



ORIGINAL ARTICLE

Heavy Metals Pollution and Health Risk Assessment of Groundwater of Bikaner Block (Rajasthan)

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KEYWORDS

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ABSTRACT: The quality of groundwater is crucial while its management is ignored. The present study investigated heavy metals pollution and health risk assessment of groundwater quality of Bikaner block (Rajasthan), India. The concentrations of heavy metals above the permissible limits can cause harm to human health. The study evaluated cancer and non-cancer health risks of heavy metals in groundwater for both children and adults based on hazard quotients (HQ), hazard indices (HI), and cancer risks (CR). Samples were collected from 26 sampling sites of Bikaner block. The physiochemical analysis of water samples was done. Selected heavy metals are Al, As, B, Cd, Cr, Co, Cu, Fe, Hg, Mn, Ni, Pb, Se, Sr, U, V, and Zn which were analyzed by inductively coupled plasma mass spectrometry (ICP-MS). Metal index (MI) and heavy metal pollution index (HPI) were evaluated. Human health risks were assessed through ingestion and skin contact routes. The hazard quotient was in the order $Hg > U > B > Sr > As > Cr > V$ for both children and adults. The HI was higher in children as compared to adults. The hazard index (HI) of more than 1 was of As, B, Cr, Hg, Sr, U, and V for adults and children. Cancer Risk of As, Cd, Cr, Ni, and Pb metals were detected and showed a higher risk for children than adults. Chromium was a major cancer risk factor in children than adults (0.000232). The results demonstrated the presence of metal pollution and metal risks to human health.

INTRODUCTION

Groundwater is a vital freshwater resource for the development of humans and the economy. It contributes to 97% of global freshwater resources consumed for drinking, irrigation, and industrial purposes. It is crucial to sustain groundwater resources for a sustainable and greener future. Utilization of groundwater for drinking and irrigation purposes needs quality investigation as groundwater contamination and its over-exploitation are growing. Hence, groundwater quality is deteriorating. It is difficult to perceive groundwater contamination. With population rise, groundwater pollution is greatly caused by underground injection of chemicals and hazardous wastes, landfills, and industrial releases. Assessment of

groundwater quality is obligatory in the current time to get an overview of the information on groundwater quality. It has a significant role in sustainable development goals (SDG) as SDGs 2, 3, and 6 are concerned with food production, health, and water security respectively.

India being the largest user of groundwater in the world is highly dependent on it. 70% of the water supply in agriculture is groundwater. It is the lifeline of the water supply. However, most of India's water problems are associated with groundwater [1]. The naturally occurring contaminants that have been widely researched in India are arsenic and fluoride. Others are iron, manganese,

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chromium, and radionuclides such as radium, radon, and uranium. The high concentrations of these geogenic groundwater contaminants may pose human health issues such as cancer, dental, and skeletal problems.

Various researches have been done on groundwater quality with special reference to heavy metal pollution, its sources, and its effects on human health. Such studies are helpful to alleviate contaminants and guard this valuable resource such as in China [2, 3], Egypt [4, 5], Ghana [6], India [7-13], Indonesia [14], Iran [15-17], Mexico [18], Nigeria [19-22], Saudi Arabia [23], South Africa [24], Sudan [25] etc.

Objective

The lack of research on heavy metal content in groundwater in Bikaner City highlights the need for the present study. The objective of the study is to estimate metal concentrations in groundwater and metal's human health risk assessment in Bikaner City of Rajasthan, India.

MATERIALS AND METHODS

Study area: Bikaner block is in the North-western part of Rajasthan and encompassed between north latitudes

27°11' to 29°03' and east longitudes 71°52' to 74°15' covering a geographical area of 30247.90 km. The block experiences an arid type of climate. Annual rainfall is in the range of 260 mm to 440 mm per year [26]. Nearly 90% of the total annual rainfall is received during the southwest monsoon which enters the block in the first week of July and withdraws in the middle of September. As the block lies in a desert area, extreme heat in summer and extreme cold in winter are the characteristics of the area. Here, the hottest month is June (36°C average) and the coldest month is January (16°C average). In the summer season, the temperature lies in the range of 28°C to 53.5°C. The winter is cold with temperatures lying in the range of -4°C to 23.2°C. The atmosphere is generally dry except during the monsoon period. The humidity is the highest in August month with a mean daily relative Humidity of 71% in the morning and 52% in the evening. The soils of the Bikaner block are predominantly light textured and weakly structured but well drained.

A total of 26 groundwater samples were collected from different locations of Bikaner block. The locations of the sampling site (Figure 1) and depth of groundwater are tabulated in Table 1.

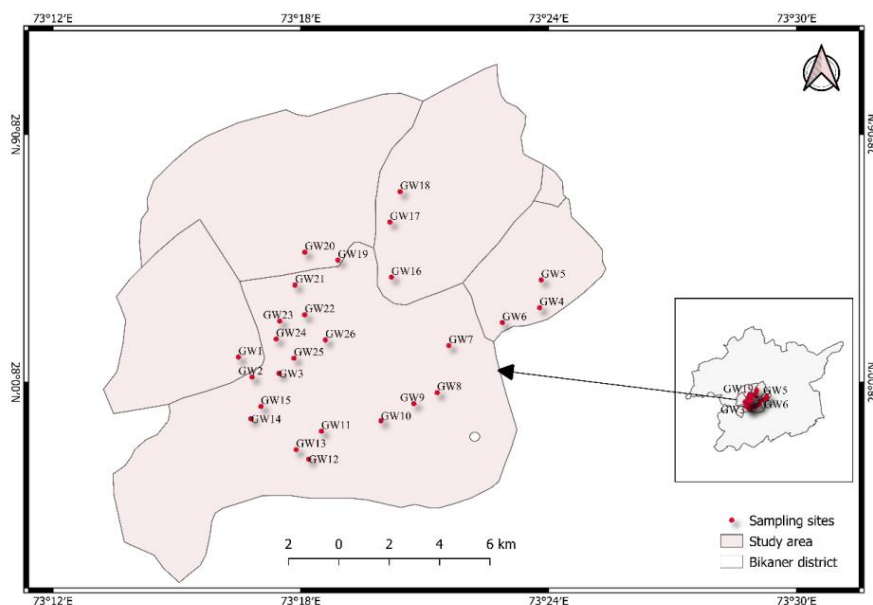


Figure 1. Locations of sampling sites in the study area (Bikaner block, Rajasthan, India).

Table 1. Depth of sampling sites of Bikaner block.

