Asian Journal of Water, Environment and Pollution, Vol. 14, No. 4 (2017), pp. 9–19.
DOI 10.3233/AJW-170032

Assessment of Heavy Metal Contamination in Groundwater of Khetri Copper Mine Region, India and Health Risk Assessment

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Received May 1, 2017; revised and accepted August 23, 2017

Abstract: The present study determines the abundance of heavy metals (Cu, Zn, Fe, Ni, Co, Mn and Pb) in the groundwater (pre and post monsoon) of the Khetri copper mine region, India and evaluates the pollution indices and risk assessment to assess the suitability of groundwater for human consumption. In majority of the groundwater samples, the concentration of heavy metals exceeds the desirable limits set by WHO, 2011 and Bureau of Indian Standards (BIS), 2012, whereas, average Fe concentration is 1.65 and 1.9 ppm during pre and post monsoon season respectively, which is above the BIS permissible limit (0.3 ppm) probably due to oxidation of iron-rich sulfides. Principal component analysis (PCA) and correlation matrix indicate a common source i.e. anthropogenic activity (mines) for Cu, Co, Ni and Mn. The calculated pollution indices namely contamination index (CI) and index of environmental risk (I_{ER}) for the heavy metals suggest that majority of the studied groundwater samples are in the slightly contaminated zone. However, a few of the samples close to mines, overburden rocks and tailings fall in the highly contaminated zone indicating their unsuitability for drinking purposes. The calculated hazard quotient for non-carcinogenic health effects is in the acceptable limit for all the groundwater samples except samples from Chaandmari (an abandoned mine), while the Health Index (HI) is in the medium range for all the samples barring a few samples.

Key words: Heavy metals, groundwater, Khetri copper mines, pollution indices, risk assessment.

Introduction

Sulphide-rich waste generated from mining activities is one of the major causes for deterioration of environment. (Fergusson, 1989). A study by Nasrabadi (2008) on groundwater surrounding the Sungun open cast copper mine in Iran shows concentrations of Fe and Al higher than the permissible limit prescribed by US Environmental Protection Agency (EPA). Bech et al. (1997) reported high concentrations of As and Cu in soil and plants around the Andes copper mine of Northern Peru.

Amari et al. (2014) found heavy metal (Cu, Fe, Pb, Cd, Zn, Co, Cr, Ni, Se and As) concentration in the groundwater from the Kettara mine area within the acceptable limits of Italian Standards, despite relatively higher concentrations of heavy metals in Acid Mine Drainage (AMD) of the mine tailings. The observed low abundances of heavy metals in the groundwater were attributed to dry climatic condition which inhibits the metal mobility (Amari et al., 2014).

In India, copper is being mined extensively since historical times at Khetri in the state of Rajasthan in north western part of the country. In the process, huge

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quantities of sulfide bearing tailings and overburden rocks are being generated and dumped in the region. On exposure to oxygen and water, sulphide-rich tailings and overburden rocks generate acid mine drainage and acidification leads to mobilisation of heavy metals into the surrounding soil and groundwater (Williams, 1975; Atkins and Pooley, 1982). Hence, assessment of groundwater quality in the mining region is important.

We present here, the results of systematic study on the heavy metal abundances in groundwater in and around the active copper mines of Khetri region covering tailings, overburden rocks and abandoned mine. In addition, we also studied two groundwater samples from ~50 km away from Khetri copper mining region in the upstream direction for comparison. The measured heavy metal concentration data in the studied groundwater samples were used to calculate the contamination index (CI), index of environmental risk (I_{ER}) and health risk assessment to assess the heavy metal contamination of the groundwater and its suitability for human consumption. To our knowledge, no systematic study has been carried out to assess the water quality and its probable health risk in the region. Proper monitoring and assessment is important to regulate the implementation of better waste management practices in the mining region.

Study Area

Khetri is famous for copper mining since historical time and it is located in the Jhunjhunu district of Rajasthan, India (Figure 1A). It is about 180 km northeast of Jaipur city the state capital, and 200 km southwest of New Delhi. It is ~370 m above MSL; latitudes N 2804.070′° and longitudes E 7549.294′°. The average rainfall in the region is ~500 mm per year. During summer, maximum temperature reaches to 45°C and minimum is 12°C, while in winter, maximum temperature reaches ~25°C and minimum is 2°C. At present in the region, mining activities are going on at three sites namely Banwas, Madhan-Kudhan and Kolihan. Mines namely Banwas and Kolihan have more than 70 Mt of ore reserve with 1.14-1.7 wt. % Cu, while Madhan-Kudhan contains 66 Mt of ore reserve with an average of 1.12-1.71 wt. % of Cu content. The ore consists of ~10 volume % sulfides mainly of chalcopyrite, pyrite and pyrrhotite, and other minerals such as quartz, amphiboles, mica, chlorite and magnetite.

