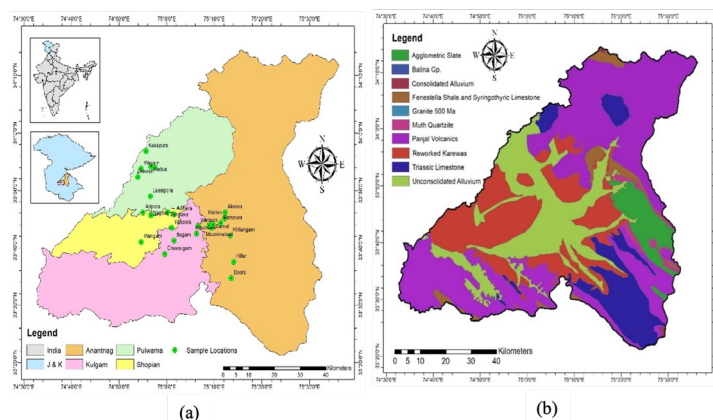


Figure 1. (a) Sampling locations (b) Geological maps of heavy metals in the study area

was taken, using Perkin Elmer Atomic Absorption Spectrophotometer Analyst 400 at Sher Kashmir University of Agriculture Science and Technology -Kashmir in the Division of Research Centre for Residue and Quality Analysis. A series of known concentrations solutions were prepared and calibration curve was plotted based on the absorbance of the said element including the blank sample and the unknown concentrations were found on the basis of absorbance [27]. AAS works based on the principle of absorption of light by atoms. The sample is atomized, usually by heating, and then exposed to a specific wavelength of light. The atoms in the sample absorb the light,

and the amount of absorption is in direct proportions to the concentration of the element being measured. By measuring the intensity of the absorbed light, the concentration of the element can be determined. AAS is preferred for heavy metal analysis due to its accuracy, sensitivity, and selectivity. It allows for the quantification of individual metals and can detect low concentrations, making it suitable for assessing heavy metal contamination in environmental samples like groundwater. Table 1 and Figure 2 shows the Concentrations of various Heavy metals in Groundwater ($\mu\text{g/l}$) found in the study area.

Table 1. Concentration of various heavy metals in groundwater ($\mu\text{g/l}$)

S no.	District	Location	Latitude	Longitude	Well Depth (ft)	Pre-Monsoon ($\mu\text{g/l}$)						Post Monsoon ($\mu\text{g/l}$)					
						Ci	Ci	Ci	Ci	Ci	Ci	(Fe)	(Mn)	(Ni)	(Pb)	(Zn)	(Cu)
						(Fe)	(Mn)	(Ni)	(Pb)	(Zn)	(Cd)	(Cu)	(Cd)	(Ni)	(Pb)	(Zn)	(Cu)
1	Shopian	Nagbal	33° 76' 10"	74° 94' 50"	100	ND	26.9	87.8	550.0	39.2	ND	16.3	ND	28.2	90.4	561.0	42.3
2		Wangam	34° 27' 50"	74° 30' 71"	100	224.6	43.8	39.2	370.0	5.4	ND	ND	235.8	46.0	40.4	377.4	5.8
3		Awnera	33° 76' 41"	75° 02' 61"	120	160.0	50.0	20.0	460.0	20.0	ND	ND	168.0	52.5	20.6	469.2	21.6
4		Zanipora	33° 77' 60"	75° 00' 41"	80	50.0	20.0	60.0	320.0	40.0	20.0	ND	52.5	21.0	61.8	326.4	43.2
5		Aripora	33° 71' 70"	74° 83' 61"	100	33.0	604.8	0.9	2.3	10.0	ND	1.0	34.7	635.0	0.9	2.3	10.8
6	Pulwama	Lassipora	33° 81' 62"	74° 94' 31"	120	ND	9.0	38.1	450.0	47.6	6.0	10.0	ND	9.5	39.2	459.0	51.4
7		Nadua	33° 81' 35"	74° 76' 31"	100	420.0	30.0	10.0	220.0	130	ND	10.0	441.0	31.5	10.3	224.4	140.4
8		Wagam	33° 89' 61"	74° 91' 10"	75	240.0	40.0	57.0	150.0	70.0	ND	20.0	252.0	42.0	58.7	153.0	75.6
9		Lajoora	33° 89' 93"	74° 95' 92"	120	350.0	30.0	44.0	390.0	20.0	ND	ND	367.5	31.5	45.3	397.8	21.6
10		Kakapura	33° 55' 35"	74° 53' 54"	100	29.6	20.0	20.0	4.5	5.4	ND	ND	31.1	21.0	20.6	4.6	5.8
11		Zeewan	33° 87' 18"	74° 89' 93"	90	214.5	10.0	34.0	3.9	103	ND	ND	225.2	10.5	35.0	4.0	111.2

Table 1. Concentration of various heavy metals in groundwater (µg/l)

12	Anantnag	Sarnal	33° 73' 28"	75° 16' 00"	100	ND	133.6	43.4	530.0	88.3	6.0	ND	ND	140.3	44.7	540.6	95.4	6.1	ND
13	Malaknag		33° 43' 25"	75° 90' 12"	80	ND	16.8	30.7	440.0	6.1	ND	ND	ND	17.6	31.6	448.8	6.6	ND	ND
14	Mattan		33° 45' 80"	75° 12' 11"	75	ND	ND	41.3	380.0	6.0	ND	ND	ND	ND	42.5	387.6	6.5	ND	ND
15	Akoora		33° 76' 89"	75° 20' 51"	80	ND	42.7	64.5	330.0	8.9	ND	ND	ND	44.8	66.4	336.6	9.6	ND	ND
16	Khilangam		33° 70' 21"	75° 22' 31"	65	ND	ND	55.0	440.0	17.7	ND	ND	ND	ND	56.7	448.8	19.1	ND	ND
17	Pulwama	Moominabad	33° 72' 41"	75° 15' 70"	100	632.9	6.7	58.2	310.0	69.0	ND	ND	664.5	7.0	59.9	316.2	74.5	ND	ND
18	Rampura		33° 73' 81"	75° 19' 12"	80	ND	23.6	50.8	530.0	110.4	0.0	0.0	0.0	24.8	52.3	540.6	119.2	ND	ND
19	Dooru		33° 57' 79"	75° 22' 60"	100	40.8	23.0	14.5	5.2	3.7	ND	20.0	42.8	24.2	14.9	5.3	4.0	ND	ND
20	Wanpoh		33° 72' 96"	75° 10' 86"	80	27.2	330.0	31.3	2.7	24.8	ND	ND	28.6	346.5	32.2	2.8	26.8	ND	ND
21	Hillar		33° 62' 54"	75° 23' 48"	120	43.1	350.0	14.6	ND	47.6	ND	ND	45.3	367.5	15.0	ND	51.4	ND	ND
22	Kulgam	Khudwani	33° 72' 32"	75° 02' 63"	100	29.5	1721	36.0	440.0	207.8	ND	ND	31.0	1807	37.1	448.8	224.4	ND	ND
23	Chawalgam		33° 64' 81"	74° 99' 34"	100	454.8	299.8	52.9	290.0	96.4	ND	ND	477.5	314.8	54.5	295.8	104.1	ND	ND
24	Yaripora		33° 72' 40"	75° 01' 81"	70	20.0	210.0	30.0	250.0	10.0	ND	ND	21.0	220.5	30.9	255.0	10.8	ND	ND
25	Bugam		33° 68' 72"	75° 02' 60"	100	ND	959.0	41.3	480.0	17.1	ND	ND	ND	1007	42.5	489.6	18.5	ND	ND