Sample number	Sampling site	Groundwater depth (feet)
GW1	Karmisar	600
GW2	Murlidhar Vyas colony	550
GW3	Nehru nagar	345
GW4	Jaipur road (shiv Badi)	350
GW5	Vrindavan Enclave	ND
GW6	Vaishno Dham	500
GW7	Shiv Badi	280
GW8	Tilak Nagar	300
GW9	Hotel Chirag	ND
GW10	Ghadsisar	650
GW11	Ganga Sahar road (old bus stand)	1000
GW12	Indira Gandhi colony	250
GW13	Bhinasar	230
GW14	Sujandesar	250
GW15	Shreeramsar	550
GW16	Karni nagar	ND
GW17	Beechwal Industrial area	400
GW18	Agricultural university	550
GW19	Rampura	200
GW20	Karni industrial area	ND
GW21	Mukta Prasad sector 2	350
GW22	Vaidhya magharam colony	400
GW23	Shree Ganga jubilee pinjrapole	250
GW24	Nathusar	ND
GW25	Mohaton ka chowk	350
GW26	Phool Bai kuwa, Joshivada	ND

Sampling and analysis

Groundwater samples were collected for physiochemical analysis in a sterilized plastic container (PVC – 500 mL) after flushing out the tap (minimum 10 minutes) to get the fresh groundwater. Then, the required quantity of water sample was collected after rinsing the container for more than 3 times. A total of twenty-six water samples were collected from bore wells and tube wells existing in Bikaner City in January 2023. The containers were sealed and the samples were protected from direct sunlight during transportation. The water pH was determined by the HACH Digital pH meter standardized with a standard buffer solution. Electrical conductivity

was determined by using a HACH digital conductivity meter standardized with KCl solution. All the parameters were analyzed according to standard methods and protocols provided in Standard Methods for the analysis of water [27]. Alkalinity was assessed by titration method. Major cations such as sodium, potassium, calcium, magnesium, and ammonium and major anions such as chloride, fluoride, nitrate, nitrite, and sulfate were assessed by ion chromatography method using the Metrohm IC instrument. Silica was measured by absorption method using a UV - VIS spectrophotometer. Metals such as Al, As, B, Cd, Cr, Co, Cu, Fe, Hg, Mn,

Ni, Pb, Se, Sr, U, V, and Zn were estimated by inductively coupled plasma mass spectrometry (ICP-MS).

Descriptive statistics were executed to find the groundwater quality of the study area. A correlation matrix was performed to assess the relation between groundwater quality parameters. Parameters with positive higher correlation coefficients were more associated and might have similar characteristics. Metal index (MI) and heavy metal pollution index (HPI) were calculated to estimate the metal pollution in groundwater [28, 29].

QGIS software (version 3.18.3) was used to do mapping of the study area and heavy metal pollution index through inverse distance weighted (IDW) type of interpolation.

Human health assessment

Assessment of metal hazards on human health was estimated by following the United States Environmental Protection Agency's human risk assessment model [30]. The model classifies human health hazards into non-carcinogenic risk and carcinogenic risk. The carcinogenic and non-carcinogenic risks of heavy metal-contaminated

water were calculated by chronic daily intake (CDI). Hazard quotient (HQ) and hazard index (HI) were applied to measure non-carcinogenic risk.

Chronic daily intake ($\text{mg kg}^{-1} \text{day}^{-1}$) of metal-containing water samples was calculated by the given formula:

$$\text{CDI} = \frac{C * \text{IR} * \text{EF} * \text{ED}}{\text{BW} * \text{AT}}$$

Where C is heavy metal concentration in water (mg L^{-1}), IR is average daily water ingestion rate (1 L per day for children and 2 L per day for adults), EF is exposure frequency (365 days per year), ED is exposure duration (6 years for children and 70 years for adults), BW is body weight (15 kg for children and 70 kg for adults), AT is the average lifetime of human exposure (2190 days for children and 25550 days for adults).

Then, the hazard quotient (HQ) was computed which expresses the non-carcinogenic risks associated with the consumption of metal-containing groundwater.

$$\text{HQ} = \frac{\text{CDI}}{\text{RfD}}$$

Where R_fD is the reference dose of metal ($\text{mg kg}^{-1} \text{day}^{-1}$) as shown in Table 2.

Table 2. Reference dose of metals for human health assessment.

Metal	Reference dose of metal ($\text{mg kg}^{-1} \text{day}^{-1}$)	
	R _f D (Ingestion)	R _f D (Dermal)
Al	1	1
As	0.0003	0.0003
B	0.2	0.2
Cd	0.0005	1.25E-05
Co	0.02	0.02
Cr	0.003	0.000075
Cu	0.04	0.04
Fe	0.7	0.14
Hg	0.0003	0.000021
Mn	0.14	0.0056
Ni	0.02	0.0008
Pb	0.0035	0.0035
Se	0.005	0.005
Sr	0.6	0.6
U	0.003	0.003
V	0.007	0.007
Zn	0.3	0.3

The Hazard Index (HI) is the summation of HQ values of all metals.

$$HI = \sum_{i=1}^n HQ$$

If the value of HI is less than 1 then water is considered to be safe for drinking. While the HI value more than 1 indicates non-carcinogenic risks.

Carcinogenic risk (CR) is the product of chronic daily intake and cancer slope factor of a particular metal. The carcinogenic risk index (CRI) is the total of all metal's carcinogenic risks.

$$CR = CDI * CSF$$

$$CRI = \sum_{i=1}^n CR$$

Where CSF is the cancer slope factor in $(\text{mg kg}^{-1} \text{day}^{-1})^{-1}$. The permissible limits of cancer risk are 10^{-6} to 10^{-4} for a single metal and it is 10^{-5} for the carcinogenic risk index. Metals like Cu, Hg, Mn, Se, and Zn are non-carcinogenic. Whereas carcinogenicity of Al, B, Co, Fe, Sr, U, and V are not determined yet. Carcinogenic risks of As, Cd, Cr, Ni, and Pb were calculated due to their known carcinogenic natures. The cancer slope factor (in $(\text{mg kg}^{-1} \text{day}^{-1})^{-1}$) of As, Cd, Cr, Ni, and Pb were 1.5, 15, 0.5, 0.91, and 0.0085 respectively for ingestion and 1.5, 600, 20, 22.75 and 0.0085 for dermal.

RESULTS AND DISCUSSION

Table 3 shows a descriptive statistical analysis of physico-chemical parameters of groundwater samples of the study area.

pH, the measure of hydrogen ions concentration in the water, is an important parameter that controls the fate of biogeochemical reactions in the water systems. The range of pH and electrical conductivity (EC) in groundwater water samples are 6.15 to 7.03 and 345 to 4804 $\mu\text{S cm}^{-1}$ respectively.

