Evaluation of the heavy metal pollution index for surface and spring water near a limestone mining area of the lower Himalayas

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Abstract Concentrations of seven heavy metals: copper, cadmium, iron, chromium, manganese, lead and zinc have been evaluated in nine spring water and eight surface water sampling locations near the limestone mining area of Sirmour district of Himachal Pradesh, India, during pre- and post-monsoon seasons. The concentrations of heavy metals have been found to be below the permissible levels of drinking water quality standards. The data have been used for the calculation of heavy metal pollution index (HPI). The HPI of spring water and surface water has been found to be far below the index limit of 100, pointing to the fact that the spring water and surface water is not polluted with respect to heavy metals despite the prolific growth of limestone mining in the region.

Keywords Heavy metal pollution index · Limestone mining · Spring water · Surface water

Introduction

Limestone mining in the ecologically fragile lower Himalayas has been a contentious issue for many years. Sirmour is the southernmost district of Himachal Pradesh State of India and covers an area of 2,825 km^2 in the lower Himalayas and Siwalik ranges. This region is very rich in limestone deposits of different grades. The two rivers, namely Giri and Tons, flow through the limestone-mining belt of the district and carry the discharges of mining activities. In the mining area, there are several springs on which the local population depends for drinking water. Because of blasting in the mining zone there is always a threat to these natural springs in terms of their damage as well as quality deterioration. Heavy metals, one of the important water quality parameters, may also get enriched in water because of mining activities. Thus, monitoring of heavy metals in spring water and surface water used for drinking purposes assumes great significance from the human health point of view. In this context monitoring of heavy metals pollution in spring water and surface waters of the limestone mining belt of Sirmour district is of paramount importance. The pollution parameters monitored for the assessment of the quality of any system give an idea of the pollution with reference to that particular parameter only. Quality indices are useful in obtaining a composite influence of all parameters of overall pollution. Quality indices make use of a series of judgements into a reproducible form and compile all the pollution parameters into some easy approach. Several methods have been proposed to develop quality indices for estimation of characteristics of surface water with water quality parameters (Horton 1965; Joung and others 1979; Landwehr 1979; Nishidia and others 1982; Tiwary and Mishra 1985). Recently, the authors (Prasad and Jaiprakas 1999) have evaluated the heavy metals pollution in groundwater and evaluated the heavy metal pollution index (HPI). In the present paper the study of overall pollution caused by heavy metals in spring water and surface water near the limestone mining area of Sirmour district has been performed using the weighted arithmetic average mean method of indexing. The concentrations of seven heavy metals, namely iron, manganese, lead, copper, cadmium, chromium and zinc, have been evaluated for nine important springs and eight important locations for surface water of Giri River and Tons River in pre- and post-monsoon seasons of a year.

Indexing approach

The HPI represents the total quality of water with respect to heavy metals. The proposed HPI is based on the weighted arithmetic quality mean method and is developed in two basic steps. First, by establishing a rating scale for each selected parameter giving weightage to select parameter and, second, by selecting the pollution parameter on which the index is to be based. The rating system

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is an arbitrary value between zero to one, and its selection depends upon the importance of individual quality considerations in a comparative way or it can be assessed by making values inversely proportional to the recommended standard for the corresponding parameter (Horton 1965; Mohan and others 1996). In the present formula, unit weightage (W_i) is taken as value inversely proportional to the recommended standard (S_i) of the corresponding parameter (Reddy 1995). Iron, manganese, lead, copper, cadmium, chromium and zinc have been monitored for the model index application. The HPI model proposed is given by (Mohan and others 1996)

$$HPI = \frac{\sum_{i=1}^{n} W_i Q_i}{\sum_{i=1}^{n} W_i} \qquad (1)$$

where Q_i is the sub-index of the ith parameter. W_i is the unit weightage of ith parameter and n is the number of parameters considered.
The sub-index (Q_i) of the parameter is calculated by

$$Q_i = \sum_{i=1}^{n} \frac{\{M_i(-)I_i\}}{(S_i - I_i)} \times 100 \qquad (2)$$

where M_i is the monitored value of heavy metal of ith parameter, I_i is the ideal value of ith parameter, S_i is the standard value of ith parameter. The sign (–) indicates the numerical difference of the two values, ignoring the algebraic sign. Generally, pollution indices are estimated for any specific use of the water. The proposed index is intended for the purpose of drinking water. The critical pollution index value for drinking water is 100.