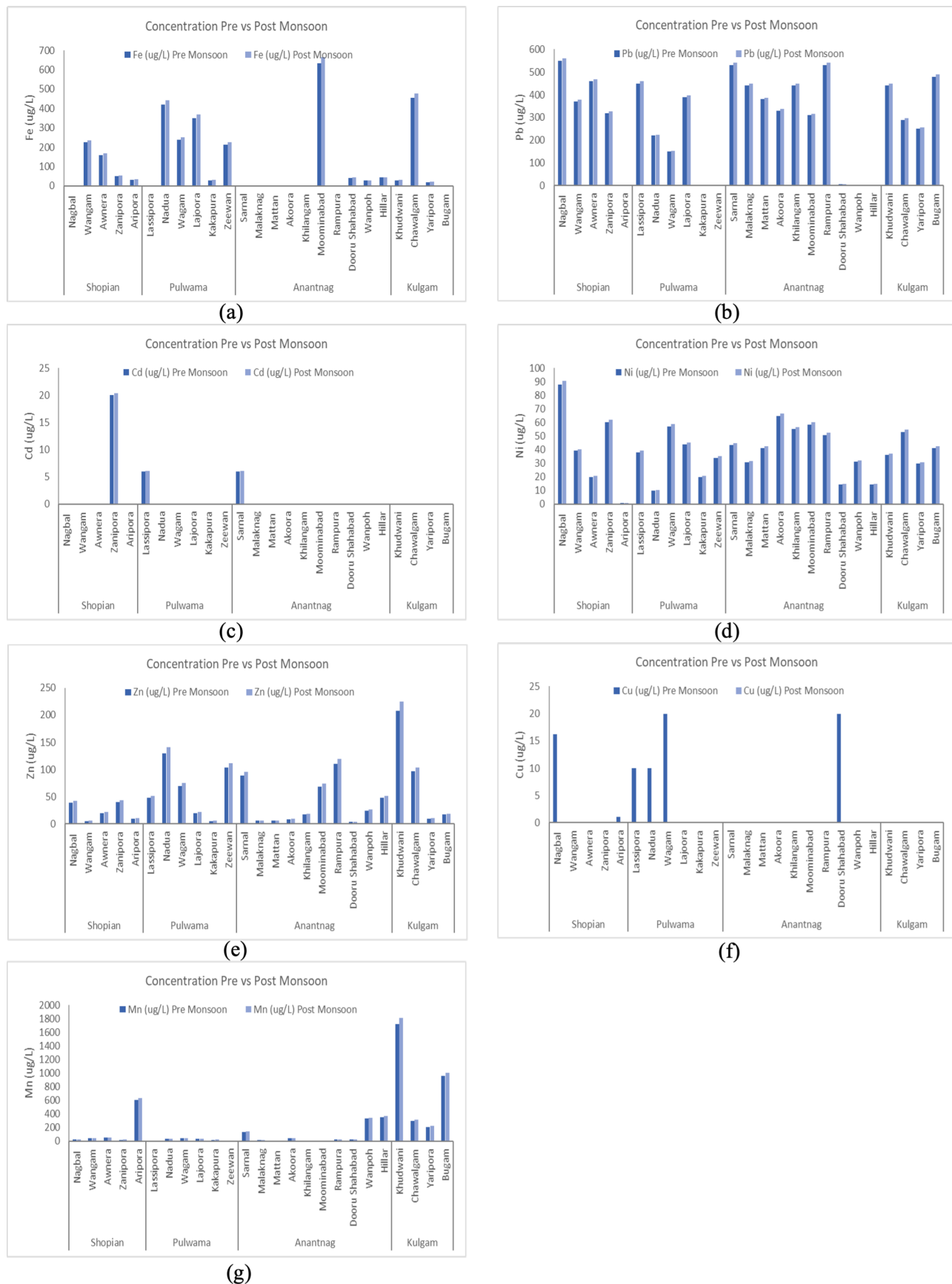


Fig 2. Graphical representation concentrations of various heavy metals in groundwater (µg/l) in Pre and Post Monsoon (a) Iron (b) Lead (c) Cadmium (d) Nickle (e) Zinc (f) Copper (g)

Heavy Metal Pollution Index

The groundwater standard in the study area has been analysed using both a complete index factor and a single factor index. The BIS 2012 acceptable limits and the concentration of heavy metal at each sampling point are related by the single factor index. The single factor index (Fi) is calculated using the following formula:

$$F_i = C_i / C_0$$

Ci is the measured concentration of heavy metal in Groundwater, and C0 is the permissible limit of the heavy metal concentration recommended by Bureau of Indian Standard for drinking water. Table 2 Shows the BIS 10500, 2012 limits of different heavy metals in drinking water.

Water quality does not meet the criteria if the value of Fi is more than 1, and it does if the value of Fi is less than 1 [28].

The comprehensive index was calculated by Nemerow Index method, this particular method was designed by two scientists named as Nemerow and Sumitomo in the year 1971, it is the most simplified pollution index and can be determined using following formula [29,30].

$$F = \sqrt{\frac{(F_{max}^2 + \bar{F}^2)}{2}}$$

In above equation the Nemerow pollution index is designated by F, Fi is a single evaluation index, and Fmax is the highest value that can be found in Fi's score value. F_{max} was calculated using following Equation (3)

$$F = \sqrt{\frac{(F_{max}^2 + \bar{F}^2)}{2}}$$

n denotes the number of sampling points assessed. Table 3 shows the water quality classification as per USEPA.

Table 2. BIS 10500:2012 Indian standard drinking water specifications in µg/l.

Heavy Metal	Fe	Pb	Zn	Cd	Ni	Cu	Mn
Permissible	300	10	15000	3	20	1500	300
Limit							
Acceptable limit	300	10	5000	3	20	50	100

Table 3. Groundwater quality classification standard as per USEPA.

S No.	Nemerow Pollution Index (F)	Water Quality Classification
1	< 0.5	Excellent
2	0.5 to 0.75	Good
3	0.75 to 1.0	Moderate
4	> 1.0	Poor

Human Health Risk

The Carcinogenic impact of presence of heavy metals present in drinking water was calculated utilising following equation:

$$R_i^c = \frac{1 - \exp(-D_i q_i)}{L}$$

In the equation above, RCi stands for the average annual risk of carcinogenesis which a carcinogen i in drinking water poses to one person. Equation (6) was used to compute Di, which stands for the average exposure dosage of carcinogen i per person daily in drinking water, and qi, which stands for the cancer slope factor of carcinogen (i) in water used for drinking purpose, mg/(kg d). The cancer slope factor (CSF) represents the increase in cancer risk per unit of exposure to the substance over a lifetime. It is a measure used in toxicology and risk assessment to estimate the potential carcinogenic risk associated with exposure to a specific chemical or substance. In the current study, a value of 15 for Cd, 8.5 for pb, and 0.84 for Ni [IRIS, WHO, CALEPA] was utilised, and L is the average life expectancy, which is believed to be 65 years in India [31].

The non- Carcinogenic health risk is calculated using the following equation:

$$R_i^n = \frac{D_i \times 10^{-6}}{RfD_i \times L}$$

In the above equation Rni denotes average annual risk caused by non-carcinogens i present in drinking water (a-1), RfDi denotes reference dose of the non-carcinogen i present in drinking water, mg/(kg.d). The RfDi values are shown in table 4.

Table 4. Reference dose of heavy metals of carcinogens and cancer slope factor

S No.	Heavy Metal	RfDi Value	Source	CSF	Source
1	Fe	0.3	USEPA 2001	-	-
2	Pb	1.4×10 ⁻³	WHO	8.5	[33]
3	Zn	3.0×10 ⁻¹	IRIS	-	-
4	Cd	1×10 ⁻³	IRIS 2011	6.1	CALEPA
5	Ni	2×10 ⁻²	IRIS 2011	0.84	CALEPA
6	Cu	5×10 ⁻³	IRIS	--	-
7	Mn	1.4×10 ⁻¹	IRIS 2011		-

The Di is calculated by the following equation:

$$Di = (CW \times IR \times EF \times ED) / (BW \times AT)$$

where body weight is denoted by BW in kg (65 kg was selected for the adults in the study area), the period of exposure is denoted by ED (70 years for the carcinogen, and 30 years for the non-carcinogen), the intake of drinking water on a daily basis is indicated by IR (a value of 2.26 L/d was used), exposure frequency is indicated by EF (365 days/year), and average exposure time is calculated as 365 × ED.

(AS per USPA 2015).

Equation (7) was used to calculate the total health risk brought on by both carcinogens and non-carcinogens in groundwater. The reference values for each risk level are shown in Table 5 according to the international standards of various authorities.

$$R = \sum_{i=1}^n R_i^c + \sum_{i=1}^n R_i^n$$

Table 5. Reference values of the risk level (a-1) set by different agencies.

