Appl Water Sci
DOI 10.1007/s13201-016-0430-3

ORIGINAL ARTICLE

Heavy metal contamination and its indexing approach for groundwater of Goa mining region, India

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Received: 28 January 2015 / Accepted: 16 May 2016

Abstract The objective of the study is to reveal the seasonal variations in the groundwater quality with respect to heavy metal contamination. To get the extent of the heavy metals contamination, groundwater samples were collected from 45 different locations in and around Goa mining area during the monsoon and post-monsoon seasons. The concentration of heavy metals, such as lead, copper, manganese, zinc, cadmium, iron, and chromium, were determined using atomic absorption spectrophotometer. Most of the samples were found within limit except for Fe content during the monsoon season at two sampling locations which is above desirable limit, i.e., 300 µg/L as per Indian drinking water standard. The data generated were used to calculate the heavy metal pollution index (HPI) for groundwater. The mean values of HPI were 1.5 in the monsoon season and 2.1 in the post-monsoon season, and these values are well below the critical index limit of 100.

Keywords Groundwater · Heavy metal · Pollution index · Seasonal variation · Goa

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Introduction

Groundwater is a valuable renewable resource and occurs in permeable geologic formations known as aquifers. Groundwater is an important resource for the agriculture purposes, industrial sectors and majorly used as potable water in India (Singh et al. 2014; Chandra et al. 2015). Water pollution not only affects water quality, but also threats human health, economic development, and social prosperity (Milovanovic 2007). Scarcity of clean and potable drinking water has emerged in recent years as one of the most serious developmental issues in many parts of West Bengal, Jharkhand, Orissa, Western Uttar Pradesh, Andhra Pradesh, Rajasthan and Punjab (Tiwari and Singh 2014). Groundwater contamination is one of the most important environmental problems in the present world, where metal contamination has major concern due to its high toxicity even at low concentration. 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 (Garbarino et al. 1995). Heavy metals enter into groundwater from variety of sources; it can either be natural or anthropogenic (Adaikpoh et al. 2005). Mining activities are well known for their deleterious effects on the water resources (Dudka and Adriano 1997; Goyal et al. 2008; Nouri et al. 2009; Verma and Singh 2013; Tiwari et al. 2016b, c, d). In general, mine tailings and other mining-related operations are the major source of contaminants, mainly of heavy metals in water (Younger 2001; Vanek et al. 2005; Vanderlinden et al. 2006; Conesa et al. 2007; Mahato et al. 2014; Tiwari et al. 2015a, 2016a).

Water quality indices are one of the most effective tools to communicate information on the quality of any water body (Singh et al. 2013a). Heavy metal pollution index (HPI) is a method that rates the aggregate influence of

Published online: 02 June 2016

individual heavy metal on the overall quality of water and is useful in getting a composite influence of all the metals on overall pollution (Mahato et al. 2014). Recently, several researchers have showing interest on assessment of water quality for the suitability of drinking purposes using water quality indices methods (Giri et al. 2010; Ravikumar et al. 2013; Singh et al. 2013b; Kumar et al. 2014; Tiwari et al. 2014, 2015a, b; Prasad et al. 2014; Logeshkumaran et al. 2014; Bhutiani et al. 2014; Panigrahy et al. 2015). The present study aimed to investigate the groundwater quality status with respect to heavy metal concentrations in mining areas of Goa. Heavy metal pollution index was used to assess the influence of overall pollution and illustrate the spatial distribution of the heavy metal concentrations in the groundwater of the study area.

Materials and methods

Study area

Goa is located between the latitudes 15°48′00″ to 14°53′54″N and longitude 74°20′13″ to 73^{0}40′33″E, on the western coast of Indian Peninsula and separated from Maharashtra by the Terekhol River in the north, Karnataka in the south, Western Ghats in the east, and Arabian Sea in the west with a cost line stretching about 105 km. Goa covers an area of 3702 km^2.