The concentration of sulfate and chloride in groundwater ranges from 10.35 to 782.28 mg L^{-1} and 34.90 to 1763.60 mg L^{-1} respectively. The sources of sulfate are dry

precipitation and weathering of gypsum rocks. Whereas, the sources of chloride in water are due to rainwater input and dry precipitation. Seven sampling sites (GW2, GW3, GW4, GW14, GW22, GW24, GW25) show a concentration of sulfate above the acceptable limit (200 to 400 mg L^{-1}) set by BIS [31]. 250 to 1000 mg L^{-1} chloride concentration is the permissible limit as per BIS which is found above the limit in two sampling sites GW3 and GW 21. The concentration of fluoride in groundwater samples is 0.121 to 2.928 mg L^{-1} . Sources of fluoride are mainly the weathering of fluorapatite and other fluoride-containing rocks. The permissible limit of fluoride concentration is 1 to 1.5 mg L^{-1} . Seven sampling sites are found beyond F permissible limits i.e., GW1, GW3, GW4, GW5, GW6, GW21, and GW23. The concentration of nitrate in groundwater samples is 3.682 to 485.913 mg L^{-1} . The source of nitrate in groundwater may be from agriculture and urban sources including chemical fertilizers and animal manure application [26]. 13 sampling sites show the concentration of nitrate above the permissible limit (45 mg L^{-1}) i.e., GW2, GW3, GW7, GW8, GW13, GW14, GW15, GW21, GW22, GW23, GW24, GW25, and GW26. The nitrite form of nitrogen is found in 6 groundwater samples and its range is 0.064 to 0.246 mg L^{-1} .

The concentration of potassium in groundwater water samples is 2.51 to 21.06 mg L^{-1} . The permissible limit of K is 10 mg L^{-1} set by WHO. Sampling sites beyond the K permissible limit are GW2, GW8, GW10, GW14, GW22, and GW26. The concentration of sodium in groundwater is 41.58 to 1226.9 mg L^{-1} . Na shows a strong correlation with K, Mg, and Ca. All sampling sites crossed the permissible limit of Na (200 mg L^{-1} of WHO). The concentration of calcium in groundwater is 17.8 to 210.4 mg L^{-1} . The source of calcium is the weathering of calcite and dolomite. Sampling site GW3 shows the concentration of Ca more than the permissible limit (75 to 200 mg L^{-1}). The concentration of magnesium in groundwater is 7.03 to 113.92 mg L^{-1} . The source of magnesium (Mg) is mainly the weathering of dolomite and magnesite. Sampling site GW2 shows a concentration of Mg more than the permissible limit (30 to 100 mg L^{-1}). The concentration of ammonium in groundwater is 0.142 to 2.408 mg L^{-1} . The permissible

limit of ammonium is 0.5 mg L⁻¹. More than 50 % of sampling sites express ammonium concentration above the permissible limit which are GW6, GW7, GW8, GW10, GW11, GW12, GW13, GW14, GW15, GW16, GW17, GW18, GW19, GW20, and GW25.

The sources of heavy metals in groundwater are rock minerals, vegetation, sands, and salts. The concentration of aluminium in groundwater samples is 0.62 to 19.74 µg L⁻¹. Arsenic concentration is found from 0.06 to 3.55 µg L⁻¹. The concentration of boron in groundwater samples is 310 to 1776 µg L⁻¹. The concentration of B above the permissible limit (1000 µg L⁻¹) is found in sampling sites GW2, GW3, GW6, GW14, GW18, and GW21. The range of cadmium concentration is 0 to 0.08 µg L⁻¹. While cobalt concentration ranges from 0 to 1.42 µg L⁻¹. The range of copper in groundwater samples is 0.12 to 4.58 µg L⁻¹. The concentration of chromium in groundwater samples is 0.05 to 12.93 µg L⁻¹. Iron concentration in groundwater samples is 0.95 to 51

µg L⁻¹. The concentration of manganese in groundwater samples is 0.04 to 366 µg L⁻¹. The permissible limit of Mn is 100 µg L⁻¹ which is found above in the GW26 sampling site. Mercury concentration is 0.02 to 10.34 µg L⁻¹. The permissible limit of Hg is 1 µg L⁻¹ which is found above in sampling sites GW1, GW2, GW3, GW4, GW5, GW6, GW8, GW11, GW12, GW14, GW16, GW21, GW23 and GW26. Nickel ranges from 0 to 2.72 µg L⁻¹. Lead ranges from 0 to 0.24 µg L⁻¹. Selenium concentration ranges from 0 to 7.22 µg L⁻¹. Strontium concentration in groundwater samples is 816 to 3774.70 µg L⁻¹. The concentration of uranium in water samples is 1.37 to 43.67 µg L⁻¹. Vanadium concentration ranges from 0.24 to 25.44 µg L⁻¹. Zinc is an essential micronutrient and beneficial element for human bodies. It is present abundantly in natural sources like soils and sediments etc. The concentration of Zn in water samples is 1.3 to 113.15 µg L⁻¹.

Table 3. Descriptive statistical analysis of physicochemical parameters of groundwater samples of the study area.

Parameter	Mean	Maximum	Minimum	Mode	Median	Range	Standard Deviation	CV	Skewness	Variance
pH	6.7	7.0	6.2	6.6	6.7	6.15-7.03	0.21	0.03	-0.68	0.04
EC (µS cm ⁻¹)	3139.4	7352.0	345.0	NA	3091.0	345-7352	1302.02	0.4	0.97	1630043
Silica (mg L ⁻¹)	10.0	13.1	5.5	9.4	9.9	5.5-13.06	1.49	0.15	-0.72	2.12
Alkalinity (mg L ⁻¹)	296.3	479.0	73.0	NA	299.1	73-479	86.87	0.3	-0.35	7255
Sodium (mg L ⁻¹)	510.6	1226.9	41.6	NA	518.4	41.6-1227	228.16	0.45	0.80	50056
Potassium (mg L ⁻¹)	9.2	21.1	2.5	NA	8.5	2.51-21.06	4.43	0.48	1.28	18.85
Calcium (mg L ⁻¹)	106.9	210.4	17.9	NA	91.1	17.88-210.4	48.07	0.45	0.55	2222
Magnesium (mg L ⁻¹)	54.8	113.9	7.3	NA	50.9	7.30-113.90-2.4	26.03	0.48	0.52	651
Ammonium (mg L ⁻¹)	0.8	2.4	0.0	0.0	0.6		0.76	1.01	0.48	0.56
Fluoride (mg L ⁻¹)	1.3	3.0	0.1	NA	1.2	0.12-2.99	0.67	0.53	1.03	0.44
Chloride (mg L ⁻¹)	652.5	1763.3	34.9	NA	681.4	34.90-1763.2	353.87	0.54	0.90	120410
Sulphate (mg L ⁻¹)	331.8	902.0	10.4	NA	288.1	10.35-902.0	214.53	0.65	1.03	44251
Nitrate (mg L ⁻¹)	89.9	485.9	3.7	NA	55.0	3.68-485.90-	102.31	1.14	2.57	10065