Agency Name	Maximum Acceptable Limit	Negligible Limit	Comment
The Swedish Environmental Protection Agency	1.0×10 ⁻⁶	-	Chemical toxins
The Dutch Ministry of Construction and the Environment	1.0×10 ⁻⁶	1.0×10 ⁻⁸	Chemical toxins
Royal Society of UK	1.0×10 ⁻⁶	1.0×10 ⁻⁷	-
International Commission on Radiological Protection	5.0×10 ⁻⁵	-	Radiation
Environmental Protection Agency of US	1.0×10 ⁻⁴	-	-

Multivariate Statistical Analysis

For the analytical data interpretation, descriptive statistical analysis (Box and Whisker plot), Pearson's correlation analysis, Cluster Analysis and Analysis of variance and principal component analysis were performed.

Pearson Correlation Analysis:

To examine the connections between the quantities of heavy metals (such as Pb, Ni, Fe, Mn, Cu and Cd) in contaminated water samples, the Pearson correlation coefficients were computed. These coefficients help to understand the co-occurrence and possible causes of pollution of the heavy metals by revealing the degree of linear correlations among them [20].

Cluster Analysis

By dividing similar data points into clusters using cluster analysis, a statistical technique, which helps evaluate how similar the structures and patterns of dataset are. Cluster analysis is a crucial tool for identifying areas with similar contamination profiles and likely pollution sources when assessing heavy metal contamination in groundwater. In this study, cluster analysis was used with Origin Pro 2018 software to determine the same source of contaminants, which are heavy metals [32].

Analysis of Variance

Analysis of variance (ANOVA) was used to look for any notable differences in the mean amounts of heavy metals in

groundwater across four districts. The Origin programme 2018 was utilised to do the statistical analysis [8,13].

Principal component analysis

Using Origin Pro 2018 software, PCA has been carried out on groundwater for quantitative analysis of complex data. Four regulating factors with eigenvalues greater than one were found in this study using principal component analysis (PCA) to look into the likely source of the water quality [33]. The varimax normalised rotation is used to calculate the loading values for each parameter under the primary PCs [8]. For every PC, a collection of related metrics with both positive and negative loading values are used to understand the fundamental procedures involved in analysing and evaluating the water quality.

For every principal component, the variance and cumulative variance (%) were obtained (PC). The variance in statistics is used to calculate dispersion, which shows how far apart data points are from their average values [8,33]. Three groups were created based on the loading values of PCs: strong > 0.75 , $0.75 > \text{moderate} > 0.5$, and $0.5 > \text{weak} > 0.4$. Less important parameter loading values (less than 0.4) were disregarded. These PCs were used to assess anthropogenic and natural processes that have an impact on water systems. By dividing the values of the laboratory-analysed data by their corresponding maximum values, the data were normalised [33]. These normalised value sets were used for PCA.

RESULTS

Box and Whisker Plots for Concentration of Heavy Metals

A boxplot, often named as "box-and-whisker" plot, usually consists of a oblong box containing three lines that denote the bottom, central, and top quartiles of the data. In addition to this, above and below the box are positioned two

points and parallel lines. The middle line within the oblong signifies the intermediate value of the dataset, while the bottom and top lines indicate the values at the first and third quartiles, respectively. The elevated and lower values in the dataset are illustrated by the points positioned above and below the box and whiskers. The vertical lines elongated from the box's edges, referred to as whiskers, generally correlate with the values at the 5% and 95% percentiles of the dataset. Figure 3 demonstrates the various variables associated with the quality of groundwater like Pb, Ni, Mn, Cd, Cu, Fe and Zn. The assessment of the heavy metal data using box whisker plot depicted their variance accurately. The mean concentrations of Mn showed a statistically notable variations as indicated by ANOVA analysis ($p < 0.05$). This could be the association linked to the presence of manganese and marshy gases in the deep aquifers of Kashmir valley. Locations like khudwani, bugam and aripora has significant variation probably due to consistency of a same origin of geological crust [28]. The introduction of manganese into the groundwater occurs as a result of leaching from minerals containing iron, facilitated by the existence of manganiferous phases [34,35]. However heavy metals Pb, Ni, Cd, Cu, Fe and Zn showed insignificant variation in the mean as $p > 0.05$, that attributes to having contrasting hydro geochemical setup.

Pearson Correlation Analysis

One approach for determining potential pollution sources is Pearson's correlation coefficient (r). The correlation between the variables is strong if the value of r varies between 0.9 and 1, moderate if the value is between 0.9 and 0.5, and bad if the value is less than 0.5 [36]. The current investigation found that Pb and Ni ($r = 0.5629$) and Mn and Zn ($r = 0.469$) had moderately positive correlations (0.5), indicating that these metals originated from the same source. This interaction between water and rocks is caused by the decomposition of pyrite and aluminosilicates. Table 6 displays the several heavy metals' Pearson's correlation coefficients.

Table 6. Pearson Correlation coefficient of seven heavy metals.

Heavy Metal	Fe	Mn	Ni	Pb	Zn	Cd	Cu
(Fe)	1	-0.1819	0.05951	-0.1084	0.28499	-0.1565	0.02409
(Mn)	-0.1819	1	-0.1806	0.04739	0.46901	-0.1298	-0.2087
(Ni)	0.05951	-0.1806	1	0.56292	0.06736	0.22038	0.10592
(Pb)	-0.1084	0.04739	0.56292	1	0.14043	0.1469	-0.1308
(Zn)	0.28499	0.46901	0.06736	0.14043	1	0.0143	0.02197
(Cd)	-0.1565	-0.1298	0.22038	0.1469	0.0143	1	-0.0585
(Cu)	0.02409	-0.2087	0.10592	-0.1308	0.02197	-0.0585	1

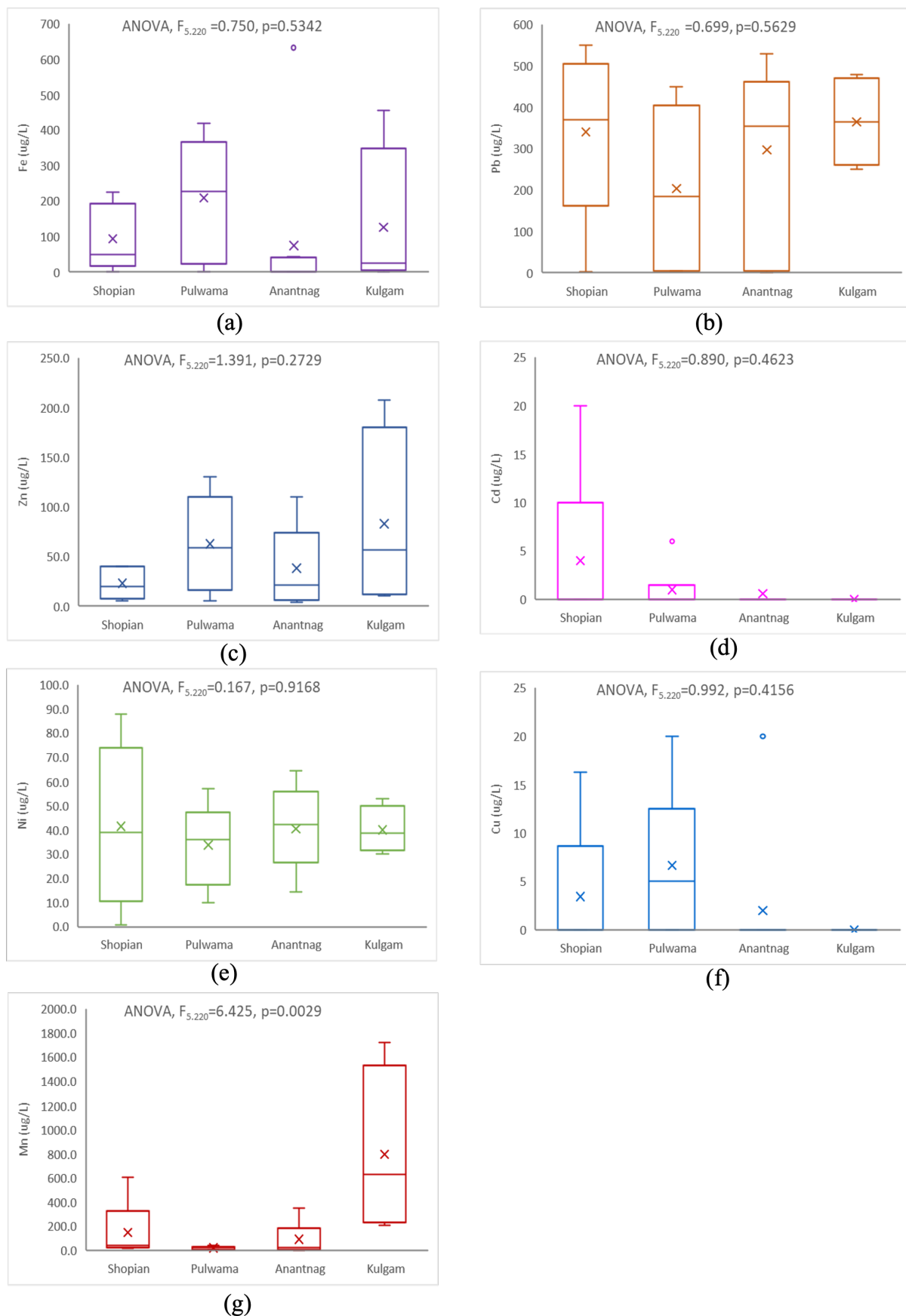


Fig 3. Boxplot illustrating the distribution of heavy metals in groundwater across various watersheds, accompanied by an analysis of variance (ANOVA) with a significance level of $p < 0.05$ (a) Iron (b) Lead (c) Zinc (d) Cadmium (e) Nickel (f) Copper (g) Manganese

