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Estimation of Heavy Metal Pollution Index for Groundwater around Integrated Industrial Estate of Terai Region, Uttarakhand, India

Surindra Negi, Vir Singh, Uma Melkania, J. P. N. Rai

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Abstract The study was carried out in the Udham Singh Nagar district of Uttarakhand to evaluate the overall quality of groundwater with respect to heavy metals using heavy metal pollution index (HPI) approach. The samples were collected from different location and analyzed for zinc (Zn), chromium (Cr), Copper (Cu), lead (Pb), iron (Fe), nickel (Ni), cadmium (Cd) and arsenic (As) concentration for pre and post-monsoon period. During both the seasons the average concentrations of Pb, Ni, Cd and As were found higher than the recommended Indian standard for drinking water. The observed values of heavy metal pollution index during pre and post-monsoon were 216.9 and 136.18 respectively, with sampling location (SL) having highest HPI value are in the order of SL6 > SL2 > SL7>SL3>SL5>SL4>SL1. Pearson's correlation coefficient analysis revealed strong association between heavy metals, Zn showed strong correlation with Ca, Pb, Fe and As, Cu is strongly associated with Pb and As and Pb is strongly correlated with Fe and As.

Keywords HPI, Groundwater, Correlation coefficient, Heavy metals, Lead.

Introduction

Water is an indispensable component of an environment to sustain life on the earth. It is required to carry out several physical, chemical and biological processes. Groundwater is being extracted for multiple purposes since ages. Irrigation sector uses 89% of groundwater, 9% is used for domestic purpose and 2% of it is used by industrial sector (Central Ground-water Board 2013). Groundwater is highly values because of certain properties which are not possessed by surface water (Rajankar et al. 2009, Goel 2000). Consumption of groundwater has always been a priority over surface water as it offers good quality of freshwater that requires minimal treatment and due to its local availability it also promises large economic benefit (Villholth 2006, UN/WWAP 2003).

However, despite being the most promising alternative of freshwater source, groundwater quality is getting deteriorated progressively. Groundwater provides supplies of freshwater to carry out different processes ; however, rapid growth of the population, urbanization and industrialization have led to increasing demand resulting in the overexploitation of groundwater, worsening its quality and making it unfit for drinking and irrigation purposes. Anthropogenic activities like agricultural activities, industrial activities, domestic sewages release harmful organic and inorganic pollutants which may infiltrate through soil and rock and reach the aquifer and pollute the groundwater. Geogenic factors like presence of arsenic, fluoride also affect the health of groundwater. Countries like India, China, Korea, Greece and America are experiencing market decline in groundwater quality (Lou et al. 2017, Yang et al. 2016). Among different States of India, North-Eastern States and

Surindra Negi*, Vir Singh, Uma Melkania, J. P. N. Rai
Department of Environmental Science, GB Pant University of Agriculture and Technology, Pantnagar (US Nagar), Uttarakhand, India
e-mail: surindranegi05@gmail.com
*Corresponding author

Table 1. Location of sampling sites.

Sl. No.	Sampling location	Latitude	Longitude	Elevation (m)	Distance from integrated industrial Estate (km) road
1.	Gangapur road	28º59′24.93″N	79º27′15.18″E	195.50	6.6
2.	Fulsunga	28º59′ 23.94′′N	79º25′28.176′′E	193.40	2.9
3.	Awas-vikas	28º59′ 21.37′′N	79º24′32.95′′E	136.6	2.0
4.	Matkota	29º0′ 31.53′′N	79º24′0.996′′E	187.10	4.1
5.	Chhatarpur	29º1′ 50.706′′N	79º23′26.664′′E	208.4	10.4
6.	Pathharchatta	29º1′ 27.18′′N	79º24′50.65′′E	197	8.2
7.	Haldi	29º0′ 45.82′′N	79º26′11.028′′E	202.6	11.8

West Bengal are several affected with fluoride, arsenic and iron contamination in groundwater (Chaurasia et al. 2012). Besides degrading the overall quality, groundwater pollution also results in loss of water supply, high clean-up costs, high costs for alternative water supplies, and / or potential health problems (Akakuru et al. 2015, 2017). Concentration of heavy metals such as copper (Cu), cadmium (Cd), chromium (Cr), lead (Pb), nickel (Ni) and zinc (Zn), above its recommended level, is of great concern due to its associated health risks as these are more persistent than organic contaminant and are highly mobile in soil (Lou et al. 2017).