Experimental

Tons River and Giri River are two main sources of water in the Sirmour district of Himachal Pradesh, India. They pass through the limestone mining belt. At some places they receive runoff water from the mines and also through the drainage flowing in the mining areas. Four sampling locations T_1, T_2, T_3 and T_4 have been selected for Tons, and four locations G_1, G_2, G_3 and G_4 for Giri River as shown in Fig. 1. Sampling locations have been selected for the assessment of water quality of the Giri River downstream of each mining area. Similarly for Tons River, sampling points have been selected downstream of the drainage because the drainage discharges mining wastes from different mining

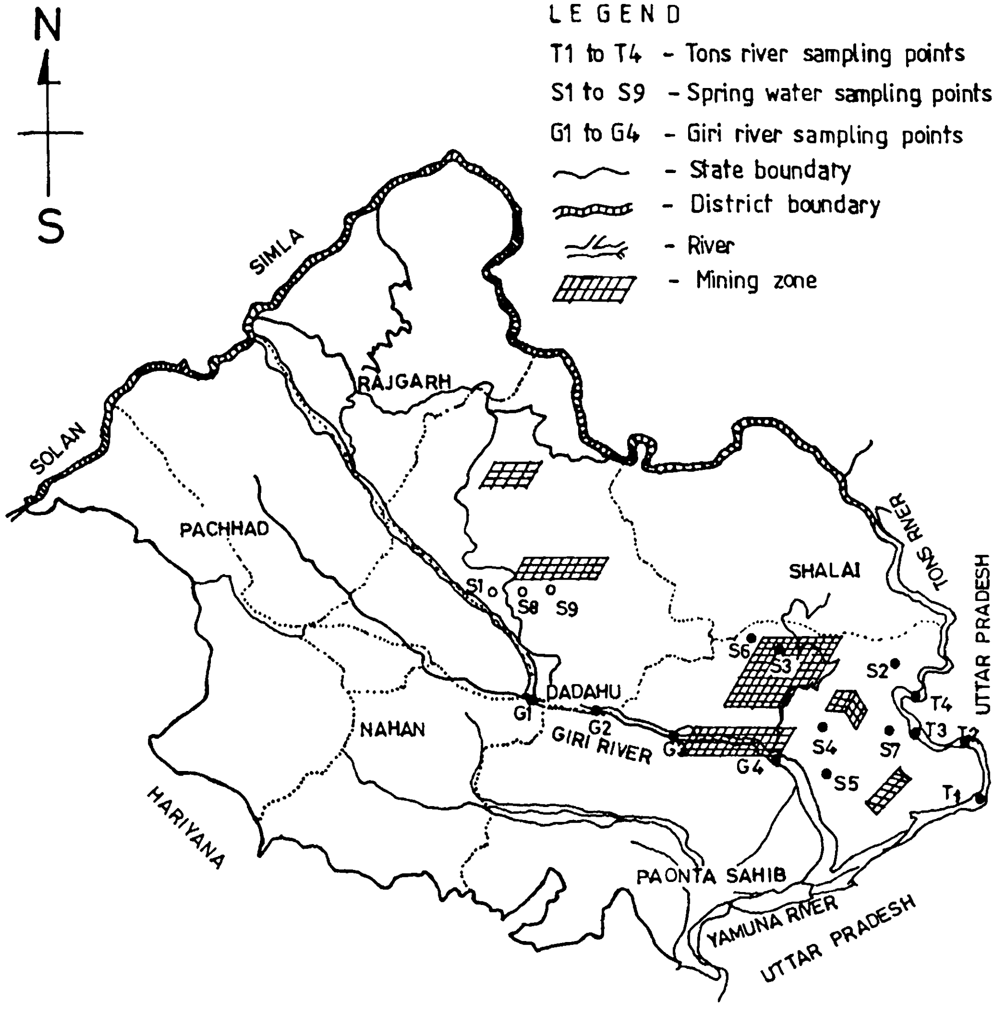

Fig. 1
Map showing sampling locations of surface and spring water near limestone area of the Sirmour District