Cluster Analysis

Cluster analysis (CA) is a statistical technique that has been used to analyse the relationship between metals and establish their nature, i.e., whether they come from natural or anthropogenic sources [28]. Hierarchical cluster analysis is used to classify the heavy metals in the research area into two main clusters, C1 and C2, as illustrated in Fig. 4. Fe, Mn, and Zn were found together in the first component, based on the initial component matrix indicators. Because it predominates throughout the entire study area, this component (C1) was designated as the "anthropogenic factor." Together, these metals account for 18% of the contamination in the research region. Auto shops, home wastewater, tyre wear and petrol combustion are probably the main sources of these metals. Pb, Ni, Cd, and Cu all showed total similarity in the second component (C2), which can be attributed to both the "natural factor" and anthropogenic factor because the composition of parent rocks and different anthropogenic activities in the study area seem to control the concentrations of these heavy metals. Based on the data, these metals account for about 41 percent of the total contamination in the area under study.

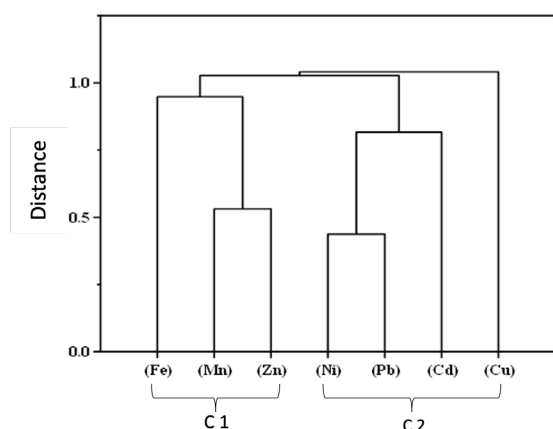


Figure 4. Dendrogram illustrating cluster analysis for seven heavy metals.

Principal component analysis

To find the group of metals with the same origin, elemental data was analysed using the PCA approach. It reduces the dataset's dimensionality and shows the relationship between the variables. All elements must be measured in the same units in order to execute PCA with the covariance function [33]. Seven measurable variables and a total of 25 monitoring points from the data matrix were used in this study to determine the categorization. The dataset's key gradients are used to calculate PC and its eigenvalues. The first four PCs had the most significant components, accounting for 78.32% of the variance in water quality overall. As shown in Table 7, the PC1, PC2, PC3, and PC4 explained 24.29%, 22.19%, 18.41%, and 13.43% of the variation, respectively. The three factors with eigenvalues > 1 (1.70, 1.55, 1.28, 0.94), after varimax rotation, were extracted from the major factor matrix. The first component (PC1), which accounts for the largest variance of 24.29%, has significant positive

loadings of Ni (0.657), Pb (0.632), and Cd (0.376), making it useful in recognising changes in water quality. Because of human and environmental influences, the PC1 factors had the biggest impact on the chemistry of the groundwater. Significant indications can leak into groundwater as a result of mineral weathering that contains silicate and salt as well as interactions between water, soils, and rocks [37]. PC2 showed significant positive loadings of Zn (0.642) and Mn (0.679), which together accounted for 22.19% of the variance and indicated the relationship with adjacent human activity. Additionally, PC3 explained 18.41% of the variance, indicating a significant positive loading of Zn (0.335), Cu (0.429), and Fe (0.730). It seems that PC3 comes from various human sources, such as car and industrial pollution (47,48). PC4 demonstrates that a large positive loading of Cu (0.81) accounts for 13.43% of the variance. The scree plot is a method for identifying multiple significant components by seeing a large split in the size of the eigen values, which causes the plot's slope to change from steep to shallow, as seen in Fig. 5(b) [8,33]. When the first three parameters are taken into account, the plot's slope changes from steep to shallow. The eigenvalues drop below one as component 3 and factor 5 are farther moved. This suggests that the best option for this investigation would be a four-component solution, which explains the overall variance of 78.32%. Most of the variables in the loadings plot of the first two PCs (PC1 and PC2) are distributed in the first and fourth quadrants depicted in Fig. 5(a). The contributions of each variable to the samples are shown by the lines passing through the origin and linking the variables. The degree of reciprocal relationship between two variable lines is indicated by their proximity [33]. The loading plot's grouping of variables (Pb, Fe, and Zn; Mn; Cu, Cd, and Ni) shows a strong positive association with one another. PCs score plots show sample attributes and offer details on how they are distributed geographically. The PCs scores plot (Fig.5(a)), which was produced with the assistance of the PC1 and PC2 components, confirms the spatial distribution and clustering of site-specific samples. Figures 5(a) and 5(b) show that samples arranged in the top quadrants have higher concentrations of maximum elements like Pb, Fe, Mn, and Zn, whereas samples in the lower quadrants have higher concentrations of Cu, Cd, and Ni. According to the groundwater scores plot shown in Fig 5 (a), the sample distributions is scattered. Moreover, the two main components, PC1 and PC2, which account for 24.29% and 24.29% of the total variance and have large loadings of (≥ 0.40), were also found to be primarily in charge of controlling the amounts of metals in the groundwater in the study area [33]. This is due to the fact that only 40% of the elements examined in the research region come under these two components with a substantial loading (0.40). In contrast, PC3 and PC4 showed substantial positive loadings of 13.43% and 18.41%, respectively, together with low variance characteristics. Because of their smaller variance, they were consequently assigned the lowest priority when it came to controlling the metal concentrations in ground water.

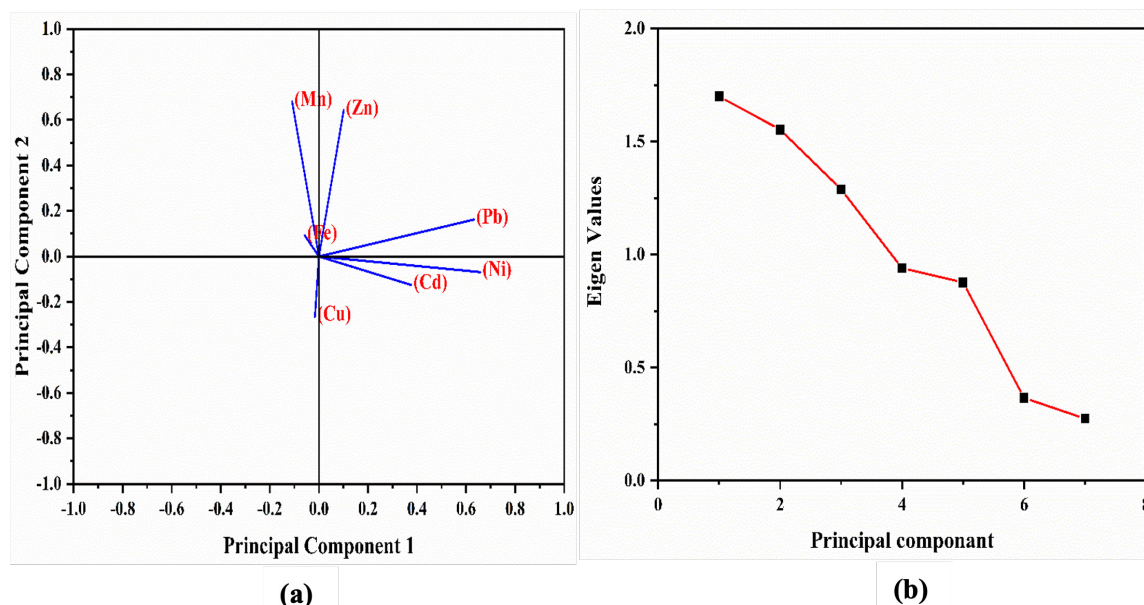


Figure 5. (a) Plot of PCA loadings scores for data set and (b) PCA scree plot of the eigen value.