The Khetri Copper Belt (KCB) is located in the north-westernmost part of Aravalli mountain ranges (AMR). The belt extends ~80 km in length from Singhana (Jhunjhunu district) in the northeast to Sangarva (Sikar district) in the southwest. Geologically, the KCB is divided into two parts i.e. northern and southern parts by the NW-SE transverse Kantli Fault (Gupta et al., 1998) (Figure 1B). The rocks of the belt belong to Delhi Supergroup, further divided into an older psammitic-dominated Alwar group and a younger pelitic-dominated Ajabgarh group (Das Gupta, 1968). The rocks of Alwar group are mainly comprised of metamorphosed mafic volcanic rocks, iron formation, conglomerate and sandstone i.e. amphibolite and feldspathic, magnetite and amphibole quartzites. The rocks of Ajabgarh group consist of metamorphosed stromatolitic carbonate, siltstone and shale, i.e. marble, phyllite, pelitic and garnet-chlorite-amphibole schists. The rocks of the northern KCB (in which the study area lies) are made up of garnet-chlorite-amphibole schists, andalusite and graphite-bearing biotite schists, phyllites and amphibole or feldspathic quartzites, folded into a number of regional synclines and anticlines (Das Gupta, 1968). Sodium-rich felsic magmatism in the form of albitites are also recorded in the region and these rocks occur along a 170 km long NNE-SSW trending lineament, named as 'albitite line' (Ray, 1990).

Hydrogeologically, the aquifer of study area is associated with quartzite, schist, phyllite, gneisses and limestone of Delhi Super Group including granites, amphibolites and pegmatites of post Delhi intrusive. Groundwater occurs under unconfined condition in the weathered mantle (thickness from 10 to 15 m) and under unconfined to semi-confined conditions in deep seated secondary porosity i.e. fractures, joints, contacts etc. of hard formation. However, the thick (15 to 140 m) and regionally extensive alluvium (composed of gravels, sand, silt, clay and kankar) which occurs surrounding the study area holds 30-70 m thick saturated zone with unconfined and semi-confined aquifers. The general groundwater flow is from hills (stretching southwest-northeast) of the study area to towards northern and eastern parts of the region (Central Groundwater Board, 2008). Water flow is relatively fast in the study area due to the steep gradient of the topography while it is considerably slow in the alluvial formations with gentle gradient. The water yield of dugwell in alluvium is 150 to 600 m^3/day and it is less than 250 m^3/day both in granites and quartzites.

Materials and Methods

Sampling and Analytical Methods

To assess the heavy metal contamination in the groundwater, the samples were collected in the immediate vicinity of the mining area (mines, tailings and overburden rocks) as well as ~10 km away from the mining area. The main constraints of sampling are hilly terrain in northwest direction and fewer habitats followed by the rapid drying of wells in the region.

A total of 17 and 23 groundwater samples were collected during pre-monsoon (March 2015) and post monsoon (October 2015) season respectively for heavy metal (Cu, Zn, Pb, Ni, Fe, Mn, and Co) analysis. During both the seasons samples were collected from the same hand pump at each sampling location, except two locations in north direction i.e. Singhana and Gujarwas where hand pumps were dried off during post monsoon season sampling. Seven new sampling sites were added during post monsoon season compared to the pre-monsoon. Additionally, two reference samples (relatively less affected by the mining activity) were also collected from areas (Bass Govind Singh and Pilani) ~50 km away from the mining region in the northwest direction and sampling locations are shown in Figure 1C. Before the sampling of water from handpump, the water was allowed to run for some time to avoid the contamination from pipe.

From each sampling site two groundwater samples were collected in narrow mouth polypropylene bottles, double rinsed with Milli-Q followed by groundwater before sampling. All the collected water samples were preserved by adding few drops of concentrated Supra-pure HNO_3 (Radojevic and Bashkin, 1999) followed by filtration and vice versa. The samples were filtered using 0.45 µm milipore filter paper and stored below 4°C prior to the analysis. pH, EC and temperature of the samples were determined at the site by portable pH (Hanna instrument, H196107) and EC (Aquapro water tester, model AP-2) meters. Heavy metals (Cu, Zn, Pb, Ni, Fe, Mn and Co) were analysed by Atomic Absorption Spectrometry (ThermoScientific, M series) using air-acetylene gas as a fuel. For the calibration of instrument, standard solutions for each heavy metal were prepared by diluting the 1000 ppm certified standard solution (Merck). During analysis, after every 10 samples, one standard solution was measured to test the accuracy and stability of the instrument. The calculated relative error was below 5% indicating the high efficiency of the heavy metal analysis. In addition to clean glassware and analytical grade reagents the samples were handled carefully to avoid the contamination during the analysis.

Statistical Analysis

Descriptive statistical parameters such as range, average, median and standard deviation were calculated to assess the distribution and variation in the heavy metal concentration in groundwater. Analysed heavy metal concentrations are compared with the World Health Organization (WHO) 2011 and Bureau of Indian Standards (BIS) 2012 limits for drinking to assess the suitability of groundwater for human consumption. The degree of association or the strength of relationship between two variables was evaluated by calculating the coefficient of correlation, *r* (Meyer, 1975). Source of heavy metals in the groundwater were identified by