Table 1
Total heavy metals concentration in surface water of Giri and Tons River of the Sirmour limestone mining area. *G_1* Giri River at Dadahu district of Sangarah and Bhootmari; *G_2* Giri River at Manal district of Manal Mines; *G_3* Giri River in the district of Sataun; *G_4* Giri River at Banganan bridge district of Rajban; *T_1* Tons River at Laldenga bridge at Kellor; *T_2* Tons River down-stream of Shiva Ka Khala; *T_3* Tons River down-stream of Banaur Ka Khala; *T_4* Tons River up-stream of Shamar Ka Khala

Parameters in mg/l	Sampling location															
	G_1		G_2		G_3		G_4		T_1		T_2		T_3		T_4	
	Pre-monsoon	Post-monsoon	Pre-monsoon	Post-monsoon	Pre-monsoon	Post-monsoon	Pre-monsoon	Post-monsoon	Pre-monsoon	Post-monsoon	Pre-monsoon	Post-monsoon	Pre-monsoon	Post-monsoon	Pre-monsoon	Post-monsoon
Fe	0.196	0.194	0.116	0.119	0.037	0.039	0.068	0.072	0.120	0.132	Nil	Nil	Nil	Nil	0.082	0.097
Mn	0.013	0.014	0.014	0.012	0.006	0.009	0.014	0.024	0.010	0.020	Nil	0.004	0.020	0.028	0.030	0.034
Pb	Nil	Nil	Nil	Nil	0.003	0.014	0.009	0.009	0.003	0.004	Nil	Nil	0.008	0.009	0.010	0.011
Cu	0.028	0.024	0.017	0.012	0.009	0.008	0.007	0.007	0.002	0.003	0.004	0.004	0.005	0.006	0.009	0.009
Cd	0.003	0.002	0.001	0.002	0.002	0.001	0.003	0.002	Nil	Nil	Nil	Nil	Nil	Nil	Nil	0.001
Cr	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	0.003	0.004	0.002	0.003	Nil	Nil
Zn	0.041	0.040	0.021	0.020	0.010	0.014	0.013	0.013	0.018	0.019	0.004	0.003	0.002	0.002	0.021	0.023

Table 2
Total heavy metals concentration in spring water of Sirmour limestone mining area. *S_1 Banaur Ka Khala; S_2 Samhar Ka Khala; S_3 Shila Ka Khala; S_4 Knajiyara Ka Khala; S_5* Tilgan Ka Khala; *S_6* Bohrar Ka Khala; *S_7* Kandon Ka Khala; *S_8* Bhootmari Ka Khala (up-stream of mines); *S_9* Bhootmari Ka Khala (down-stream of mines)

Parameters in mg/l	Sampling location																	
	S_1		S_2		S_3		S_4		S_5		S_6		S_7		S_8		S_9	
	Pre-monsoon	Post-monsoon	Pre-monsoon	Post-monsoon	Pre-monsoon	Post-monsoon	Pre-monsoon	Post-monsoon	Pre-monsoon	Post-monsoon	Pre-monsoon	Post-monsoon	Pre-monsoon	Post-monsoon	Pre-monsoon	Post-monsoon	Pre-monsoon	Post-monsoon
Fe	0.310	0.274	0.098	0.099	0.200	0.105	0.910	0.813	0.320	0.291	0.060	0.050	0.120	0.108	0.230	0.212	0.350	0.331
Mn	0.030	0.032	0.012	0.028	0.200	0.012	0.050	0.054	0.011	0.015	0.010	0.012	0.008	0.009	0.011	0.015	0.012	0.012
Pb	0.020	0.019	0.012	0.012	Nil	0.012	0.007	0.009	Nil	Nil	0.011	0.017	0.012	0.011	Nil	Nil	Nil	Nil
Cu	0.010	0.009	0.010	0.009	0.007	0.006	0.012	0.013	0.014	0.014	0.006	0.005	0.010	0.009	0.020	0.015	0.010	0.014
Cd	Nil	0.003	Nil	0.001	0.002	0.001	0.001	0.001	Nil	Nil	0.001	0.001	0.002	0.002	0.003	0.002	Nil	0.001
Cr	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Zn	0.050	0.043	0.019	0.019	0.012	0.014	0.025	0.024	0.026	0.021	0.020	0.012	0.020	0.020	0.030	0.026	0.030	0.030

Table 3
HPI calculation for surface water of Sirmour limestone mining area. Σ W_i=0.22536 Σ W_iQ_i=2.1108; *HPI*=9.3663