Table 7. Principal component loadings for metals in groundwater.

Heavy Metal	Coefficients of PC1	Coefficients of PC2	Coefficients of PC3	Coefficient Of PC4
(Fe)	-0.0573	0.09196	0.73042	-0.4863
(Mn)	-0.1094	0.67964	-0.2536	0.24547
(Ni)	0.65771	-0.0688	0.1988	0.03786
(Pb)	0.63258	0.16258	-0.0826	-0.0512
(Zn)	0.10079	0.6423	0.33586	0.16664
(Cd)	0.37631	-0.1251	-0.2425	0.00809
(Cu)	-0.0163	-0.2651	0.4292	0.81938

Single-Factor Evaluation

Groundwater samples totalling 25 were examined in pre and post monsoon season for the presence of heavy metals, and the results showed that the concentrations of these metals can be categorised as follows: $Pb > Mn > Fe > Zn > Ni > Cu > Cd$. Furthermore, coefficient of variation was greater than 1 at majority of the sampling points, hydro-chemical properties of the groundwater showed inconsistency in both the seasons. Locations like Hillar and Chawalgam has insignificant variation in pre and post monsoon season probably due to consistency of a similar source of origin (geological crustal) during both seasonal periods [28]. Comparison of seven heavy metals when done with the BIS for ground water quality (Table 8), it was observed that the quality of 19 water samples did not comply the Pb and Ni concentra-

tion requirement as per BIS, accounting to 76% for each element in pre monsoon seasons and in post monsoon season 19 and 21 water samples did not comply the Pb and Ni concentration requirement as per BIS, accounting to 76% and 84% for each element respectively. Additionally, the concentration of manganese was greater than permissible limits at 5 and 6 locations in pre and post monsoon seasons respectively accounting to 20% and 24%. The findings indicated that Pb, Ni, Fe, and Mn contamination existed in the local groundwater. Figure 6 depicts the spatial distribution map of Iron, Lead, Copper, Cadmium, Nickel, Manganese, Zinc concentrations.

Table 8. Statistical characteristics of heavy metals in ground water (µg/l)

Index	Pre-Monsoon (µg/l)								Post Monsoon (µg/l)							
	Ci	Ci	Ci	Ci	Ci	Ci	Ci	Ci	Ci	Ci	Ci	Ci	Ci	Ci	Ci	Ci
	(Fe)	(Mn)	(Ni)	(Pb)	(Zn)	(Cd)	(Cu)	(Fe)	(Mn)	(Ni)	(Pb)	(Zn)	(Cd)	(Cu)	(Fe)	(Cu)
Max (conc.)	632.9	550.0	207.8	20.0	87.8	20.0	1721.4	664.5	561.0	224.4	20.4	90.4	0.0	1807.5		
Min (conc.)	0.0	0.0	3.7	0.0	0.9	0.0	0.0	0.0	0.0	4.0	0.0	0.9	0.0	0.0		
Sampling points exceeding	4.0	19.0	0.0	3.0	19.0	0.0	5.0	4.0	19.0	0.0	3.0	21.0	0.0	6.0		
BIS limit (Each)	16%	76%	0%	12%	76%	0%	20%	16%	76%	0%	12%	84%	0%	24%		
Exceeding the standard (%)	118.8	293.9	48.2	1.3	39.0	3.1	200.0	124.7	299.8	52.0	1.3	40.2	0.0	210.0		
Mean	176.0	192.3	50.7	4.2	19.6	6.5	389.7	184.8	196.2	54.8	4.3	20.2	0.0	409.2		
Standard Deviation	1.48	0.65	1.05	3.31	0.50	2.12	1.95	1.48	0.65	1.05	3.31	0.50	2.04	1.95		
Coefficient of variation (100%)	240.0	40.0	57.0	150.0	70.0	ND	20.0	252.0	42.0	58.7	153.0	75.6	ND	ND		

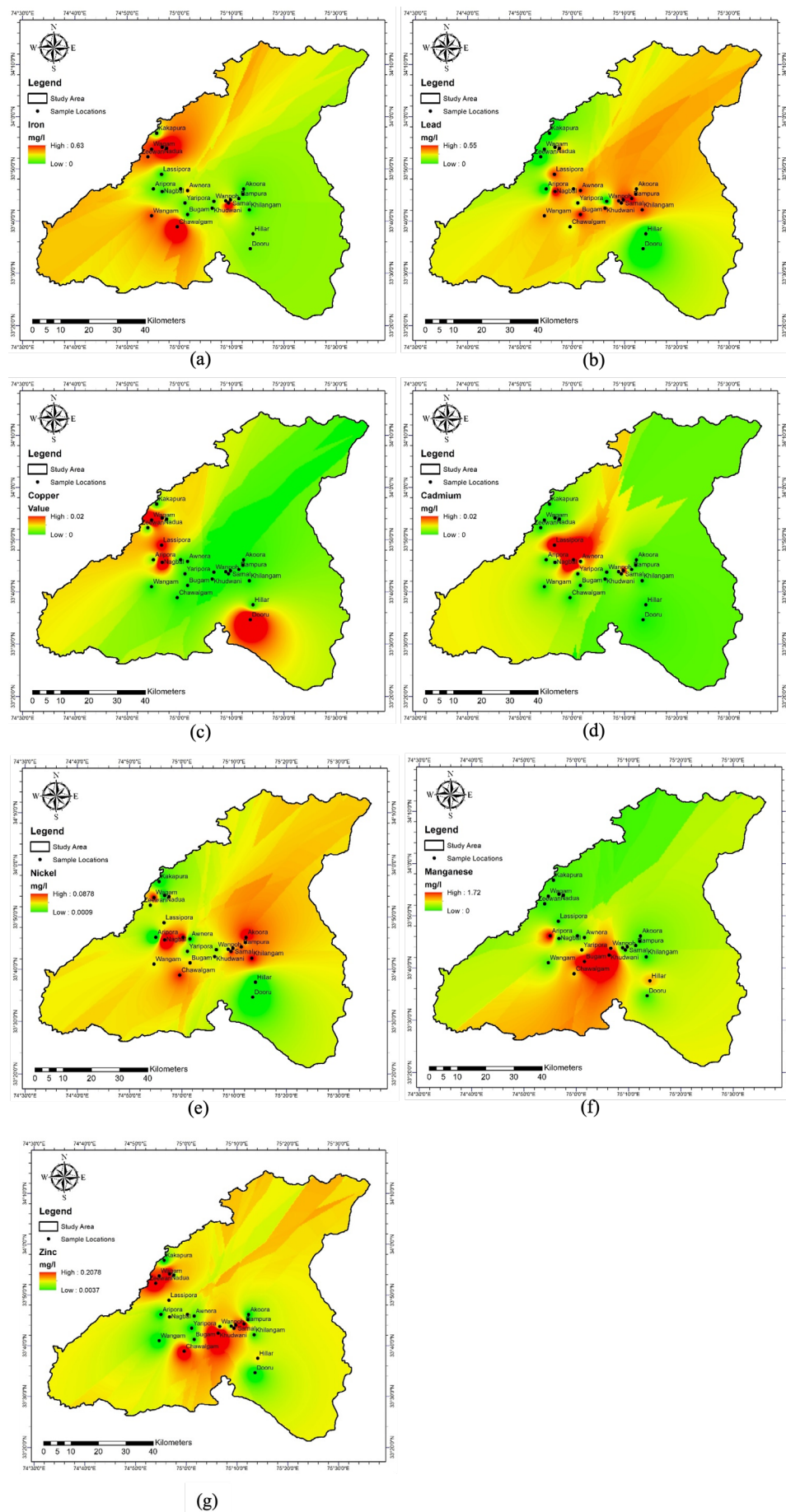


Figure 6. Spatial distribution of heavy metals: (a) Iron (b) Lead (c) Copper (d) Cadmium (e) Nickel (f) Manganese (g) Zinc in the research area.