Geology of Goa

Occurrence of iron ore is restricted to Bicholim formation of Archaean metamorphic in age belonging to Goa Group of Dharwar Super Group. Bicholim formation is represented by Quartz-chlorite/amphibolites schist with lenses of metabasalt, sills of metagabbro, carbonaceous and manganiferous chert, quartzite, phyllite with banded iron formation Quartz-sericite schist and magnesium limestone. Schematic section of Geology of Goa was shown in Fig. 1.

Groundwater aquifers in Goa

The mining belt in Goa has two known aquifers, viz., top laterite layer and the powdery iron ore formation at depth. The top layer with laterite cover is quite extensive in the area and even though mining activities have denuded some of these areas, still some areas are left out, with sufficient laterite cover. Herein, the water is under perched water table condition. The friable powdery iron ore at depth is porous, permeable, and completely saturated with water. The ore bodies (aquifers) are exposed and water seeps into the mine pits under pressure from them during mining operations and particularly due to large amount of monsoon rainfall in Goa. The depth to water level ranged from 1.69 to 26.09 mbgl during the monsoon and from 2.17 to 19.23 mbgl in the post-monsoon season.

Field sampling and experimental procedure

Samples were collected from 45 different locations during the monsoon and post-monsoon seasons, respectively (Fig. 2). Criteria for selections of sampling stations were based on the locations of different industrial units (mining) and lands use pattern to quantify heavy metal concentration. The depth of open wells was between 25 and 30 m. Sampling had been done for the month of July (monsoon) 2013 and October (post-monsoon) 2013. The pH values were measured in the field using a portable pH meter (multiparameter PCS Tester series 35). The total dissolved solid (TDS) value was measured using the TDS meter instrument (model no 651E). For the analysis of the heavy metals, samples were preserved in 100 mL polypropylene bottles by adjusting pH < 2 with the help of ultra-pure nitric acid. All samples have been digested, concentrated, and prepared for the analysis by atomic absorption spectrophotometer (AAS) methods using model: GBC-Avanta.

Indexing approach

Water quality and its suitability for drinking purpose can be examined by determining its quality index (Mohan et al. 1996; Prasad and Kumari 2008; Prasad and Mondal 2008; Tiwari et al. 2015a) by heavy metal pollution index methods. The HPI represents the total quality of water with respect to heavy metals. The HPI is based on weighted arithmetic quality mean method and developed in two steps. First by establishing a rating scale for each selected parameters giving weightage and second by selecting the pollution parameters on which the index is to be based. The rating system is 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 for the corresponding parameter (Horton 1965; Mohan et al. 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. Iron, manganese, lead, copper, cadmium, chromium, and zinc have been monitored for the model index application. The HPI model proposed is given by Mohan et al. (1996).

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

where Q_i is the sub-index of the ith parameter. W_i is the unit weightage of the ith parameter, and n is the number of parameters considered.