						0.246				
Nitrite (mg L⁻¹)	0.0	0.2	0.0	0.0	0.0	0-0.2	0.07	2.09	2.07	0.00
Al (µg L⁻¹)	2.7	19.7	0.6	1.1	1.4	0.58-19.74	4.47	1.64	3.28	19.25
As (µg L⁻¹)	0.7	3.6	0.1	0.5	0.5	0.06-3.55	0.69	0.98	2.97	0.46
B (µg L⁻¹)	827.0	1777.0	310.0	NA	826.0	310-1777	310.92	0.38	0.95	92954
Cd (µg L⁻¹)	0.0	0.1	0.0	0.0	0.0	0-0.08	0.02	0.95	3.34	0.00
Co (µg L⁻¹)	0.1	1.4	0.0	0.0	0.0	0-1.42	0.31	2.59	3.74	0.09
Cr (µg L⁻¹)	4.6	12.9	0.1	0.5	4.3	0.05-12.93	4.34	0.95	0.61	18.08
Cu (µg L⁻¹)	0.7	4.6	0.1	0.5	0.4	0.12-4.58	0.94	1.29	3.11	0.85
Fe (µg L⁻¹)	4.2	51.1	1.0	NA	2.3	0.95-51.1	9.63	2.28	4.98	89.13
Hg (µg L⁻¹)	1.9	10.3	0.0	0.2	1.1	0-10.34	2.59	1.35	2.22	6.43
Mn (µg L⁻¹)	17.9	366.1	0.0	NA	3.1	0.04-366	71.19	3.98	5.06	4873.58
Ni (µg L⁻¹)	0.1	2.7	0.0	0.0	0.0	0-2.72	0.53	5.10	5.10	0.27
Pb (µg L⁻¹)	0.0	0.2	0.0	0.0	0.0	0-0.24	0.06	1.81	2.73	0.00
Se (µg L⁻¹)	2.5	7.2	0.0	NA	2.4	0-7.22	1.54	0.61	1.10	2.29
Sr (µg L⁻¹)	1680.5	3774.7	260.3	NA	1502.7	260.25-3774.7	859.64	0.51	0.75	710553
U (µg L⁻¹)	14.0	43.7	1.4	NA	12.1	1.37-43.67	8.97	0.64	1.50	77.44
V (µg L⁻¹)	10.5	25.4	0.2	NA	9.0	0.24-25.44	5.82	0.55	0.64	32.52
Zn (µg L⁻¹)	31.2	113.2	1.3	NA	17.8	1.3-113.15	33.73	1.08	1.51	1094

Hydrochemical characteristics

The major ions analyzed are plotted on a Hill-Piper trilinear diagram (Figure 2) which displays their uneven distribution. The diagram is comprised of two triangles at the base and one diamond shape at the top to represent the major significant cations and anions responsible for

the nature of groundwater. Calcium cation demonstrates more than 80% dominance. Whereas, anions carbonate and bicarbonate have 2-65% dominance and chloride and sulphate show dominance from 38-82%.

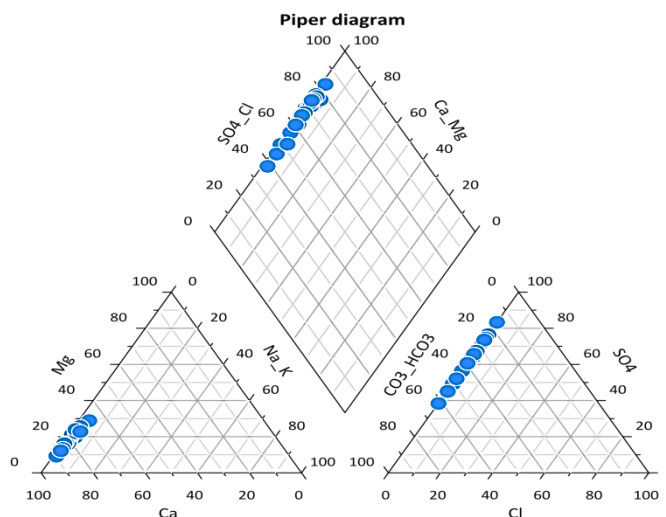


Figure 2. Piper diagram showing hydrochemical facies of groundwater of the study area.

Correlation matrix

The correlation matrix of various groundwater quality parameters including heavy metals is created and analyzed (Table 4). Parameters like pH, EC, alkalinity, silica, major anions, cations, and heavy metals are significantly correlated, reflecting more than 0.50 positive correlation values. Further, Na^+ vs EC, Alkalinity vs Mg/Nitrate, K^+ vs Ca^{2+} and Mg^{2+} , HCO_3^- vs Alkalinity, sulfate, and nitrate indicate the most relevant correlation having a significant impetus on the overall assessment of the quality of groundwater than any other major essential and physical parameters. A critical analysis of the correlation matrix indicates that sulfate is positively correlated with EC, Na^+ , Ca^{2+} , Mn, and Cl⁻. Similarly, Na^+ is positively correlated with EC. Ca^{2+} is positively correlated with EC, Na^+ , Mg^{2+} , and K^+ . Ca and Mg are also strongly related to Sr with 0.91 and 0.93 values respectively. Further, Fe is positively correlated with nitrate and Al^{+3} . Mn shows a strong positive relation with Ni (1.0). Cadmium and cobalt are strongly related to Mn and Ni. Uranium is positively correlated to nitrate (0.83 correlation value) and it contributes to alkalinity (0.82 correlation value). Positive correlations between metals signify their common sources. The positive correlations are also seen in As-B (0.77), Co-Cd (0.79), Fe-Al (0.54), Pb-B (0.47), Pb-Hg (0.33), Sr-B (0.46), Sr-Co (0.40), U-B (0.61), U-Co (0.37), U-Sr (0.76), V-Al (0.38), V-As (0.76), V-Cr (0.45), V-U (0.28), V-Se (0.47), Zn-B (0.20), Zn-Cd (0.50), Zn-Co (0.42), Zn-Mn (0.26), Zn-Ni (0.26), Zn-Pb (0.43), Zn-Sr (0.24) and Zn-

U (0.41).

Heavy metal pollution load

Table 5 represents the metal index values of the study area. All the selected heavy metals come in very pure or pure class except Hg and V. MI values of 1.9 and 2.6 are shown by Hg and V respectively denoting slight and moderate effects of both metals. Overall, the study area has a cumulative metal index value of 6.7 and shows characteristics of being seriously affected by metals.