Comprehensive Evaluation

The score of water quality of individual sample point is demonstrated in Table 9. In both the seasons Out of 25 samples, the quality of one sample was excellent, the quality of 2 samples were good, the quality of 2 samples were moderate and 20 water samples had a very poor-quality accounting to 4%, 8%, 8% and 80% respectively. The Excellent and good quality water accounted 12%, suggesting that the quality of water in the research area was very poor and majority of the sampling sites were contaminated. The results found in comprehensive evaluation validated the results of single factor evaluation.

Human Health Risk Assessment

Non-Carcinogenic Risk Assessment

The recommended values for risk limit suggested by some institutions are presented in Table 5. The derived non-carcinous health risk value of following heavy metals viz, lead, nickel, iron, manganese, zinc, copper and cadmium are depicted in the table 10 and 11 for pre monsoon season and post monsoon season, showing maximum value at 8.88×10^{-4} and 9.06×10^{-4} in pre and post monsoon season respectively. The results indicate that the level of non-carcinous health risk induced by zinc, nickel, lead and manganese in the groundwater of said area is very high and can cause serious harm to human health. It has been revealed after the calculation of non-carcinogenic health risk the following seven heavy metals can be graded as $Pb > Ni > Mn > Cd > Cu > Fe > Zn$. Among these lead and manganese are contributing the most, accounting 96%, 92% respectively, of the total health risk values.

Carcinogenic Health Risk Assessment

Table 10 and 11 show the carcinogenic health risk assessment for pre and post monsoon season respectively. The carcinogenic risk value for lead was found between 0 and 2.31×10^{-3} and 0 and 2.35×10^{-3} in pre and post monsoon season respectively. 24 samples exceeded the maximum acceptable Pb level recommended by The Dutch Ministry of construction and Environment, The Royal society and The Swedish Environmental Protection Agency. Nineteen

samples (76%) exceeded the permissible limit recommended by US environmental Protection Agency and International Commission on Radiological Protection for lead in both the seasons. The carcinogenic risk value for Cadmium was found between 0 and 6.51×10^{-5} in pre monsoon and 0 and 6.64×10^{-5} in post monsoon season. Three samples accounting 12% exceeding the maximum acceptable limits recommended for cadmium by The Dutch Ministry of construction and Environment, The Royal society, and The Swedish Environmental Protection Agency. One sample accounting 4 % exceeds the maximum acceptable limits recommended for cadmium by International Commission on Radiological Protection in both the seasons. The carcinogenic risk value for Nickel was found between 0 and 3.9×10^{-5} in pre monsoon season and 0 and 4.06×10^{-5} in post monsoon season. 24 samples exceeded the maximum acceptable Ni level recommended by The Dutch Ministry of construction and Environment, The Royal society and The Swedish Environmental Protection Agency accounting 96% in both the seasons. The results show a clear picture of carcinogenic health risk in the groundwater of the study area and the relevant authorities should seriously take the health risk into consideration.

Overall Health Risk Assessment

Tables 10 and 11 demonstrate that the carcinogenic risk assessment value is the main cause of the overall health risk. The average carcinogenic risk in pre monsoon season throughout the 25 sampling points was 4.27×10^{-4} , or 72.41% of the total health risk, while the average non-carcinogenic risk was 27.59%. and for post monsoon season the average carcinogenic risk throughout the 25 sampling points was 4.35×10^{-4} , or 72.38% of the total health risk, while the average non-carcinogenic risk was 27.62%. The findings demonstrated that both carcinogenic risk and non-carcinogenic risk contribute to the overall health risk of the study area's ground water. However, the risk of cancer is slightly higher than the risk of other diseases. Lead requires particular attention in the aforementioned study region as it accounts for 71% of the carcinogenic health risk.

Table 9. The calculation of Nemerow pollution index (F)

S No.	Location	Pre-Monsoon										Post Monsoon															
		Fi	Fi	Fi	Fi	Fi	Fi	Fi	F _{max}	F	F	(Fe)	F _i	(Pb)	F _i	(Zn)	F _i	(Cd)	F _i	(Ni)	F _i	(Cu)	(Mn)	F _i	F _{max}	F	F
		(Fe)	(Pb)	(Zn)	(Cd)	(Ni)	(Cu)	(Mn)																			
1	Nagbal	0	55	0	0	4.39	0.01	0.09	55	8.5	27.83	0	56.1	0	0	4.52	0.01	0.09	56.1	8.68	28.38						
2	Wangam	0.75	37	0	0	1.96	0	0.15	37	5.69	18.72	0.79	37.74	0	0	2.02	0	0.15	37.74	5.81	19.09						
3	Awnera	0.53	46	0	0	1	0	0.17	46	6.81	23.25	0.56	46.92	0	0	1.03	0	0.18	46.92	6.96	23.72						
4	Zanipora	0.17	32	0	6.67	3	0	0.07	32	5.99	16.28	0.18	32.64	0	6.8	3.09	0	0.07	32.64	6.11	16.6						
5	Shopian	0.11	0.23	0	0	0.05	0	2.02	2.02	0.34	1.02	0.12	0.23	0	0	0.05	0	2.12	2.12	0.36	1.07						
6	Lassipora	0	45	0	2	1.9	0.01	0.03	45	6.99	22.77	0	45.9	0	2.04	1.96	0.01	0.03	45.9	7.13	23.23						
7	Nadua	1.4	22	0.01	0	0.5	0.01	0.1	22	3.43	11.13	1.47	22.44	0.01	0	0.52	0.01	0.11	22.44	3.51	11.36						
8	Wagam	0.8	15	0	0	2.85	0.01	0.13	15	2.69	7.62	0.84	15.3	0.01	0	2.94	0.01	0.14	15.3	2.75	7.77						
9	Lajoora	1.17	39	0	0	2.2	0	0.1	39	6.07	19.73	1.23	39.78	0	0	2.27	0	0.11	39.78	6.2	20.13						
10	Kakapura	0.1	0.45	0	0	1	0	0.07	1	0.23	0.51	0.1	0.46	0	0	1.03	0	0.07	1.03	0.24	0.53						
11	Zeewan	0.72	0.39	0.01	0	1.7	0	0.03	1.7	0.41	0.87	0.75	0.4	0.01	0	1.75	0	0.04	1.75	0.42	0.9						
12	Sarnal	0	53	0.01	2	2.17	0	0.45	53	8.23	26.82	0	54.06	0.01	2.04	2.24	0	0.47	54.06	8.4	27.35						
13	Malaknag	0	44	0	0	1.53	0	0.06	44	6.51	22.24	0	44.88	0	0	1.58	0	0.06	44.88	6.65	22.68						
14	Mattan	0	38	0	0	2.06	0	0	38	5.72	19.21	0	38.76	0	0	2.13	0	0	38.76	5.84	19.6						
15	Akoora	0	33	0	0	3.23	0	0.14	33	5.2	16.7	0	33.66	0	0	3.32	0	0.15	33.66	5.3	17.04						
16	Khilangam	0	44	0	0	2.75	0	0	44	6.68	22.25	0	44.88	0	0	2.83	0	0	44.88	6.82	22.7						
17	Moominabad	2.11	31	0	0	2.91	0	0.02	31	5.15	15.71	2.22	31.62	0	0	3	0	0.02	31.62	5.27	16.03						
18	Rampura	0	53	0.01	0	2.54	0	0.08	53	7.95	26.8	0	54.06	0.01	0	2.62	0	0.08	54.06	8.11	27.33						
19	Dooru	0.14	0.52	0	0	0.73	0.01	0.08	0.73	0.21	0.38	0.14	0.53	0	0	0.75	0.01	0.08	0.75	0.22	0.39						
20	Wanpoh	0.09	0.27	0	0	1.57	0	1.1	1.57	0.43	0.81	0.1	0.28	0	0	1.61	0	1.16	1.61	0.45	0.84						
21	Hillar	0.14	0	0	0	0.73	0	1.17	1.17	0.29	0.6	0.15	0	0	0	0.75	0	1.23	1.23	0.3	0.63						
22	Khudwani	0.1	44	0.01	0	1.8	0	5.74	44	7.38	22.31	0.1	44.88	0.01	0	1.85	0	6.02	44.88	7.55	22.76						
23	Chawalgam	1.52	29	0.01	0	2.65	0	1	29	4.88	14.7	1.59	29.58	0.01	0	2.72	0	1.05	29.58	4.99	15						
24	Yaripora	0.07	25	0	0	1.5	0	0.7	25	3.9	12.65	0.07	25.5	0	0	1.55	0	0.74	25.5	3.98	12.9						
25	Bugam	0	48	0	0	2.06	0	3.2	48	7.61	24.3	0	48.96	0	0	2.13	0	3.36	48.96	7.78	24.79						