Heavy metal is a general collective term, which applies to the group of metals and metalloids with atomic density greater than 4000 kg m^3, or five times more than water (Singh and Kama 2017, Garbarino et al. 1995). Efforts have been made by different authors to develop several water quality estimation indices including Mohan et al. (1996), Tziritis et al. (2014) and Tamasi and Cini (2004). The application of these methods generally depends on the data available and the solicited results (Arslan et al. 2017, Horton 1965, Nishida et al. 1982). The present study has been carried out to investigate the seasonal variation in heavy metal concentration in groundwater around the integrated industrial settlement in Terai region of Uttarakhand, India.

Materials and Methods

Study area

The study was carried out in the Rudrapur city of Udham Singh Nagar district of Uttarakhand which falls under the Terai belt of the Himalayan foothills and is surrounded by Nainital district, Champawat district, Nepal and few districts of Uttar Pradesh in the north, northeast, east and west and south direction respectively. The city lies within 28.98^{o}N latitude and 79.40^{o}E longitude at an elevation of 243.8 meter above sea level. Rudrapur city covers a total area of 27.65 km^2, housing the population of 140,857 as per the 2011 census of India. The area falls under subtropical zone with 3 different seasons, viz. summers (March–May), monsoon season (June–September) followed by winters (October–February). On average, it receives annual rain about 1400 mm. The maximum temperature goes up to 42^{o}C in summers whereas it decreases up to 4^{o}C in the winters. Shallow to medium brown forest soil of alluvial nature is observed. The district hosts a number of automobiles and agro based industries and is also known for its agricultural set-ups. Due to the presence of shallow aquifers in the Terai region, maximum number of hand pumps and tube wells can be observed in the study area that caters the demands of freshwater supply. Being the industrial hub, the city is experiencing population spurt which in turn leads to the overexploitation and contamination of groundwater. For information regarding sampling locations see Table 1.

Geology of study area

The Terai region is the deposition ground for south flowing Himalayan Rivers. Therefore, it is mainly composed of clay, silt, sand, gravel and boulders derived from the denudation of Himalayan rocks. The study area forms a part of it. Bhabar, close to

Table 2. Descriptive statistical analysis of heavy metals of different locations for pre and post-monsoon season.

Sl. No.	Metals	Pre-monsoon season Min	Max	Mean±SD	Post-monsoon season Min	Max	Mean±SD	Standards for drinking water IS: 10500 ; 2004 Desirable limit	Permissible limit
1.	Zinc	0.083	0.71	0.316±0.202	0.024	0.866	0.349±0.25	5	15
2.	Chromium	0.003	0.058	0.0234±0.017	0.001	0.053	0.012±0.01	0.05	No relaxation
3.	Copper	0.001	0.052	0.007±0.013	.001	0.044	0.005±0.01	0.05	1.5
4.	Lead	0.029	0.293	0.10±0.09	0.01	0.61	0.074±0.11	.05	No relaxation
5.	Iron	0.101	1.64	0.46±0.036	0.012	1.26	0.28±0.2	0.3	1
6.	Nickel	0.01	0.089	0.032±0.016	.002	0.1	0.038±0.02	0.02	No relaxation
7.	Cadmium	0.004	0.091	0.042±0.02	0.001	0.061	0.017±0.015	0.003	0.01
8.	Arsenic	0.001	1.4	0.11±0.228	0.003	1.3	0.147±0.28	0.05	No relaxation