The heavy metal pollution index of selected heavy metals in the study area is calculated which is displayed in Figure 3 and Table 6. HPI value of Al was maximum in GW 4 and GW 8 (0.045). As had the highest HPI of 0.256 in GW 9 and GW 26. The highest HPI of B, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Sr, U, V, and Zn were 0.132 (GW 3), 17.2 (GW 1), 0.029 (GW 26), 0.928 (GW 1), 0.001 (all samples), 0.171 (GW 1), 532.9 (GW 4), 0.229 (GW 26), 2.57 (GW 1), 5.12 (GW 1), 3.57 (GW 14), 0.012 (GW 2), 2.50 (GW 2), 15.91 (GW 26), and 0.002 (all samples) respectively. Mercury (Hg) was highly involved in heavy metal pollution of groundwater. The value of HPI more than 100 was observed in 7 sampling sites with decreasing order of GW 4 (536.14) > GW 21 (442.26) > GW 11 (316.41) > GW 6 (203.01) > GW 5 (173.49) > GW 26 (153.65) > GW 3 (140.51) making them unsuitable for drinking purposes due to high mercury pollution (Table 7). The decreasing order of heavy metal pollution index with more than 1 value is Hg > Cd > V > Pb > Se > Ni > U.

Table 5. Metal Index (MI) values of the study area.

Metal	Metal Index Values	Metal Index Class	Characteristics of MI class
Cu	0.000487	less than 0.3	Very Pure
Zn	0.002079		
Co	0.002362		
Pb	0.003115		
Ni	0.005231		
Cd	0.005256		
Al	0.01365		
As	0.014085		
Fe	0.014106		
Mn	0.059615		
Cr	0.091177		
Se	0.252462		
Sr	0.420116	0.3 to 1	Pure
U	0.465103		
B	0.827003		
Hg	1.919615	1 to 2	Slightly affected
V	2.621635	2 to 4	Moderately affected
Cumulative MI	6.717096	More than 6	Seriously affected
Mean MI	0.395123	0.3 to 1	Pure

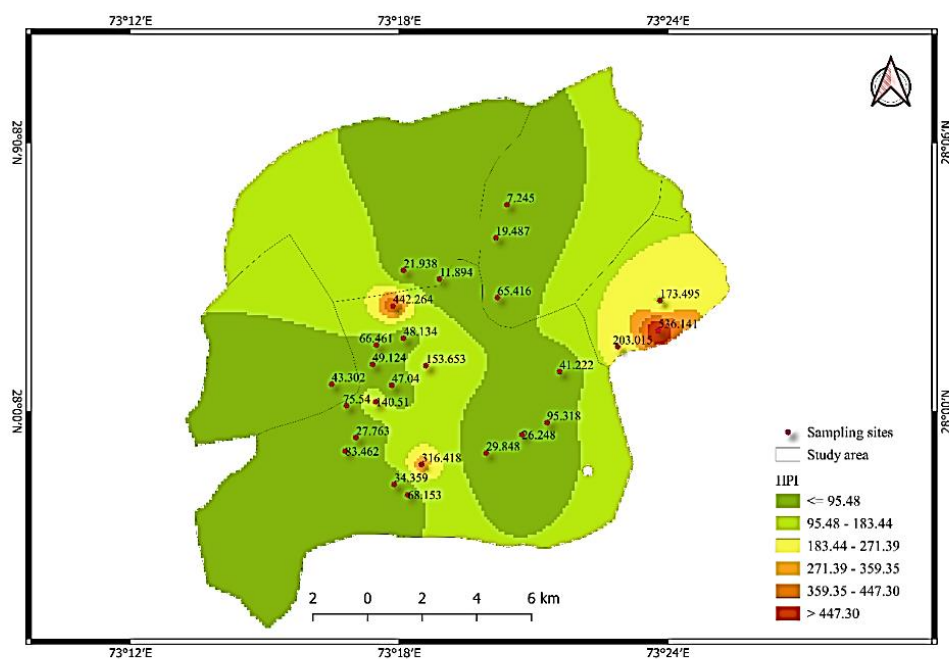


Figure 3. Spatial distribution of heavy metal pollution index of the study area.

Table 6. Heavy metal pollution index of selected heavy metals of the study area.

Sample N.	Al	As	B	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Sr	U	V	Zn
GW1	0.044	0.231	0.039	17.122	0.001	0.928	0.001	0.171	9.792	0.085	2.577	5.123	2.891	0.004	0.668	3.624	0.002
GW2	0.044	0.233	0.082	0.115	0.016	0.008	0.001	0.001	66.999	0.079	0.000	0.010	1.716	0.012	2.501	3.720	0.002
GW3	0.043	0.250	0.132	0.172	0.000	0.004	0.001	0.001	124.722	0.085	0.000	0.124	0.783	0.009	1.378	12.804	0.002
GW4	0.045	0.232	0.043	0.115	0.000	0.177	0.001	0.002	532.903	0.083	0.000	0.082	1.232	0.003	0.641	0.580	0.002
GW5	0.044	0.248	0.045	0.057	0.000	0.126	0.001	0.003	165.952	0.083	0.000	0.021	1.124	0.004	0.375	5.411	0.002
GW6	0.041	0.217	0.074	0.057	0.000	0.259	0.001	0.001	198.937	0.086	0.000	0.000	1.917	0.002	0.744	0.676	0.002
GW7	0.043	0.242	0.020	0.057	0.002	0.267	0.001	0.001	31.438	0.080	0.000	0.031	1.665	0.006	0.620	6.748	0.002
GW8	0.045	0.249	0.006	0.172	0.001	0.161	0.001	0.001	81.945	0.082	0.000	0.010	0.670	0.006	1.328	10.638	0.002
GW9	0.044	0.256	0.020	0.057	0.000	0.010	0.001	0.002	10.308	0.083	0.000	0.005	0.000	0.001	0.078	15.381	0.002
GW10	0.043	0.237	0.019	0.057	0.002	0.015	0.001	0.001	17.008	0.065	0.000	0.052	0.124	0.007	0.699	11.516	0.002
GW11	0.042	0.239	0.025	0.115	0.000	0.174	0.001	0.003	305.105	0.078	0.000	0.010	0.490	0.004	0.588	9.543	0.002
GW12	0.043	0.248	0.017	0.057	0.000	0.012	0.001	0.003	54.630	0.086	0.000	0.010	2.701	0.003	0.316	10.026	0.002
GW13	0.043	0.245	0.011	0.057	0.001	0.174	0.001	0.001	25.254	0.082	0.000	0.010	1.355	0.003	0.395	6.724	0.002
GW14	0.044	0.232	0.053	0.000	0.003	0.146	0.001	0.001	73.184	0.083	0.000	0.005	3.721	0.008	1.396	4.582	0.002
GW15	0.016	0.166	0.038	0.057	0.002	0.032	0.001	0.001	20.100	0.082	0.000	0.000	1.551	0.004	1.331	4.381	0.002
GW16	0.044	0.245	0.013	0.115	0.000	0.156	0.001	0.001	54.630	0.083	0.000	0.005	0.856	0.005	0.344	8.914	0.002
GW17	0.044	0.252	0.022	0.057	0.000	0.005	0.001	0.001	7.215	0.086	0.000	0.000	1.000	0.004	0.386	10.412	0.002
GW18	0.043	0.238	0.054	0.057	0.000	0.265	0.001	0.002	1.031	0.086	0.000	0.000	0.706	0.004	0.513	4.244	0.002
GW19	0.022	0.227	0.016	0.057	0.000	0.112	0.001	0.029	0.000	0.084	0.000	0.000	1.268	0.006	0.703	9.365	0.002
GW20	0.044	0.253	0.036	0.057	0.000	0.089	0.001	0.001	10.308	0.086	0.000	0.000	0.923	0.005	0.921	9.212	0.002
GW21	0.043	0.251	0.054	0.115	0.000	0.004	0.001	0.002	429.827	0.078	0.000	0.000	1.556	0.007	1.208	9.116	0.002
GW22	0.038	0.248	0.040	0.057	0.004	0.010	0.001	0.001	36.592	0.082	0.000	0.005	1.304	0.010	1.221	8.520	0.002
GW23	0.044	0.245	0.050	0.057	0.000	0.089	0.001	0.001	56.692	0.086	0.000	0.000	1.876	0.003	0.688	6.627	0.002
GW24	0.042	0.252	0.023	0.000	0.000	0.028	0.001	0.001	37.623	0.085	0.000	0.000	1.469	0.010	0.778	8.810	0.002
GW25	0.041	0.236	0.009	0.115	0.000	0.017	0.001	0.001	34.015	0.086	0.000	0.005	0.515	0.003	0.182	11.813	0.002
GW26	0.044	0.256	0.031	0.458	0.029	0.001	0.001	0.001	134.514	0.229	0.350	0.000	1.046	0.007	0.771	15.912	0.002