Heavy metals	Mean concentration value (M_i) (ppb) n=16	Standard permissible value (S_i) (ppb)	Highest desirable value (I_i) (ppb)	Unit weightage (W_i)	Sub index (Q_i)	$W_i \times Q_i$
Fe	79.5	1,000	100	0.001	2.2777	0.0022
Mn	15.75	300	100	0.0033	42.125	0.1390
Pb	5.0	50	–	0.020	10.00	0.200
Cu	9.625	1,000	50	0.001	4.25	0.0042
Cd	1.0625	10	–	0.100	10.625	1.0625
Cr	0.700	10	–	0.100	7.00	0.700
Zn	16.5	15,000	5,000	0.00006	49.83	0.0029

Table 4
HPI calculation for spring water of Sirmour limestone mining area. Σ W_i=0.2253 Σ W_iQ_i=1.6401; *HPI*=7.2796

Heavy metals	Mean conc. value (M_i) (ppb) n=18	Standard permissible value (S_i) (ppb)	Highest desirable value (I_i) (ppb)	Unit weightage (W_i)	Sub index (Q_i)	$W_i \times Q_i$
Fe	271.16	1,000	100	0.001	19.017	0.0190
Mn	19.61	300	100	0.0033	40.195	0.1326
Pb	7.888	50	–	0.02	15.776	0.3155
Cu	10.722	1,000	50	0.001	4.134	0.0041
Cd	1.166	10	–	0.1	11.66	1.166
Cr	0.000	10	–	0.1	0.000	0.000
Zn	24.50	15,000	5,000	0.00006	49.755	0.0029

areas into it. Almost all the important locations of springs, S_1 to S_9, marked in Fig. 1, have been covered to assess their water quality as they are the only sources of drinking water supply in this hilly area. Sampling has been done in pre-monsoon (May–June) and post-monsoon (October–November) seasons of the year to evaluate variations in annual concentration of heavy metals.

Collection of water samples

Water samples from surface waters and spring waters were collected just below the water surface using 1-l polythene bottles, which had been cleansed by soaking in 10% nitric acid overnight and rinsed with distilled water on the day of sampling. At the sampling site, the bottles were rinsed twice with water to be sampled prior to filling. Each sample was treated with 10 ml 6 N HNO_3 solution. The samples were filtered immediately upon arrival at the laboratory using a 0.45-µm millipore membrane filter and kept in the dark before analysis.

Sample preparation

An aliquot of 500 ml of each water sample was taken into a beaker, digested on a hot plate and reduced to the volume less then 50 ml. The digested sample was poured into a 50-ml volumetric flask and the volume was made up by distilled water, which was used before to rinse the digested sample beaker. The prepared sample was kept in the dark at room temperature about 1 week, before being analysed by flame atomic absorption spectrophotometry (GBC 902) and inductively coupled plasma spectrophotometry (GBC Integra XM).

Determination of iron, manganese, copper, cadmium and zinc

Analysis of these elements was performed by flame atomic absorption spectrophotometry. Standard solutions were prepared by dissolving pure elements in an appropriate acid, and different dilutions were prepared according to requirements. According to the manual, the instrument was calibrated with standard solutions and analysis of iron, manganese, copper, cadmium and zinc was performed at 248.3, 279.5, 324,7, 228.8 and 213.9 nm, respectively. Three replicates were run for each sample and the instrument was recalibrated after analysis of 10 samples. Overall precision, expressed as percent relative standard deviation (RSD) was obtained for all the samples. Analysis precision for Fe, Mn, Cu, Cd and Zn was 1.10, 0.39, 0.73, 3.44 and 0.54 RSD, respectively. Because the samples were concentrated during digestion, the result obtained was calculated to get the actual concentration.