the Himalayan foothills, forming the northern border with Terai is the main intake area. The formation is favorable to percolate the water laterally from the Bhabar to Terai with a hydraulic gradient of approximately 2.97 m/km (Annual Report 2008-2009) and the Older Alluvium further south. The hydrogeology of the study area suggests the existence of shallow unconfined aquifers as well as deep confined aquifers separated by impervious clay. Artesian conditions are restricted to the Terai zone. Central Groundwater Board has constructed 159 artesian wells at Basai, Kashipur, Bazpur, Nagaland, Rudrapur. The drilled depth is found to be from 84.4 m to 433.0 m below ground level, with free-flowing head up to 8.69 m above ground level. Further, the hydraulic conductivity of the aquifers in the study area was reported to be in the range of 25–243 m/day. The transmissivity values of these shallow aquifers were observed to be in a range of 300 to 8800 m^2/day, while the yield of the aquifers ranged from 10 to 50 liter per second (CGWB 2013).

Sample collection and experimental method

The sampling of groundwater was performed during post-monsoon and pre-monsoon season, in the month of January and May 2018, respectively. Total 35 groundwater samples were collected from 7 different locations covering the study area. The sampling criterion adopted the method of measuring the distance of Integrated Industrial Estate from the sampling points. High density polyethylene bottles (1L) were used and were rinsed with ethanol thrice, prior to sampling. The samples were taken to the laboratory, for that purpose, pH < 2 was adjusted by adding nitric acid and stored in refrigerator at 4°C for further analysis. The samples were digested and analyzed for heavy metal concentration using atomic absorption spectrophotometry (Perkin-Elmer atomic absorption spectrometer (Model 3110).

Heavy metal pollution index (HPI) approach

HPI method indicates the overall water quality with regard to heavy metals. The HPI is based on weighted arithmetic quality mean method and was developed in 2 steps. Firstly, by assiging rating or weightage (Wi) to the selected parameters and secondly, by selecting the pollution parameters on which the index has to be based. The rating system uses an arbitrary value between 0 and 1 and its selection depends upon the importance of individual quality concentrations in a comparative way or it can be assessed by making values inversely proportional to the recommended standard (Si) for the corresponding parameter (Horton 1965, Mohan et al. 1996). Heavy metals like copper zinc, lead and cadmium were monitored for developing the application model index. The permissible or critical pollution index value for drinking water is 100. The HPI modelgiven below is proposed by Mohan et al. (1996).

$$HPI = \sum_{i=1}^{n} WiQi / \sum_{i=1}^{n} Wi$$

Where, Wi is the unit weightage given to the i^{th}

Table 3a. HPI for pre-monsoon season.

Sl. No.	Heavy metals	Mi (ppb)	Ii (IS : 10500) (ppb)	Si (IS : 10500) (ppb)	Wi	Qi	WiQi
1.	Cr	23	50	No relaxation	0.02	0.46	0.0092
2.	Cu	7.77	50	1500	0.0006	0.518	0.0003
3.	Pb	100.3	50	NR	0.02	200.6	4.01
4.	Fe	463.1	300	1000	0.001	46.31	0.046
5.	Ni	32.9	20	No relaxation	0.05	164.5	8.22
6.	Cd	42.1	3	10	0.1	421	42.2
7.	As	110	50	No relaxation	0.02	220	4.4
8.	Zn	316	5000	15000	0.06	2.1	0.126
					∑Wi=0.2716		∑WiQi=58.9115
						HPI=216.9	

Table 3b. HPI for post-monsoon season.