Table 10. Health risk assessment (a-1), pre-monsoon

S No.	Location	Health Risk Assessment, Pre-Monsoon										
		Non-Carcinogenic Risk					Carcinogenic Risk					Total Health Risk
		Fe	Pb	Zn	Cd	Ni	Cu	Mn	Pb	Cd	Ni	
1	Nagbal	0	8.8x10-4	2.9x10-7	0	9.9x10-6	7.3x10-6	4.3x10-7	2.3x10-3	0	3.9x10-5	3.2x10-3
2	Wangam	1.6x10-6	5.9x10-4	4.0x10-8	0	4.4x10-6	0	7.0x10-7	1.5x10-3	0	1.7x10-5	2.2x10-3
3	Awnera	1.2x10-6	7.4x10-4	1.5x10-7	0	2.2x10-6	0	8.0x10-7	1.9x10-3	0	8.9x10-6	2.7x10-3
4	Zanipora	3.7x10-7	5.1x10-4	3.0x10-7	4.5x10-5	6.7x10-6	0	3.2x10-7	1.3x10-3	6.5x10-5	2.6x10-5	2.0x10-3
5	Shopian	2.49x10-7	3.7x10-6	7.5x10-8	0	1.0x10-7	4.5x10-7	9.7x10-6	1.0x10-5	0	4.0x10-7	2.5x10-5
6	Lassipora	0	7.2x10-4	3.5x10-7	1.3x10-5	4.3x10-6	4.5x10-6	1.4x10-7	1.9x10-3	1.9x10-5	1.7x10-5	2.7x10-3
7	Nadua	3.16x10-6	3.5x10-4	9.7x10-7	0	1.1x10-6	4.5x10-6	4.8x10-7	9.6x10-4	0	4.4x10-6	1.3x10-3
8	Wagam	1.8x10-6	2.4x10-4	5.2x10-7	0	6.4x10-6	9.0x10-6	6.4x10-7	6.6x10-4	0	2.56x10-5	9.5x10-4
9	Lajoora	2.6x10-6	6.3x10-4	1.5x10-7	0	4.9x10-6	0	4.8x10-7	1.6x10-3	0	1.9x10-5	2.3x10-3
10	Kakapura	2.2x10-7	7.2x10-6	4.0x10-8	0	2.2x10-6	0	3.2x10-7	2.0x10-5	0	8.9x10-6	3.9x10-5
11	Zeewan	1.6x10-6	6.3x10-6	7.7x10-7	0	3.8x10-6	0	1.6x10-7	1.7x10-5	0	1.5x10-5	4.5x10-5

Table 10. Health risk assessment (a-1), pre-monsoon

S No.	Location	Health Risk Assessment, Pre-Monsoon											Total Health Risk
		Non-Carcinogenic Risk					Carcinogenic Risk						
		Fe	Pb	Zn	Cd	Ni	Cu	Mn	Pb	Cd	Ni		
12	Sarnal	0	8.5x10-4	6.6x10-7	1.3x10-5	4.9x10-6	0	2.1x10-6	2.2x10-3	1.9x10-5	1.9x10-5	3.1x10-3	
13	Malaknag	0	7.1x10-4	4.6x10-8	0	3.4x10-6	0	2.7x10-7	1.8x10-3	0	1.3x10-5	2.6x10-3	
14	Mattan	0	6.1x10-4	4.5x10-8	0	4.6x10-6	0	0	1.6x10-3	0	1.8x10-5	2.2x10-3	
15	Akoora	0	5.3x10-4	6.7x10-8	0	7.2x10-6	0	6.8x10-7	1.4x10-3	0	2.9x10-5	2.0x10-3	
16	Khilangam	0	7.1x10-4	1.3x10-7	0	6.2x10-6	0	0	1.8x10-3	0	2.4x10-5	2.6x10-3	
17	Moominabad	4.7x10-6	5.0x10-4	5.2x10-7	0	6.5x10-6	0	1.0x10-7	1.3x10-3	0	2.6x10-5	1.8x10-3	
18	Rampura	0	8.5x10-4	8.3x10-7	0	5.7x10-6	0	3.8x10-7	2.2x10-3	0	2.2x10-5	3.1x10-3	
19	Dooru	3.0x10-7	8.3x10-6	2.7x10-8	0	1.6x10-6	9.0x10-6	3.7x10-7	2.3x10-5	0	6.5x10-6	4.9x10-5	
20	Wanpoh	2.0x10-7	4.3x10-6	1.8x10-7	0	3.5x10-6	0	5.3x10-6	1.2x10-5	0	1.4x10-5	3.9x10-5	
21	Hillar	3.2x10-7	0	3.5x10-7	0	1.6x10-6	0	5.6x10-6	0	0	6.5x10-6	1.4x10-5	
22	Khudwani	2.2x10-7	7.1x10-4	1.5x10-6	0	4.0x10-6	0	2.7x10-5	1.8x10-3	0	1.6x10-5	2.6x10-3	

Table 11. Health risk assessment (a-1), post-monsoon

S No.	Location	Health Risk Assessment, Pre-Monsoon											Total Health Risk
		Non-Carcinogenic Risk					Carcinogenic Risk						
		Fe	Pb	Zn	Cd	Ni	Cu	Mn	Pb	Cd	Ni		
1	Nagbal	0	9.0x10-4	3.1x10-7	0	1.0x10-5	7.3x10-6	4.5x10-7	2.3x10-3	0	4.0x10-5	3.3x10-3	
2	Wangam	1.7x10-6	6.0x10-4	4.3x10-8	0	4.5x10-6	0	7.4x10-7	1.6x10-3	0	1.8x10-5	2.2x10-3	
3	Awnera	1.2x10-6	7.5x10-4	1.6x10-7	0	2.3x10-6	0	8.4x10-7	1.9x10-3	0	9.2x10-6	2.7x10-3	
4	Zanipora	3.9x10-7	5.2x10-4	3.2x10-7	4.6x10-5	6.9x10-6	0	3.3x10-7	1.4x10-3	6.6x10-5	2.7x10-5	2.0x10-3	
5	Shopian	2.6x10-7	3.7x10-6	8.1x10-8	0	1.0x10-7	4.5x10-7	1.0x10-5	1.0x10-5	0	4.1x10-7	2.6x10-5	
6	Lassipora	0	7.4x10-4	3.8x10-7	1.3x10-5	4.4x10-6	4.5x10-6	1.5x10-7	1.9x10-3	2.0x10-5	1.7x10-5	2.7x10-3	
7	Nadua	3.3x10-6	3.6x10-4	1.0x10-6	0	1.1x10-6	4.5x10-6	5.0x10-7	9.8x10-4	0	4.6x10-6	1.3x10-3	
8	Wagam	1.9x10-6	2.4x10-4	5.7x10-7	0	6.6x10-6	9.0x10-6	6.7x10-7	6.8x10-4	0	2.6x10-5	9.7x10-4	
9	Lajoora	2.7x10-6	6.4x10-4	1.6x10-7	0	5.1x10-6	0	5.0x10-7	1.7x10-3	0	2.0x10-5	2.3x10-3	
10	Kakapura	2.3x10-7	7.4x10-6	4.3x10-8	0	2.3x10-6	0	3.3x10-7	2.0x10-5	0	9.2x10-6	4.0x10-5	
11	Zeewan	1.7x10-6	6.4x10-6	8.3x10-7	0	3.9x10-6	0	1.7x10-7	1.8x10-5	0	1.5x10-5	4.6x10-5	