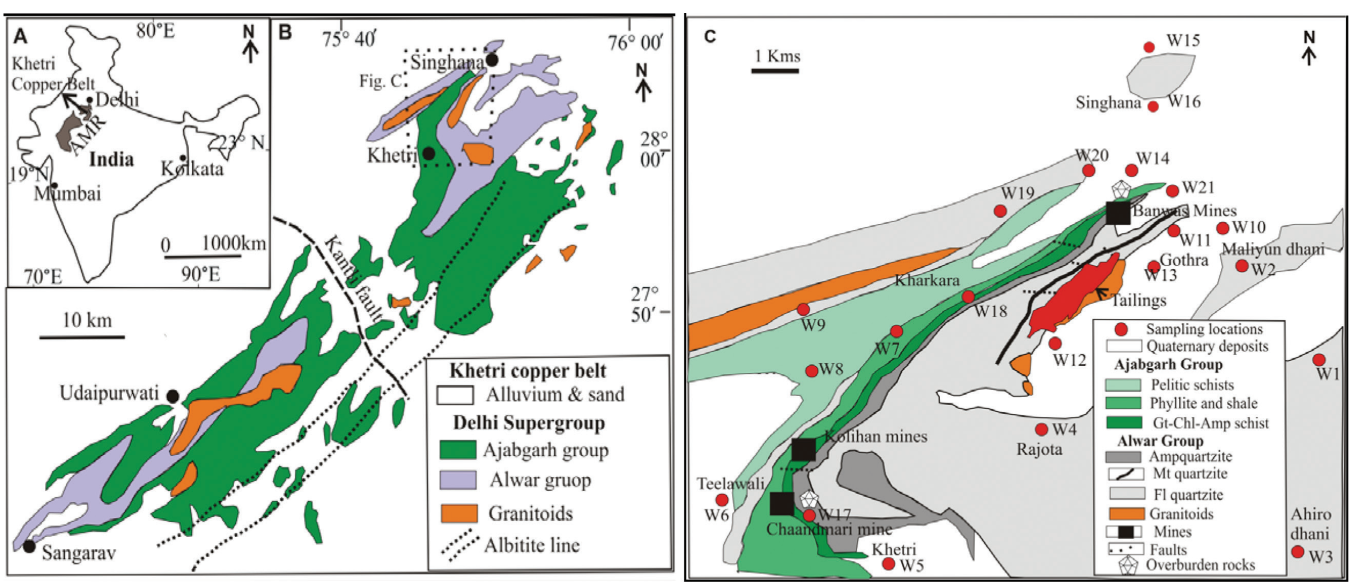


Figure 1: Map of India showing (A) the location of Khetri belt, Rajasthan, (B) Geology of Khetri copper belt (after Kaur and Mehta, 2005; Kaur et al., 2006; Knight et al., 2005) and (C) Groundwater sampling locations.

Principal Component Analysis (PCA) and correlation matrix. IBM SPSS 19 version and Golden Grapher version 10 along MS word 2007 were used for all the data processing.

Pollution Indices and Risk Assessment

The popular pollution indices namely contamination index (CI) and index of environmental risk (I_{ER}) were used to assess the enrichment of heavy metals and the probability of adverse impact on environment due to high concentration of heavy metals. The measured concentrations of individual elements and the maximum permissible limit set by BIS 2012 were used to calculate the pollution indices (contamination index and index of environmental risk) and health risk assessment.

Contamination Index (CI)

CI (Adamu, 2015) is calculated to assess the enrichment of heavy metals in groundwater samples with respect to maximum permissible limits of BIS 2012 for individual element using Eq. (1)

$$CI = \{(Cu \div 1.5) + (Zn \div 15) + (Fe \div 0.3) + (Co \div 0.2) + (Ni \div 0.02) + (Mn \div 0.3) + (Pb \div 0.01)\} \div 7 \quad (1)$$

where CI is the contamination index, and Cu, Zn, Fe, Co, Ni, Mn and Pb are the measured concentration at each sampling site divided by the maximum permissible limit for the element. CI has been classified into three categories namely CI < 1 (not contaminated); CI 1-5 (slightly contaminated) and CI > 5 (contaminated).

Index of Environmental Risk (I_{ER})

I_{ER} is a numerical value used to predict the probability of the occurrence of the negative impact on environment by means of specific contaminations (Rapant and Kordík, 2003).

In the present study, I_{ER} is calculated to assess the magnitude of adverse impact of the concentrations of heavy metals on the water and to characterize overall contamination state in the Khetri copper mine region. I_{ER} for individual groundwater sample is calculated by the following equations (Eq. 2 and 3):

$$I_{ER} = \sum_{i=1}^{n} Q_{Eri} \quad (2)$$

$$Q_{Eri} = \frac{AC_i}{RC_i} - 1 \quad (3)$$

where I_{ER} is the overall index of environmental risk of the sample, Q_{Eri} is the index of environmental risk quotient of the i^{th} element, AC_i is the measured concentration of the i^{th} element and RC_i is the maximum permissible concentration limit (BIS, 2012) of i^{th} element. The I_{ER} classification scale (Rapant et al., 2009) and the categorization of studied samples into different I_{ER} scale are given in Table 1.

Table 1: Scale for index of environmental risk along with the number of Khetri groundwater samples falling in different risk range

I_{ER} values	*Risk magnitude*	*Samples within the range of I_{ER} values (n = 23)*
0	No risk	W18, W23
≤ 1	Very low risk	W8, W9, W10, W22
≤ 3	Low risk	W15, W19
≤ 5	Medium risk	W1, W2, W4, W20
≤ 10	High risk	W5, W6, W7, W11, W12, W16
≤ 15	Very high risk	W13, W21
≥ 15	Extremely high risk	W3, W14, W17

The risk scale is after Rapant et al. (2009).