Sl. No.	Elements	Mi (ppb)	Ii (IS : 10500) (ppb)	Si (IS : 10500) (ppb)	Wi	Qi	WiQi
1.	Cr	12.8	50	NR	0.02	25.6	0.512
2.	Cu	5	50	1500	0.0006	0.33	0.00019
3.	Pb	74	50	NR	0.02	148	2.96
4.	Fe	280	300	1000	0.001	28	0.028
5.	Ni	38.1	20	NR	0.05	190.5	9.525
6.	Cd	17.71	3	10	0.1	177.1	17.71
7.	As	147.5	50	NR	0.02	295	5.9
8.	Zn	349	5000	15000	0.06	2.32	0.139
					∑Wi=0.2716		∑WiQi=36.77419
						HPI=136.18	

parameter, Qi is the sub-index of the i^{th} parameter and n is the number of parameter used for indexing approach.

The sub-index Qi can be calculated by:

$$Qi = \sum_{i=1}^{n} \frac{(Mi - Ii)}{(Si - Ii)} \times 100$$

Where, Mi is the monitored value of i^{th} parameters, Ii is the ideal value of i^{th} parameters and Si is the standard value of i^{th} parameters. The expression (Mi-Ii) indicates the numerical difference of the 2 values, ignoring the algebraic sign.

Statistical analysis

Pearson's correlation matrix for monitored heavy metals under Principal Component Analysis (PCA) was formed for both the seasons using XLSTAT software.

Results and Discussion

Heavy metal concentration in groundwater

The mean value and other statistical measure of analyzed heavy metals for 2 seasons are shown in Table 2. The observed values of heavy metals were compared with the Indian drinking water standards IS : 10500. It was observed that during pre and post-monsoon period the average concentration of Zn, Cr and Cu in the groundwater sample of the study area were within the recommended level whereas the mean concentration of Pb, Ni, Cd and As were beyond the permissible limit with the exception, where mean concentration of Fe was found higher than the recommended level during pre-monsoon as compared to post-monsoon. During pre-monsoon season the mean value of Pb, Fe and Cd increased by about 35%, 64% and 147% respectively, whereas Ni and As showed marked decrease in the concentration by 15%

Table 4a. Pearson's correlation coefficient matrix of heavy metals for pre-monsoon.

Vari-ables	Zn	Cr	Cu	Pb	Fe	Ni	Cd	As
Zn	**1**	– 0.457	0.811	0.998	0.717	– 0.349	–0.889	0.596
Cr	– 0.457	**1**	– 0.192	– 0.461	– 0.443	0.348	0.192	– 0.223
Cu	0.811	– 0.192	**1**	0.790	0.311	– 0.326	–0.600	0.548
Pb	0.998	– 0.461	0.790	**1**	0.724	– 0.367	–0.905	0.573
Fe	0.717	– 0.443	0.311	0.724	**1**	0.169	–0.785	0.258
Ni	– 0.349	0.348	– 0.326	– 0.367	0.169	**1**	0.163	– 0.498
Cd	– 0.889	0.192	– 0.600	– 0.905	– 0.785	0.163	**1**	–0.339
As	0.596	– 0.223	0.548	0.573	0.258	– 0.498	–0.339	**1**

Table 4b. Pearson's correlation coefficient matrix of heavy metals for post-monsoon.

Vari-ables	Zn	Cr	Cu	Pb	Fe	Ni	Cd	As
Zn	**1**	– 0.094	0.453	0.354	0.581	– 0.043	0.175	0.271
Cr	– 0.094	**1**	– 0.136	0.115	– 0.016	0.130	– 0.133	0.020
Cu	0.453	– 0.136	**1**	0.227	– 0.053	0.055	0.145	0.036
Pb	0.354	0.115	0.227	**1**	0.190	– 0.078	– 0.102	–0.025
Fe	0.581	– 0.016	– 0.053	0.190	**1**	– 0.166	0.064	0.290
Ni	– 0.043	0.130	0.055	– 0.078	– 0.166	**1**	0.353	–0.182
Cd	0.175	– 0.133	0.145	– 0.102	0.064	0.353	**1**	–0.131
As	0.271	0.020	0.036	– 0.025	0.290	– 0.182	– 0.131	**1**

and 25% when compared to post-monsoon season. Udham Singh Nagar district is also known as food bowl due to high rate of agricultural production and several agro-based and other industries ; therefore, anthropogenic activities are the major cause of the groundwater contamination.