Table 11. Health risk assessment (a-1), post-monsoon

S No.	Location	Health Risk Assessment, Pre-Monsoon											Total Health Risk
		Non-Carcinogenic Risk					Carcinogenic Risk						
		Fe	Pb	Zn	Cd	Ni	Cu	Mn	Pb	Cd	Ni		
12	Sarnal	0	8.7x10-4	7.1x10-7	1.3x10-5	5.0x10-6	0	2.2x10-6	2.2x10-3	2.0x10-5	2.0x10-3	3.2x10-3	
13	Malaknag	0	7.2x10-4	4.9x10-8	0	3.5x10-6	0	2.8x10-7	1.9x10-3	0	1.4x10-5	2.6x10-3	
14	Mattan	0	6.2x10-4	4.8x10-8	0	4.8x10-6	0	0	1.6x10-3	0	1.9x10-5	2.3x10-3	
15	Akoora	0	5.4x10-4	7.2x10-8	0	7.5x10-6	0	7.2x10-7	1.4x10-3	0	2.9x10-5	2.0x10-3	
16	Khilangam	0	7.2x10-4	1.4x10-7	0	6.4x10-6	0	0	1.9x10-3	0	2.5x10-5	2.6x10-3	
17	Moominabad	5.0x10-6	5.1x10-4	5.6x10-7	0	6.7x10-6	0	1.1x10-7	1.3x10-3	0	2.6x10-5	1.9x10-3	
18	Rampura	0	8.7x10-4	8.9x10-7	0	5.9x10-6	0	4.0x10-7	2.2x10-3	0	2.3x10-5	3.1x10-3	
19	Dooru	3.2x10-7	8.5x10-6	3.0x10-8	0	1.6x10-6	9.0x10-6	3.9x10-7	2.4x10-5	0	6.7x10-6	5.0x10-5	
20	Wanpoh	2.1x10-7	4.4x10-6	2.0x10-7	0	3.6x10-6	0	5.5x10-6	1.2x10-5	0	1.4x10-5	4.1x10-5	
21	Hillar	3.4x10-7	0	3.8x10-7	0	1.7x10-6	0	5.9x10-6	0	0	6.7x10-6	1.5x10-5	
22	Khudwani	2.3x10-7	7.2x10-4	1.6x10-6	0	4.1x10-6	0	2.9x10-5	1.9x10-3	0	1.6x10-5	2.6x10-3	

Table 11. Health risk assessment (a-1), post-monsoon

S No.	Location	Health Risk Assessment, Pre-Monsoon												Total Health Risk
		Non-Carcinogenic Risk						Carcinogenic Risk						
		Fe	Pb	Zn	Cd	Ni	Cu	Mn	Pb	Cd	Ni			
23	Chawalgam	3.6x10-6	4.7x10-4	7.8x10-7	0	6.1x10-6	0	5.0x10-6	1.2x10-3	0	2.4x10-5	1.8x10-3		
24	Yaripora	1.5x10-7	4.1x10-4	8.1x10-8	0	3.4x10-6	0	3.5x10-6	1.1x10-3	0	1.3x10-5	1.5x10-3		
25	Bugam	0	7.9x10-4	1.3x10-7	0	4.8x10-6	0	1.6x10-5	2.0x10-3	0	1.9x10-5	2.9x10-3		
	Total	2.3x10-5	1.2x10-2	9.8x10-6	7.3x10-5	1.1x10-4	3.4x10-5	8.4x10-5	3.2x10-2	1.0x10-4	4.5x10-4	4.5x10-2		
	Mean	3.1x10-7	9.1x10-4	6.9x10-7	5.5x10-6	8.4x10-6	2.6x10-6	6.2x10-6	2.4x10-3	8.0x10-6	3.3x10-4	3.7x10-3		

DISCUSSION

Human activities and Environmental negligence:

The ignorant behaviour of people towards the environment, haphazard disposal of anthropogenic wastes, use of excess agricultural chemicals, untreated sewage discharges and clay and silty lithology has caused the deterioration of groundwater in Kashmir valley [38,39].

Sources and health impacts of iron and manganese:

Based on previous research it is found that salinity of groundwater is not an issue in the UT of Jammu and Kashmir, however the problem of iron, manganese contamination prevails. Deep aquifers in Kashmir valley have iron and marshy gases contributing to the contamination. Manganese leaches into the groundwater from iron bearing minerals due to presence of manganiferous phases [34,35]. Alluvium based aquifer, limestone and shales contribute to the iron and manganese contamination in the groundwater of Kashmir valley [40].

Manganese and iron are important heavy metals for human body, if consumed in the right or prescribed proportions. However, a slight increase in the consumption of the following elements can cause damage to the human health. According to WHO and EPA, the standard concentration of iron in drinking water is 0.1mg/l. Elevated levels of iron is associated with increasing heart disease, Hyperkeratosis, altered pigmentation and other illnesses like arthritis, endocrine problems, diabetes and also liver disease. Likewise, WHO and EPA, prescribe the standard concentration of manganese in drinking water is 0.05mg/l. Manganese if present excess in water imparts color, odor, or taste to the drinking water [19]. Exceeded values of manganese can cause Alzheimer's disease and various respiratory disorders. High exposure of manganese is also associated neurological problems in children including difficulty in speech, loss of memory and retard behaviour [41].

Lead contamination, causes and health impacts:

Lead is a hazardous component; it is injurious even in minor quantities. WHO and BIS has set the permissible limit of lead as 0.001mg/l in drinking water. Lead is both carcinogenic and non- carcinogenic depending upon the concentration consumption. Exceeded limit of lead consumption causes brain damage, anxiety, central nervous system damage and kidney failure [42]. Lead contamination can occur due to excavation, industrial and recycling activities. Delivery of drinking water through lead pipes can also cause lead contamination. Long term effects to human health like high blood pressure and kidney damage. In addition, it causes miscarriage, premature birth in pregnant ladies. Lead toxicity is more prominent in children causing irreversible health impacts mainly related to brain and nervous system development. The Public health impact of chemicals: knowns and unknowns nearly 50% of 2 million fatality is caused due to known exposure was due to lead in 2019 as is presented in a report furnished by world health

organisation in 2021. [19].

Sources and health effects of nickel and cadmium:

Nickle and cadmium are some of the heavy metals that are cancerous to humans and their chronic exposure increases the possibility of cancer [36,43]. The exposure to Nickle contamination causes allergies to skin, Lung Fibrosis and lung cancer and other cancers related to respiratory system. Mechanism behind cancers caused by Nickle is unknown however few research show that the mechanism might be genetic or epigenetic. Ni-enriched insecticides/fertilizers used in the agricultural activities could be the primary cause of contamination in groundwater samples [44,45].

According to WHO and EPA, the standard concentration of Cd in potable water is 0.005 mg/l. Cd is one of the most poisonous metals which is produced as a byproduct of zinc manufacturing. This metal if ingested by humans can lead to a very serious impact to human body. It causes a liver disease known as hepatotoxicity. It also causes various kidney related infections leading to kidney failures [46]. Considering the presence of the above toxic elements in the groundwater of our study area it is necessary for the relevant Government authorities to take effective measures to strengthen the protection from these elements.

CONCLUSION

The findings of the present study have shed light on the distressing reality of heavy metal contamination in the aquifers of four districts in South Kashmir. Both natural and human-induced activities were found to play a significant role in compromising the water quality of the study area. Notably, Pb emerged as the most predominant contaminant, with contamination levels ranking in the order of $Pb > Mn > Fe > Zn > Ni > Cu > Cd$. The highest health risks were associated with lead and nickel, with lead accounting for 72% of the carcinogenic health risk. It is, therefore, imperative to accord special attention to mitigating the levels of lead, manganese, iron, and nickel in the area's groundwater. The results of this study provide a valuable insight into the extent of heavy metal contamination in groundwater and its adverse impact on human health, thereby enabling researchers to build on this foundation. Furthermore, the transformation of paddy agricultural lands to orchards in Kashmir has augmented the risk of groundwater contamination due to the excessive use of chemicals. It is, therefore, recommended to establish a dedicated groundwater department in Kashmir to analyse and monitor the quality of groundwater and curb its deterioration. It is incumbent on the authorities to prioritize these four elements, raise awareness, and implement measures to mitigate their deleterious impact on health.

Notations

Abbreviation

AAS: Atomic Absorption Spectroscopy

APHA: American Public Health Association

BIS: Bureau of Indian Standards

CALEPA: California Environmental Protection Agency

Cd: Degree of Contamination

EPA: Environment Protection Act

PCA: Principal Component Analysis

CA: Cluster Analysis

IRIS: Integrated Risk Information System

ND: Not Detected

NPI: Nemerow Pollution Index

WHO: World Health Organisation

CGWB: Central Groundwater Board

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DATA AVAILABILITY STATEMENT

The author confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

USE OF AI FOR WRITING ASSISTANCE

Not declared.

ETHICS

There are no ethical issues with the publication of this manuscript.

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