Table 5
Heavy metal pollution index of individual surface water. Mean *HPI*=9.6485

Surface water	HPI value	Deviation (%)
Giri River	10.3177	+6.93
Tons River	8.9794	–6.93

Determination of chromium and lead

These two elements were determined by inductively coupled plasma spectrophotometry (GBC Integra XM) according to standard methods (Arnold and others 1992). Standard solutions were purchased from Aldrich chemical company (USA). Appropriate dilutions of standards were prepared according to requirements. The instrument was

Table 6
Heavy metal pollution index of spring water at various sampling locations. Mean *HPI*=6.3392

Sampling point	HPI	Mean deviation	Deviation (%)
S1	8.4407	+2.1015	+33.15
S2	4.9665	–1.3727	–21.65
S3	8.3945	+2.0553	+32.42
S4	6.6143	+0.2751	+4.33
S5	0.7672	–5.5720	–87.89
S6	3.6355	–2.7037	–42.65
S7	11.6236	+5.2844	+83.36
S8	9.5988	+3.2596	+51.41
S9	3.0120	–3.3272	–52.48

calibrated with standard solutions of hexavalent chromium and lead at 205.552 and 220.353 nm. The samples for chromium analysis were treated with few drops of potassium permanganate followed by gentle heating to convert Cr (III) to Cr (IV). The analytical precision for Cr and Pb was 1.02 and 1.01 RSD, respectively. The results obtained were calculated to get the actual concentration of metals.

Results and discussion

The evaluation of concentration of the seven heavy metals Fe, Mn, Pb, Cu, Cd, Cr and Zn in pre- and post-monsoon seasons in the surface water of Giri River (G_1–G_4) and Tons River (T_1–T_4) is given in Table 1. The concentration of these heavy metals is well below the permissible limit of drinking water standards. The concentration of iron was found to be at a maximum at six sampling points (G_1,G_2,G_3,G_4,$T_1$and T_4) out of a total of eight points in the Giri and Tons Rivers, whereas chromium was found in only two sampling locations (T_2 and T_3) of the Tons river. The concentrations of these heavy metals in nine spring water samples (S_1–S_9) for pre- and post-monsoon seasons are given in Table 2. In these spring waters, iron was also found at a maximum and chromium was not detected at all in any of the samples.

The variation in the concentration of heavy metals in river and spring water in two different seasons has been found to be insignificant. Both the surface water and spring water samples in and around the mining belt have been found to be safe from the heavy metals pollution. These monitored data have been used to evaluate the HPI for surface water and spring water to assess the validity of the proposed index model.

The HPI has been determined for surface water and spring water by taking the mean concentration value of heavy metals for both the seasons using Eq. (1). The detailed calculation of the pollution index with unit weightage (W_i) and standard permissible value (S_i) are presented for surface water in Table 3 and spring water in Table 4. The heavy metal pollution index calculated with mean concentration values of all metals, including all sampling points of the surface and spring water for both the seasons is 9.3663 and 7.2796, respectively; values that are well below the critical index value of 100. The calculated index values indicate that, in general, the surface and spring waters are not contaminated with respect to heavy metal pollution.

The HPI of surface waters of the Giri and Tons Rivers was also calculated separately. For this calculation, all the four sampling points of each river, including all the seven heavy metals evaluated in pre- and post-monsoon season, were used. The HPI calculated separately for Giri and Tons Rivers is 10.3177 and 8.9794, respectively, and is given in Table 5. This enables us to assess the quality of water at each river and compare them with respect to heavy metal pollution. Although the HPI of both rivers is far below the critical index value of 100, the index value of the Giri River is greater than that of the Tons River, indicating that the Giri River receives more pollutants through wastewater discharged into it than the Tons River.

The HPI of all the spring water sampling points has also been calculated separately. For each calculation, it includes all the seven heavy metals determined in pre- and post-monsoon seasons at each point and is given in Table 6. Mean deviation and percentage deviation from the mean HPI value has been calculated for each sampling point. Four sampling points (S_2, S_5, S_6 and S_9) of spring water show that the index values are lower than the mean value and the percentage deviation is on the negative side, which indicates a better quality of water with respect to heavy metals. The remainder of the five sampling points (S_1, S_3, S_4, S_7 and S_8) show index values are more than mean HPI value. The method used to calculate HPI has been found to be very useful to study and compare variations of over-all pollution levels, which includes many parameters and is also very useful to assess the overall pollution level with respect to heavy metals.

Conclusion

The HPI model used here has been proven to be a very useful tool in evaluating the overall pollution level of surface water and spring water in terms of heavy metals. The HPI calculated for surface waters and spring waters of Sirmour limestone mining area has been found to be far below the index limit of 100. This shows that the surface water and spring water are not polluted with respect to heavy metals despite the prolific growth of mining and other allied activities in the zone.

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