Heavy metal pollution index

The mean of monitored values (Mi) of all the 8 heavy metals, desirable values (Ii) and permissible values (Si) as per the IS : 10500 guidelines and unit weightage (Si) assigned to each heavy metals were taken into the consideration for the calculation of heavy metal pollution index for both the seasons as shown in Tables 3a and 3b. The HPI values for both the season were found higher than the proposed critical pollution index value of 100 (Mohan et al. 1996). Further, it can be observed that HPI value of pre-monsoon season is higher than the HPI value of post-monsoon. The experimental observations indicated that the groundwater was critically polluted and not fit for drinking purpose. HPI was also calculated for the selected sampling locations whereall the values of HPI were found > 100. Based on the calculation of HPI value for different sampling locations, the locations having higher mean HPI value for both the seasons were in the increasing order of, SL6 > SL2 > SL7 > SL3 > SL5 > SL4 > SL1. It was observed that among different sampling locations, groundwater sample collected from SL6 had highest HPI value i.e. 221.57 and was found critically polluted due to elevated level of heavy metal concentration, which might be due to the fact that the location was very close to one of the automobile industries, i.e. 2.2 km and also surrounded by large agricultural area which influences the overall quality of groundwater. The distance of sampling location SL2 from the center of integrated Industrial Estate is about 2.9 km hence this can be the major cause of heavy metal pollution. Sampling location SL1 was found to have lowest mean value of HPI i.e. 116.2.

Principal component analysis

Correlation matrix was determined at 5% level of significance using Principal component analysis (PCA) for heavy metals is shown in Tables 4a and 4b for both the seasons. It is a technique to measure the degree of association among different variables.

Such association is likely to lead to reasoning about causal relationship between the variables. The Pearson correlation coefficient is denoted as r and its value ranges –1 to +1, which shows the negative and positive relationship between the 2 variables. Among the studied heavy metals, Zn showed strong positive correlation with Cu, Pb, Fe and As. Similarly, Cu is strongly associated with Pb and As ; likewise Pb is strongly correlated with Fe and As. The positive relationship shown in the Table among different heavy metals indicated the same source of input (Mishra et al. 2018), i.e. possibly due to combined effect of industrial as well as agricultural activities.

Conclusion

The study was carried out to assess the groundwater contamination due to heavy metals. The groundwater samples were collected from seven different locations during pre and post-monsoon. The mean concentration of Pb, Ni, Cd and As was found higher than the permissible limit as per given by IS : 10500, whereas mean concentration of Zn, Cr, and Cu were within the permissible limit. Heavy metal pollution indexing approach was applied to the observed concentration of 8 heavy metals (Zn, Cr, Cu, Pb, Fe, Ni, Cd and As) to assess the influence of heavy metal on the overall water quality of groundwater. The HPI values were found above the critical value of 100, i.e. 216.9, during pre-monsoon and 1.36.18 during post-monsoon. It can be concluded that the groundwater of the study area is critically polluted and unfit for drinking purposes. Also, HPI was calculated for individual locations and the location having highest HPI value are in the order of SL6 > SL2 > SL7 > SL3 > SL5 > SL4 > SL1. The combined effect of industrial and agricultural activities was found responsible for the heavy metal pollution of groundwater of location SL6. Pearson's correlation coefficient matrix determined the positive and negative relationship between heavy metals under study where Zn showed strong positive correlation with Cu, Pb, Fe and As. Similarly, Cu is strongly associated with Pb and As ; likewise Pb is strongly correlated with Fe and As. The remediation of groundwater contamination is difficult and expensive as compared to surface water. Therefore, periodic evaluation of groundwater quality is the need of the hour to detect the contamination at the initial stage and prevent further deterioation by adopting certain preventive measures.

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