Risk Assessment

Risk assessment is defined as the process of estimating the probability of occurrence of adverse health effects as a function of hazard and exposure over a specified time period. The health risk assessment of individual heavy metal or metalloid is a quantification of the risk level which is expressed as carcinogenic or non-carcinogenic (USEPA, 2009). The two principal toxicity risk factors evaluated are the slope factor (SF) for carcinogen risk characterization, and the reference dose (RfD) for non-carcinogen risk characterization (USEPA, 1997, 1999; USEPA IRIS http:// www.epa.gov/iris/). The oral RFD (mg/kg/day) is different for each element i.e. Cu (4×10^{-2}), Zn (0.3), Fe (0.7), Co (2×10^{-2}), Ni (2×10^{-2}), Mn (1.4×10^{-1}) and Pb (3.5×10^{-3}) (USEPA IRIS http://www.epa.gov/iris/). The estimations of magnitude, frequency and duration of human exposure to each heavy metal or metalloid in the environment are typically reported as average daily dose (ADD) (USEPA, 1992), as shown in Eq. (4):

$$ADD = (C \times IR \times EF \times ED) \div (BW \times AT) \quad (4)$$

where ADD is the average daily dose (mg/kg/day), C is the mean concentration (mg/L) of heavy metal, IR is the water intake rate (3.45 L/day for adults) (Apambire et al., 1997), EF is the exposure frequency (365 days/year), ED is the exposure duration (70 years), BW is the average body weight (60 kg), and AT is the average time (25,550 days, i.e., 70 years × 365 days/year) (Roychowdhury et al., 2003).

The hazard quotient (HQ) for non-carcinogenic health risk is calculated by following equation (Eq. 5):

$$HQ = \frac{ADD}{RfD} \quad (5)$$

where ADD (exposure intake) and RfD (reference dose) are in mg/kg/day. For the risk assessment in case of mixture of contaminants, the individual HQs are combined to get the hazard index (HI) (Eq. 6). Based on calculated HQ/HI values, samples were placed in different categories of non-carcinogenic health effects i.e. <0.1(very low), ≥ 0.1 < 1 (low), ≥ 1 < 4 (medium) and ≥4 (high) (USEPA, 1999).

$$HI = \Sigma HQ \quad (6)$$

Results and Discussion

The physico-chemical parameters such as pH, EC and concentration of heavy metals in the groundwater of Khetri region are summarized in Table 2. Average pH of groundwater lies near neutral during both pre and post monsoon. It varies from 4.3 to 7.7 with an average of 7.1 in pre monsoon while it is 4.6 to 8.3 with an average of 7.3 in post monsoon. Lowest pH of 4 is observed in the mine waters of abandoned Chaandmari (W17) during both the seasons due to the presence of sulfides.

EC in the groundwater of study area varies from 350 to 3543 µs/cm with an average of 1974 µs/cm during pre monsoon, and from 170 to 5350 µs/cm with an average of 2049 µs/cm during post monsoon. The observed high variation in the EC is due to the presence of mines and/or rapid depletion of groundwater table in the region. The increase in average EC from pre monsoon to post monsoon is probably due to leaching of ions during monsoon season. The maximum EC 3543 µs/cm is found at W15 during pre monsoon, and 5350 µs/cm at W16 during post monsoon season. Both W15 and W16 lie in the northern direction of mines, and groundwater table is depleting at faster rate as both the hand pumps from the area were found dried during second (post monsoon) season sampling. The sampling sites close to mines have high EC in both the seasons indicating more dissolution of minerals. EC at W11 is 2900 µs/cm during pre monsoon and at W13, W21 and W11 the EC is 3064, 2744 and 2814 µs/cm respectively during post monsoon.

Cu concentration ranges from 0.17 to 8.19 ppm with an average of 0.66 ppm during pre monsoon, and 0.09 to 9.04 ppm with an average of 0.49 ppm during post monsoon. The mine water of abandoned Chaandmari (W17) has exceptionally high concentration of Cu i.e. 8.19 and 9.04 ppm and Mn i.e. 7.38 and 6.74 ppm during pre and post monsoon respectively. However, concentration of Fe is low i.e. 0.28 and 0.26 ppm during pre and post monsoon respectively which may be due to precipitation of Fe at pH 4. In the acid mine drainage, the iron is present as ferric ion and Fe^{3+} ions get precipitated at pH 3-4 (Balintova and Petrilakova, 2011).

The average concentration of Fe is 1.65 and 1.9 during pre and post monsoon respectively. The increase in Fe concentration during the post monsoon compared to pre monsoon may be due to leaching of sulfides. The sampling sites close to mines (W5, W6, W11 and W21), tailing dam (W12 and W13) and overburden rocks (W14 and W20) have high concentration of Fe compared to those at distant locations indicating the high mobility of Fe as it is more susceptible to environmental conditions. The Kanjaniyun dhani (W14) which is close to overburden rocks have high concentration of Fe 10.4 and 6.53 ppm during pre and post monsoon respectively. The mining has been going on in the hilly region of study area and mine waste including overburden rocks and tailings are also being dumped in the hills. The sampling sites i.e. W8, W9, W18 and W19 located in the western direction have low Fe concentration compared to eastern and northern direction samples as the groundwater flow is from hills (stretching southwest-northeast) towards northern and eastern parts. Fe concentration is found high in all samples except two reference samples (W22 and W23) indicating that the source for high concentration of Fe is the mines. Pyrite and pyrrhotite in addition to chalcopyrite are present in the Khetri copper ore and all are the potential source for Fe. It is observed that the concentration of Fe and Zn in groundwater neighbouring the overburden materials are much higher compared to Cu. The Cu has low mobility as it can be easily absorbed by the carbonates, phylosilicates and organic matter (Kabata-Pendias and Pendias, 2001).