Table 7. Heavy metal Pollution Index (HPI) of groundwater samples.

Sample Code	HPI	Quality for drinking	Explanations
GW1	43.302	Suitable	
GW2	75.54	Suitable	
GW3	140.51	Unsuitable	Hg is highly involved (HPI value 124.72).
GW4	536.141	Unsuitable	Hg is highly involved (HPI value 532.90).
GW5	173.495	Unsuitable	Hg is highly involved (HPI value 165.95).
GW6	203.015	Unsuitable	Hg is highly involved (HPI value 198.93).
GW7	41.222	Suitable	
GW8	95.318	Suitable	
GW9	26.248	Suitable	
GW10	29.848	Suitable	
GW11	316.418	Unsuitable	Hg is highly involved (HPI value 305.10).
GW12	68.153	Suitable	
GW13	34.359	Suitable	
GW14	83.462	Suitable	
GW15	27.763	Suitable	
GW16	65.416	Suitable	
GW17	19.487	Suitable	
GW18	7.245	Suitable	
GW19	11.894	Suitable	
GW20	21.938	Suitable	
GW21	442.264	Unsuitable	Hg is highly involved (HPI value 429.82).
GW22	48.134	Suitable	
GW23	66.461	Suitable	
GW24	49.124	Suitable	
GW25	47.04	Suitable	
GW26	153.653	Unsuitable	Hg is highly involved (HPI value 144.51).
Mean HPI	108.74	Unsuitable	

Health risk assessment

Non-carcinogenic health risk assessment of metals in water samples are shown in Figure 4 and Table 8. The hazard index (HI) is the tool to calculate the non-carcinogenic health risk of metals. HI values of dermal contact were less than 1 in both children and adults. Whereas the HI values of ingestion showed varied patterns. In adults, the values of HI (ingestion) more than 1 were found in five water samples i.e., GW 2 (1.09), GW 4 (1.54), GW6 (1.07), GW11 (1.02), and GW 21 (1.32). While the values of HI (ingestion) in children was more than 1 in 91 % of water samples except for sampling sites GW 9 (0.25), GW 12 (0.809), GW 13

(0.961), GW 17 (0.716) and GW 25 (0.79). In children, metal-specific HI (ingestion) values of more than 1 were found for As (4.06), B (7.16), Cr (2.60), Hg (11.09), Sr (4.85), U (8.06), and V (2.59). Similarly, HI (ingestion) values of more than 1 were found in adults of As (1.85), B (3.07), Cr (1.12), Hg (4.75), Sr (2.08), U (3.45) and V (1.11).

The carcinogenic risk of metals in water samples is displayed in Figure 5 and Table 9. The value of CR beyond the permissible limit was found in children exposed to Cr-containing water (2.3×10^{-4}). Arsenic, cadmium, nickel, and lead were within acceptable levels

in both children and adults. Carcinogenic risk index (CRI) values were above the permissible limit in children (2.63×10^{-4}) and adults (1.41×10^{-4}) which indicates a potentially great cancer risk from drinking groundwater.

The cancer risk was mainly attributed to Cr (66.7% in children and 65.5% in adults) and As (20.3% in children and 21.5% in adults).

Table 8. Non-carcinogenic health risk of heavy metals.

Heavy metals	Statistical parameter	Children		Adult	
		Hazard Quotient (Ingestion)	Hazard Quotient (Dermal)	Hazard Quotient (Ingestion)	Hazard Quotient (Dermal)
Al	Mean	0.000182	1.2E-07	0.000078	7.02E-08
	Maximum	0.001316	8.6856E-07	0.000564	5.076E-07
	Minimum	3.86667E-05	2.552E-08	1.66E-05	1.4914E-08
	SD	0.000298278	1.96863E-07	0.000128	1.1505E-07
	CV	1.63888957	1.63888957	1.63889	1.63888957
	Variance	8.89697E-08	3.87552E-14	1.63E-08	1.3237E-14
As	Mean	0.156496	0.001033	0.071282	6.0363E-05
	Maximum	0.788889	0.000521	0.338095	0.00030429
	Minimum	0.013333	8.8E-06	0.006667	5.1429E-06
	SD	0.153869	0.000102	0.065363	5.935E-05
	CV	0.983216	0.983216	0.916969	0.98321646
	Variance	0.023676	1.03E-08	0.004272	3.5224E-09
B	Mean	0.275668	0.001819	0.118143	0.00010633
	Maximum	0.592323333	0.000390933	0.253853	0.00022847
	Minimum	0.103343333	6.82066E-05	0.04429	3.9861E-05
	SD	0.103640817	6.84029E-05	0.044417	3.9976E-05
	CV	0.37596287	0.37596287	0.375963	0.37596287
	Variance	0.010741419	4.67896E-09	0.001973	1.5981E-09
Cd	Mean	0.002103	0.000555	0.000901	8.1099E-07
	Maximum	0.010667	7.04E-06	0.004571	4.1143E-06
	Minimum	0	0	0	0
	SD	0.002002	1.32E-06	0.000858	7.7209E-07
	CV	0.952032	0.952032	0.952032	0.95203217
	Variance	4.01E-06	1.75E-12	7.36E-07	5.9612E-13
Co	Mean	0.000394	2.6E-06	0.000169	1.5181E-07
	Maximum	0.004733	3.12E-06	0.002029	1.8257E-06
	Minimum	0	0	0	0
	SD	0.001021	6.74E-07	0.000437	3.9367E-07
	CV	2.593138	2.593138	2.593138	2.59313782
	Variance	1.04E-06	4.54E-13	1.91E-07	1.5498E-13
Cr	Mean	0.101308	0.05349	0.043418	3.9076E-05
	Maximum	0.287333333	0.00018964	0.123143	0.00011083
	Minimum	0.001111111	7.33333E-07	0.000476	4.2857E-07