Hence, observed heavy metal concentrations in the groundwater from the study area shows that water samples collected close to mining area (W5, W6, W11 and W21), tailing dam (W12 and W13) and waste dumps (W14 and W20) have high abundances of heavy metals. The measured concentrations of each element (Cu, Zn, Fe, Co, Ni, Mn and Pb) are compared to those set by the BIS 2012 and WHO 2011 water quality standards (Table 3) which revealed that heavy metal concentration in majority of the water samples exceeds the permissible limits. In the region, the groundwater

Table 2: Description of physico-chemical parameters of groundwater samples from Khetri copper mine region during pre- and post-monsoon seasons (all concentration are in ppm)

Sample code	Sample location	Pre-Monsoon									Post-Monsoon								
		pH	*EC**	*Cu*	*Zn*	*Fe*	*Co*	*Ni*	*Mn*	*Pb*	*pH*	*EC**	*Cu*	*Zn*	*Fe*	*Co*	*Ni*	*Mn*	*Pb*
W1	Kakarai	7.3	2715	0.18	2.49	0.16	0.03	0.11	0.11	0.05	7.5	3534	0.09	1.81	0.33	0.08	0.09	0.14	0.03
W2	Maliyun Dhani	7.2	933	0.19	0.37	0.63	0.10	0.10	0.09	BDL	7.2	1876	0.11	1.16	1.78	0.09	0.11	0.16	BDL
W3	Ahiro Dhani	7.2	1006	0.17	1.12	1.22	0.06	0.09	0.12	BDL	7.7	1035	0.10	0.40	9.42	0.09	0.13	0.24	BDL
W4	Rajota	7	1882	0.19	0.15	1.37	0.08	0.11	0.12	BDL	7.1	2207	0.13	0.37	2.13	0.06	0.05	0.23	BDL
W5	Khetri	6.7	2394	0.19	0.31	1.95	0.07	0.11	0.16	0.03	6.9	2499	0.11	0.22	0.61	0.09	0.13	0.14	BDL
W6	Teelawali	7.7	615	0.23	2.92	1.05	0.09	0.08	0.14	0.07	8.3	590	0.11	1.66	2.16	0.09	0.11	0.25	BDL
W7	Meghawali Dhani	7.6	715	0.22	0.46	1.35	0.07	0.09	0.11	0.02	7.9	680	0.12	0.32	4.43	0.06	0.09	0.23	BDL
W8	Khakara Devran	7.3	1006	0.23	0.11	0.32	0.13	0.10	0.09	BDL	7.7	1088	0.13	0.62	0.43	0.08	0.10	0.22	BDL
W9	Kharkara Rajputan	7.3	1850	0.23	1.62	0.50	0.06	0.08	0.13	0.01	7.5	1827	0.13	1.36	0.59	0.08	0.10	0.23	BDL
W10	River bed	7.6	1801	0.21	2.31	0.19	0.03	0.10	0.11	0.01	8.2	1975	0.14	3.15	0.37	0.08	0.10	0.23	BDL
W11	Khetri Nagar	7	2900	0.21	0.89	1.15	0.09	0.07	0.12	0.01	7.5	2813	0.15	1.11	2.41	0.09	0.12	0.24	BDL
W12	Bhargda Dhani	7.2	3061	0.38	7.14	2.65	0.04	0.08	0.16	0.03	7.3	1969	0.19	6.69	1.04	0.05	0.09	0.24	BDL
W13	Near tailing	7.2	1398	0.20	1.76	2.29	0.08	0.12	0.21	0.05	7.2	3067	0.17	8.51	3.29	0.11	0.09	0.32	BDL
W14	Kanjaniyun Dhani	7.5	2638	0.24	0.77	10.40	0.10	0.11	0.23	BDL	7.2	2730	0.15	0.46	6.53	0.10	0.12	0.29	BDL
W15	Gujarwas	7.2	3543	0.21	0.34	0.34	0.39	0.07	0.53	0.01	7.3	1160	0.16	0.72	0.27	0.06	0.09	0.19	BDL
W16	Singhana	7.1	3228	0.22	1.31	2.25	0.07	0.12	0.13	0.01	7.0	5350	0.17	4.21	1.62	0.10	0.08	0.30	BDL
W17	Chaandbari	4.3	3501	8.19	0.51	0.28	1.00	1.70	7.38	BDL	4.6	3546	9.04	0.49	0.26	1.01	1.69	6.74	BDL
W18	Bhand Bhatiar	-	-	-	-	-	-	-	-	-	7.6	929	0.11	0.41	0.18	0.06	0.10	0.18	BDL
W19	Bawadi Dhani	-	-	-	-	-	-	-	-	-	8.2	2495	0.12	0.05	0.29	0.09	0.10	0.70	BDL
W20	Banwas	-	-	-	-	-	-	-	-	-	7.6	1285	0.14	6.12	1.20	0.06	0.11	0.29	BDL
W21	Guest house	-	-	-	-	-	-	-	-	-	7.2	2744	0.20	0.67	4.07	0.08	0.11	0.34	BDL
W22	Bass Govind Singh	-	-	-	-	-	-	-	-	-	6.6	2614	0.16	0.03	0.21	0.09	0.11	0.23	BDL
W23	Pilani	-	-	-	-	-	-	-	-	-	7.5	1427	0.16	0.06	0.17	0.06	0.09	0.17	BDL
	Min	4.30	350	0.17	0.11	0.16	0.03	0.07	0.09	BDL	4.6	170	0.09	0.03	0.17	0.05	0.05	0.14	BDL
	Max	7.70	3543	8.19	7.14	10.40	1.00	1.70	7.38	0.07	8.3	5350	9.04	8.51	9.42	1.01	1.69	6.74	0.03
	Average	7.08	1974	0.69	1.45	1.65	0.15	0.19	0.58	0.02	7.3	2049	0.53	1.77	1.90	0.12	0.17	0.54	BDL
	Median	7.20	1866	0.21	0.89	1.15	0.08	0.10	0.13	0.01	7.5	1969	0.14	0.67	1.04	0.08	0.10	0.23	BDL
	STDEV	0.76	1057	1.93	1.70	2.39	0.23	0.39	1.76	0.02	0.73	1144	1.86	2.37	2.33	0.20	0.33	1.36	0.01