	SD	0.096362553	6.35993E-05	0.041298	3.7168E-05
	CV	0.951186927	0.951186927	0.951187	0.95118693
	Variance	0.009285742	4.04487E-09	0.001706	1.3815E-09
Cu	Mean	0.001218	8.04E-07	0.000522	4.6978E-07
	Maximum	0.007633	5.04E-06	0.003271	2.9443E-06
	Minimum	0.0002	1.32E-07	8.57E-05	7.7143E-08
	SD	0.001571	1.04E-06	0.000673	6.0612E-07
	CV	1.290228	1.290228	1.290228	1.29022832
	Variance	2.47E-06	1.08E-12	4.54E-07	3.6739E-13
Fe	Mean	0.000403	2.66E-07	0.000173	1.5546E-07
	Maximum	0.004866	3.21E-06	0.002085	1.8768E-06
	Minimum	9.05E-05	5.97E-08	3.88E-05	3.4898E-08
	SD	0.000917	6.05E-07	0.000393	3.5368E-07
	CV	2.275076	2.275076	2.275076	2.27507605
	Variance	8.41E-07	3.66E-13	1.54E-07	1.2509E-13
Hg	Mean	0.426581	0.000282	0.182821	0.00016454
	Maximum	2.297778	0.001517	0.984762	0.00088629
	Minimum	0	0	0	0
	SD	0.574692	0.000379	0.246297	0.00022167
	CV	1.347204	1.347204	1.347204	1.34720447
	Variance	0.330271	1.44E-07	0.060662	4.9136E-08
Mn	Mean	0.008516	5.62E-06	0.00365	3.2849E-06
	Maximum	0.174333	0.000115	0.074714	6.7243E-05
	Minimum	1.9E-05	1.26E-08	8.16E-06	7.3469E-09
	SD	0.033902	2.24E-05	0.014529	1.3076E-05
	CV	3.980715	3.980715	3.980715	3.98071506
	Variance	0.001149	5.01E-10	0.000211	1.7099E-10
Ni	Mean	0.000349	2.3E-07	0.000149	1.3451E-07
	Maximum	0.009067	5.98E-06	0.003886	3.4971E-06
	Minimum	0	0	0	0
	SD	0.001778	1.17E-06	0.000762107	6.8585E-07
	CV	5.09902	5.09902	5.099019514	5.09901951
	Variance	3.16E-06	1.38E-12	5.80808E-07	4.7038E-13
Pb	Mean	0.000593	3.92E-07	0.000254	2.2889E-07
	Maximum	0.004571	3.02E-06	0.001959	1.7633E-06
	Minimum	0	0	0	0
	SD	0.001073	7.08E-07	0.00046	4.1369E-07
	CV	1.807424	1.807424	1.807424	1.80742427
	Variance	1.15E-06	5.01E-13	2.11E-07	1.7114E-13
Se	Mean	0.033662	2.22E-05	0.014426	1.2984E-05
	Maximum	0.096267	6.35E-05	0.041257	3.7131E-05
	Minimum	0	0	0	0

	SD	0.020582	1.36E-05	0.008821	7.9387E-06
	CV	0.611436	0.611436	0.611436	0.61143589
	Variance	0.000424	1.85E-10	7.78E-05	6.3023E-11
Sr	Mean	0.186718	0.000123	0.080022	7.202E-05
	Maximum	0.419411	0.000277	0.179748	0.00016177
	Minimum	0.028917	1.91E-05	0.012393	1.1154E-05
	SD	0.095515	6.3E-05	0.040935	3.6842E-05
	CV	0.511547	0.511547	0.511547	0.51154721
	Variance	0.009123	3.97E-09	0.001676	1.3573E-09
	U	Mean	0.310068	0.000205	0.132886
Maximum		0.970444	0.00064	0.4159048	0.00037431
Minimum		0.030444	2.01E-05	0.0130476	1.1743E-05
SD		0.199434	0.000132	0.0854719	7.6925E-05
CV		0.643195	0.643195	0.6431947	0.64319468
Variance		0.039774	1.73E-08	0.0073054	5.9174E-09
V		Mean	0.099872	6.59E-05	0.042802
	Maximum	0.242286	0.00016	0.103837	9.3453E-05
	Minimum	0.002286	1.51E-06	0.00098	8.8163E-07
	SD	0.055388	3.66E-05	0.023738	2.1364E-05
	CV	0.554592	0.554592	0.554592	0.55459167
	Variance	0.003068	1.34E-09	0.000563	4.5642E-10
	Zn	Mean	0.006928	4.57E-06	0.002969
Maximum		0.025144	1.66E-05	0.010776	9.6986E-06
Minimum		0.000289	1.91E-07	0.000124	1.1143E-07
SD		0.007496	4.95E-06	0.003212	2.8912E-06
CV		1.081859	1.081859	1.081859	1.08185899
Variance		5.62E-05	2.45E-11	1.03E-05	8.3588E-12
Hazard Index		Mean	1.61	0.001063	0.690
	Maximum	5.937062	0.002378	1.544019	0.00138962
	Minimum	0.180072	0.000165	0.107097	9.6387E-05
	SD	1.349541	0.000511	0.332582	0.00029885
	CV	26.69672	0.480925	0.478765	0.4809247
	Variance	0.427581	2.61E-07	0.110611	8.9312E-08

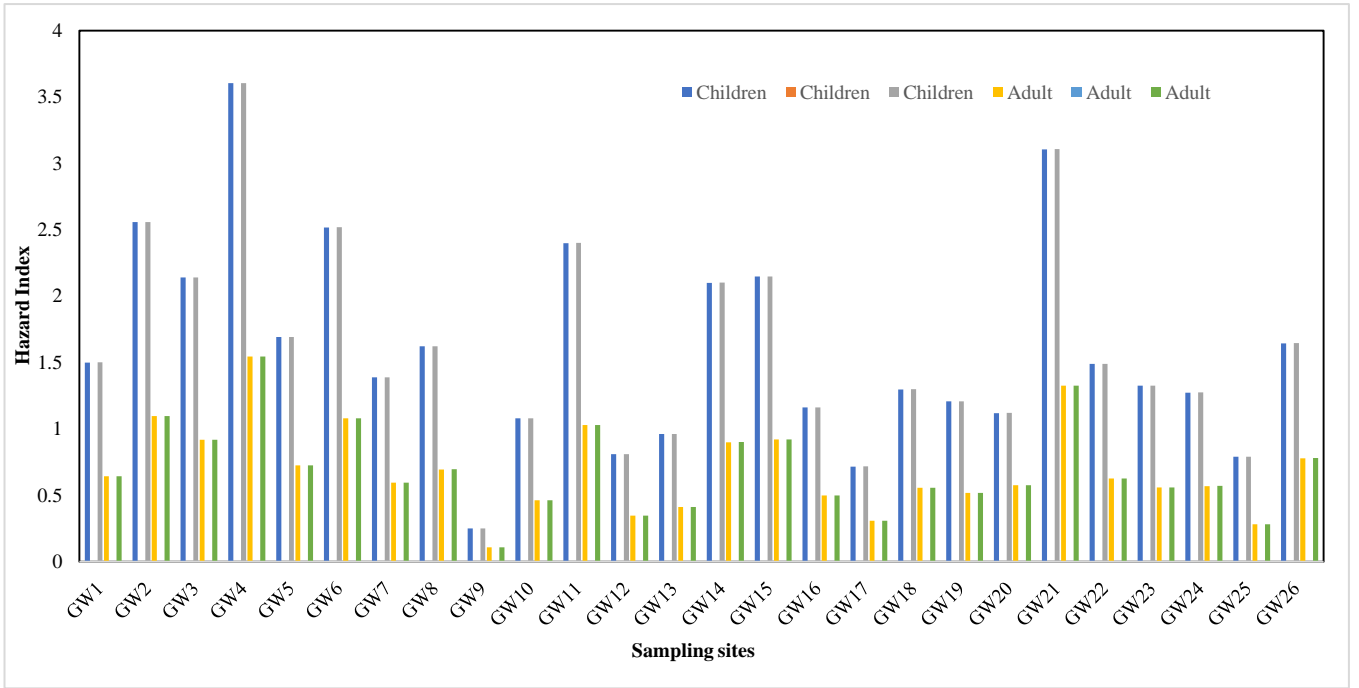


Figure 4. Hazard Index of the study area.

Table 9. Carcinogenic health risk of heavy metals.

Heavy metals	Children			Adult		
	Cancer Risk (Ingestion)	Cancer Risk (Dermal)	Total cancer Risk	Cancer Risk (Ingestion)	Cancer Risk (Dermal)	Total cancer Risk
As	7.04E-05	4.65E-07	7.08879E-05	3.02E-05	1.58E-07	3.03389E-05
Cd	1.58E-05	4.16E-06	1.99323E-05	6.76E-06	1.41E-06	8.16936E-06
Cr	0.000152	8.02E-05	0.000232197	6.51E-05	2.72E-05	9.23231E-05
Ni	6.35E-06	2.09E-07	6.55611E-06	2.72E-06	7.1E-08	2.79099E-06
Pb	1.77E-05	4.66E-07	1.81199E-05	7.57E-06	1.58E-07	7.72391E-06
CRI	0.000262	4.66E-07	0.000263	0.000112	2.9E-05	0.000141

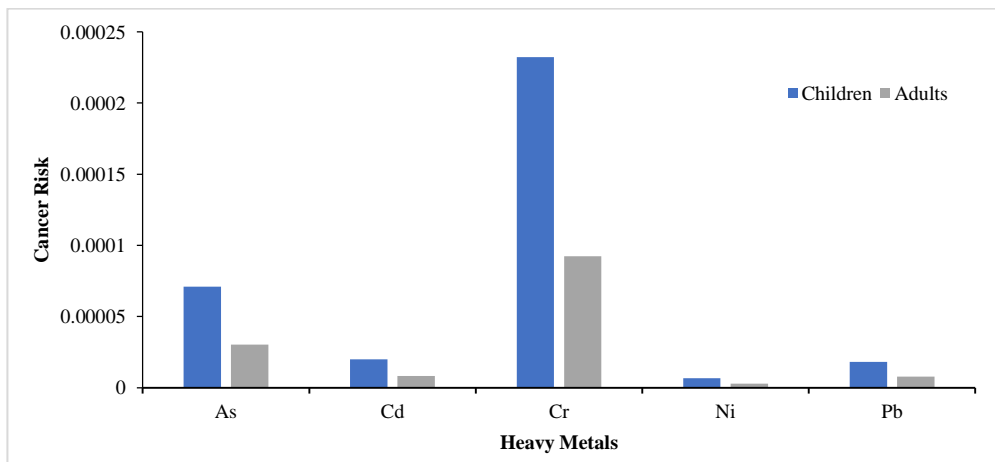


Figure 5. Carcinogenic health risk of heavy metals on children and adults.

CONCLUSIONS

The physio-chemical parameters of groundwater of the Bikaner block were studied at 26 locations in the city. Parameters such as fluoride, chloride, nitrate, sulfate, sodium, potassium, calcium, ammonium, magnesium, boron, mercury, and manganese were above the permissible limits of drinking water. Sodium concentrations were beyond the permissible limits in all samples. Parameters such as ammonium, nitrate, mercury, sulfate, fluoride, boron, and potassium had crossed the permissible limits in Shree Ramsar, Sujandesar, Indira Gandhi colony, Tilak Nagar, Shiv Badi and Vaishno Dham sampling sites of the study area respectively. Most water quality parameters were positively correlated with each other. The high concentrations of these cations and anions in groundwater indicate its overexploitation. Which emphasized generating awareness about the presence of these ions and adopting groundwater treatment technologies for sustainable utilization of the resource. The non-carcinogenic risk (HI) and the carcinogenic risks (CRI) were greater than the acceptable limit. The health of children was at greater risk. Henceforth, the study would be helpful to instigate necessary action for metal removal and groundwater management in Bikaner City.

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Conflicts of interest

There is no conflict of interest to declare.

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