BDL – Below Detection limit * – Unit of EC (µs/cm)

Table 3: Comparison of heavy metal concentration in groundwater from Khetri copper mine region with the BIS, 2012 and WHO, 2011 water quality standards

Parameters	*WHO limit (2011)*	*BIS Desirable limit*	*BIS Permissible limit*	*Number of samples exceeding the limit*			
				Pre-Monsoon (n = 17)		*Post-Monsoon (n = 23)*	
				Desirable	*Permissible*	*Desirable*	*Permissible*
Cu	2	0.05	1.5	16	1	16	1
Zn	3	5	15	1	-	3	-
Fe	-	0.3	0.3*	-	14	-	18
Co	-	0.03	0.2	16	1	22	1
Ni	.07	0.02	0.02*	-	17	-	23
Mn	0.4	0.1	0.3	13	2	16	7
Pb	.01	0.01	0.01*	-	6	-	1

* – No Relaxation

depth is ~40 m. The high leaching of heavy metals is probably due to the presence of faults near the mines and tailings and secondly, underground mining activities close to the groundwater table are going on.

Cu, Fe, Co, Ni and Mn exceed the desirable limit of BIS 2012 for drinking water in majority of the samples during both the seasons. Pb concentration exceeds the permissible limit in six samples during pre monsoon while it is only one sample during post monsoon, may be due to dilution effect. Ni concentration exceeds the permissible limit in all the samples during both the seasons. Similarly, Fe concentration exceeds the permissible limits in 14 and 18 samples during pre and post monsoon. Hence, Fe and Ni concentration exceeds the permissible limits in more number of samples, while Cu, Mn and Co exceeds the desirable limits in more number of samples.

A Ficklin diagram (Ficklin et al., 1992) is used to classify the studied water samples on the basis of total metal concentration and pH (Figure 2). It is found that most of the samples lie near neutral and high metal region except two reference samples (W22 and W23) that lies in neutral and low metal region, while, sample from an abandoned Chaandmari mine (W17) lie in acidic and high metal concentration region.

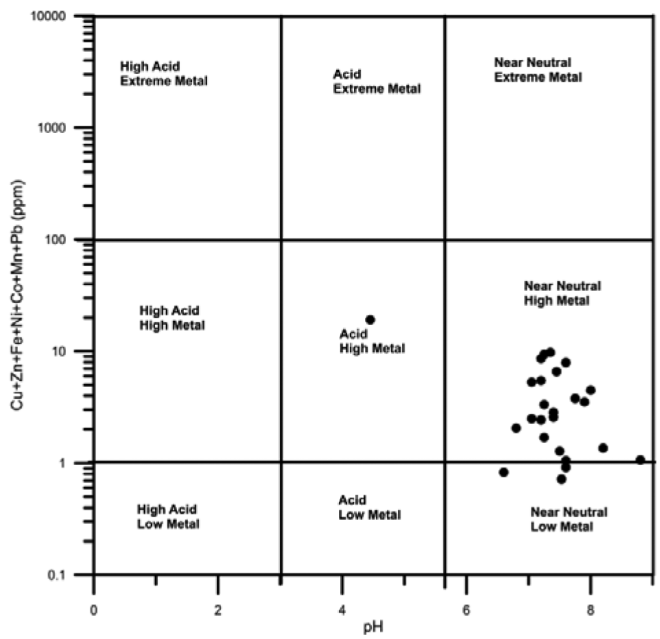


Figure 2: Ficklin diagram showing the classification of Khetri groundwater samples on the basis of total metal concentration vs pH.

Source Identification

To identify the source for heavy metals in the groundwater, the correlation matrix was used for both pre and post monsoon. The strong correlation among the heavy metals suggests their common source. During pre and post monsoon seasons, pH is negatively correlated with the Cu (-0.702 and -0.820, $p > 0.01$), Co (-0.671 and -0.820, $p > 0.01$), Ni (-0.703 and -0.814, $p > 0.01$) and Mn (-0.694 and -0.80, $p > 0.01$) interfaces that with decrease in pH of water the concentration of these elements increases in the water (Table 4). EC does not show any strong correlation with the heavy metal concentration, may be because EC is mostly controlled by the major ions concentration rather the trace elements concentration.

Cu has a strong positive correlation with Co (0.938, $p > 0.01$), Ni (0.999, $p > 0.01$) and Mn (0.998, $p > 0.01$), probably due to common source for these elements in the groundwater. However, Zn and Fe show a negative correlation with these elements which may be due to precipitation or exchange of these elements with other cations. Co also shows strong correlation with Ni (0.933, $p > 0.01$) and Mn (0.955, $p > 0.01$), and Ni with Mn (0.997, $p > 0.01$). Three principal components (PCs) with eigen values >1 were extracted for heavy metals in ground water during pre and post monsoon. The PCA lead to a reduction of the initial dimension of the dataset to three components, which explain 90.85 and 89.56% of the data variation in pre and post monsoon respectively. The results of the PCA for pre and post monsoon are given in Table 5.

Table 4: Correlation coefficient among heavy metals for pre-monsoon and post-monsoon seasons groundwater samples

Pre Monsoon									
	pH	*EC*	*Cu*	*Zn*	*Fe*	*Co*	*Ni*	*Mn*	*Pb*
pH	1	-0.582*	-0.702**	-0.002	0.033	-0.671**	-0.703**	-0.694**	0.371
EC		1	0.368	0.204	0.192	0.434	0.360	0.383	-0.266
Cu			1	-0.108	-0.133	0.938**	0.999**	0.998**	-0.211
Zn				1	0.059	-0.231	-0.135	-0.134	0.376
Fe					1	-0.153	-0.127	-0.132	-0.150
Co						1	0.933**	0.955**	-0.236
Ni							1	0.997**	-0.212
Mn								1	-0.206
Pb									1
Post Monsoon									
pH	1	-0.469*	-0.820**	0.055	0.125	-0.820**	-0.814**	-0.800**	0.016
EC		1	0.279	0.263	-0.039	0.309	0.265	0.284	-0.097
Cu			1	-0.096	-0.138	0.996**	0.998**	0.997**	-0.069
Zn				1	0.002	-0.100	-0.111	-0.098	-0.104
Fe					1	-0.117	-0.120	-0.134	-0.186
Co						1	0.997**	0.995**	-0.061
Ni							1	0.995**	-0.065
Mn								1	-0.067
Pb									1

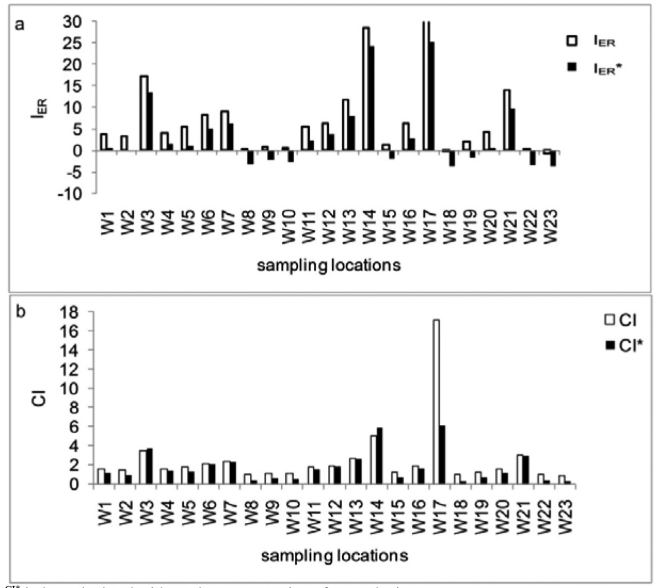
* – Correlation is significant at the 0.05 level (2-tailed)
** – Correlation is significant at the 0.01 level (2-tailed)

Table 5: Principal component analysis (PCA) for heavy metal concentration

	Pre-monsoon			*Post-monsoon*		
Parameter	*PC 1*	*PC 2*	*PC 3*	*PC 1*	*PC 2*	*PC 3*
Mn	0.990	0.105	0.077	0.995	0.045	0.057
Cu	0.986	0.117	0.089	0.994	0.059	0.072
Ni	0.985	0.099	0.081	0.994	0.049	0.071
Co	0.969	0.028	0.000	0.990	0.026	0.028
Pb	-0.301	0.791	-0.049	-0.181	0.796	-0.060
Zn	-0.237	0.715	0.483	-0.166	0.639	0.579
Fe	-0.165	-0.385	0.865	-0.174	-0.411	0.811
Eigen value	4.036	1.319	1.004	4.038	1.220	1.011
% of variance	57.65	18.85	14.35	57.69	17.431	14.440
Cumulative %	57.65	76.50	90.85	57.69	75.12	89.56

The first component (PC1) for groundwater during pre and post monsoon shows the strong association among Cu, Co, Ni and Mn which explains the 57.65 and 57.69% of variance respectively. These elements are found in abundant quantity in association with sulfide ores; hence their source is mining activities. The PC1 explains the anthropogenic source (i.e. mines) with the highest % of variance for both pre and post monsoon.

In the second component (PC2), the association of Zn and Pb was identified with 18.85 and 17.43% of variance during pre and post monsoon respectively. The presence of Pb in the soil explains that their source is weathering of parent rock, as the Pb is found in trace quantity (1 ppm) in the tailings (Punia and Siddaiah, 2017 unpublished data). Zn is also found associated with the sulfides in nature. Hence, the PC2 explains the mixed source (geogenic or anthropogenic). The third component (PC3) contains only Fe with variance of 14.35 and 14.44% of variance during pre and post monsoon respectively. The source of Fe is also anthropogenic as it is present in both oxide (hematite and magnetite) and sulfide (pyrite and pyrrhotite) minerals; hence it shows variation with respect to other elements depending upon the environmental conditions.



CI* index calculated without the concentration of Co and Ni
I_{ER}* index calculated without the concentration of Co and Ni

Figure 3: Bar graph showing (a) I_{ER} and (b) CI values for groundwater at each sampling location from Khetri copper mine region.

Pollution Indices and Risk Assessment

The abundance and distribution of heavy metals alone are not sufficient to assess their possible environmental impacts; therefore different types of pollution indices were calculated to assess the heavy metal pollution status of groundwater. The pollution level of groundwater samples is classified into different categories on the basis of scales given in literature which provides more details about the status of pollution.

Almost all the studied samples of Khetri copper mine region are in the slightly contamination range (1-5) excepting two samples namely W8 and W18, and the two reference samples (W22 and W23) which are in the safe zone (<1). Two samples namely W14 (close to overburden rocks) and W17 (abandoned mine) with CI values of 5 and 17 respectively are higher than the defined numerical value (>5) for high contamination (Figure 3). Hence, both these sample sites are highly contaminated on the basis of calculated CI values. In terms of I_{ER} values the water quality is highly degraded (≥5) for all the samples except samples from W8, W9, W10, W12, W15, W18 and W19 sites. The details of the samples falling in different categories of environmental risk are given in Table 1. The highest I_{ER} values 29 and 113 are found at W14 and W17 respectively and both fall in the extremely high risk (≥15) zone.

It is found that in the study area, the concentrations of Co and Ni contribute more in enhancing the numerical values for I_{ER} and CI. The I_{ER} which is higher in almost all the samples decreases to below 3 which is a limit for highly contamination category after excluding the concentration of Co and Ni from the I_{ER} calculation. However, in eight samples (W3, W6, W7, W12, W13, W14, W17 and W21) the I_{ER} values remain high (above 3) after excluding the concentration of Co and Ni from the calculations.

The calculated HI numerical values for Cu, Zn, Fe, Ni, Co, Mn and Pb for all the samples are shown in Figure 4. The hazard quotient for all the elements is within the acceptable range (<1), except W17 sample which is having ~40 (high >4). The calculated health index (HI) varies from 1 to 4 for all the samples, which is in medium range (≥ 1 <4) for non-carcinogenic health risk except samples from W5, W8 and W18 and two reference samples (W22 and W23). Hence, the consumption of groundwater could probably cause non-carcinogenic health impacts on the human beings in the region.

Conclusions

The heavy metal (Cu, Ni, Co, Fe and Mn) concentration data on groundwater samples for both pre and post monsoon from the Khetri mining region shows that

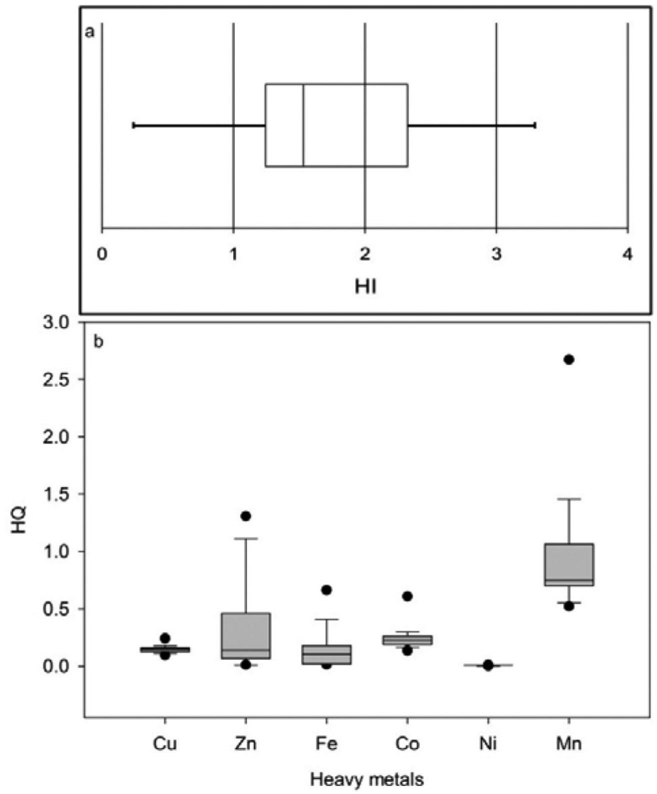


Figure 4: Box plot showing the calculated values of (a) HI and (b) HQ for groundwater samples (using average concentration of pre- and post-monsoon) for non-carcinogenic health effects at Khetri copper mine region.

their abundances in majority of the samples exceeds the desirable limits set by WHO, 2011 and BIS, 2012. However, Fe is found in much higher concentration (1.65 and 1.90 ppm during pre and post monsoon respectively) and exceeds the permissible limit (WHO and BIS) in almost all the samples in both the seasons, which is due to leaching of iron-rich sulfides. In addition, Fe is more mobile in the groundwater relative to Cu due to its high sensitivity to redox conditions.

The correlation matrix ($p > 0.01$) and PCA (57% of variance) indicate an anthropogenic source (sulfide mineral from the mines) for Cu, Co, Ni and Mn in the groundwater of the region. Lack of correlation between Fe and heavy metals is due to occurrence of Fe as oxides, silicates and carbonates in addition to sulphides as well as its high sensitivity to changing environment. pH shows significant negative correlation with Cu, Co, Ni and Mn at $p > 0.01$ and confirms the decrease in pH of water with the contamination while EC does not show any strong correlation with the heavy metal as EC is mostly controlled by the major ion chemistry.

The calculated pollution indices namely CI and I_{ER} indicate that most of the studied groundwater samples are in the slightly contaminated zone (1-5) and above the high risk zone (>10) respectively, and a few of the samples fall in the highly contaminated (>5) and extremely risk zone (>15). It is found that the hazard quotient for non-carcinogenic health effects is in the acceptable limit (<1) for all the groundwater samples except samples from Chaandmari mine (~40), whereas the Health Index (HI) is in the medium range (≥ 1 <4) for all the samples indicating the average suitability of groundwater for drinking purposes except few samples.

Acknowledgements

We thank the Dean, School of Environmental Sciences, JNU for encouragement and DST (Purse-Phase-II) and UGC (UPE-II) for financial support. AP acknowledges the University Grant Commission for Junior Research Fellowship.

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