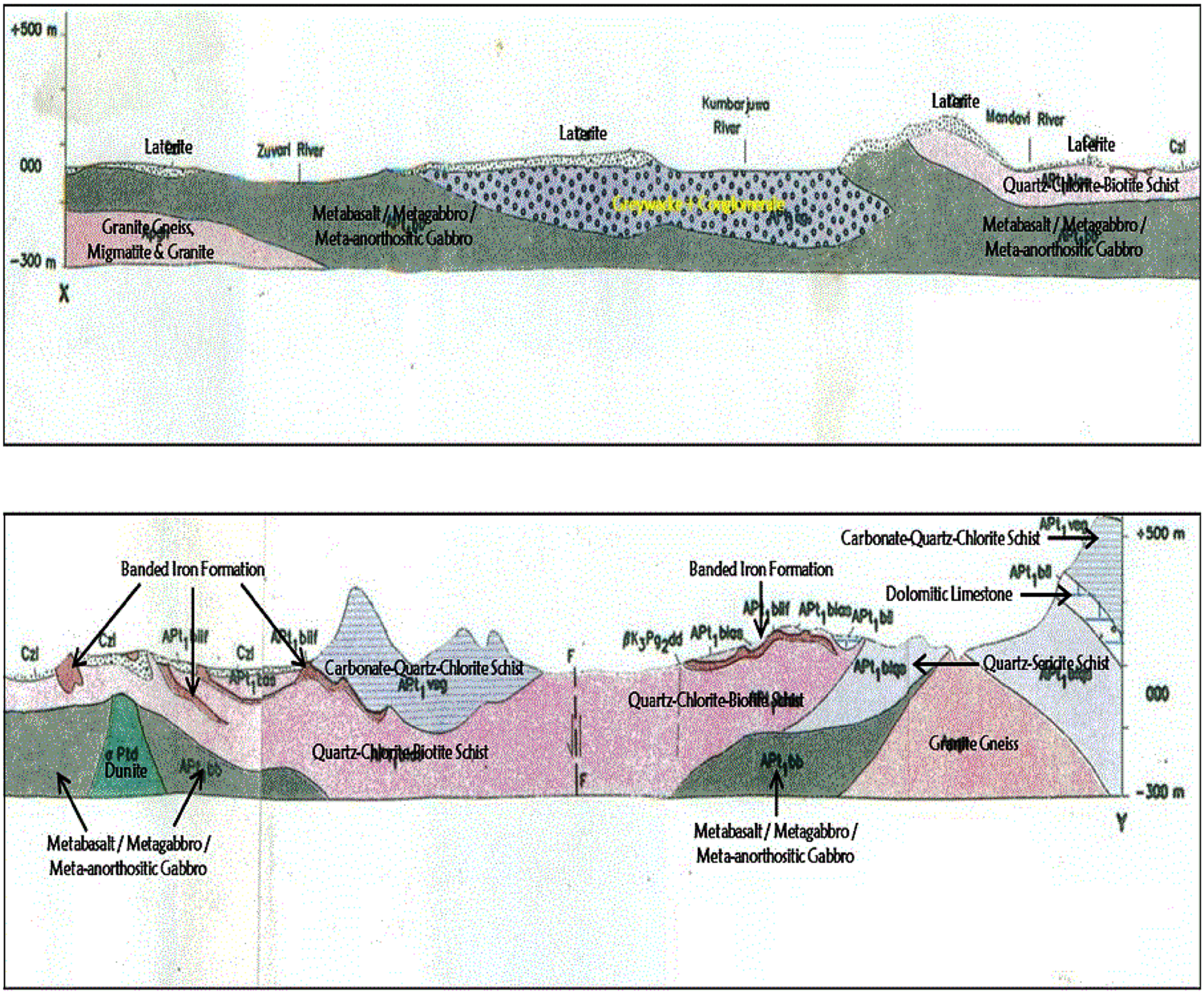

Fig. 1 Schematic section of geology of Goa

The sub index (Q_i) of the parameter is calculated by

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

where M_i is the monitored value of heavy metal of the ith parameter, I_i is the ideal value (maximum desirable value for drinking water) of the ith parameter; S_i is the standard value (highest permissive value for drinking water) of the ith parameter. The (–) indicates the numerical difference of the two values, ignoring the algebraic sign. The critical pollution index of HPI value for drinking water was given by Prasad and Bose (2001) is 100. However, a modified scale using three classes has been used in the present study after Edet and Offiong (2002). The classes have been demarcated as low, medium, and high for HPI values <15, 15–30, and >30, respectively. The proposed index is intended for the purpose of drinking water.

Results and discussion

The results were separated into two parts: (1) HPI calculation for groundwater during the monsoon and post-monsoon seasons (Table 1) and (2) statistical variation (range, mean, and standard deviation) among various heavy metals (Table 2).

The pH of the groundwater samples were found to be ranged between 4.5 and 7.1 and with a mean of 5.9 for the monsoon season, while the post-monsoon season water samples varied from 5.5 to 8.2 and with a mean 6.0, clearly indicating acidic to slightly alkaline nature of the groundwater samples in both the seasons. In the monsoon and post-monsoon seasons, about 84–87 % of the groundwater samples have a value lower than the desirable limit of 6.5, as per the Indian standard of drinking water (BIS 2003). The above values usually indicate the presence of

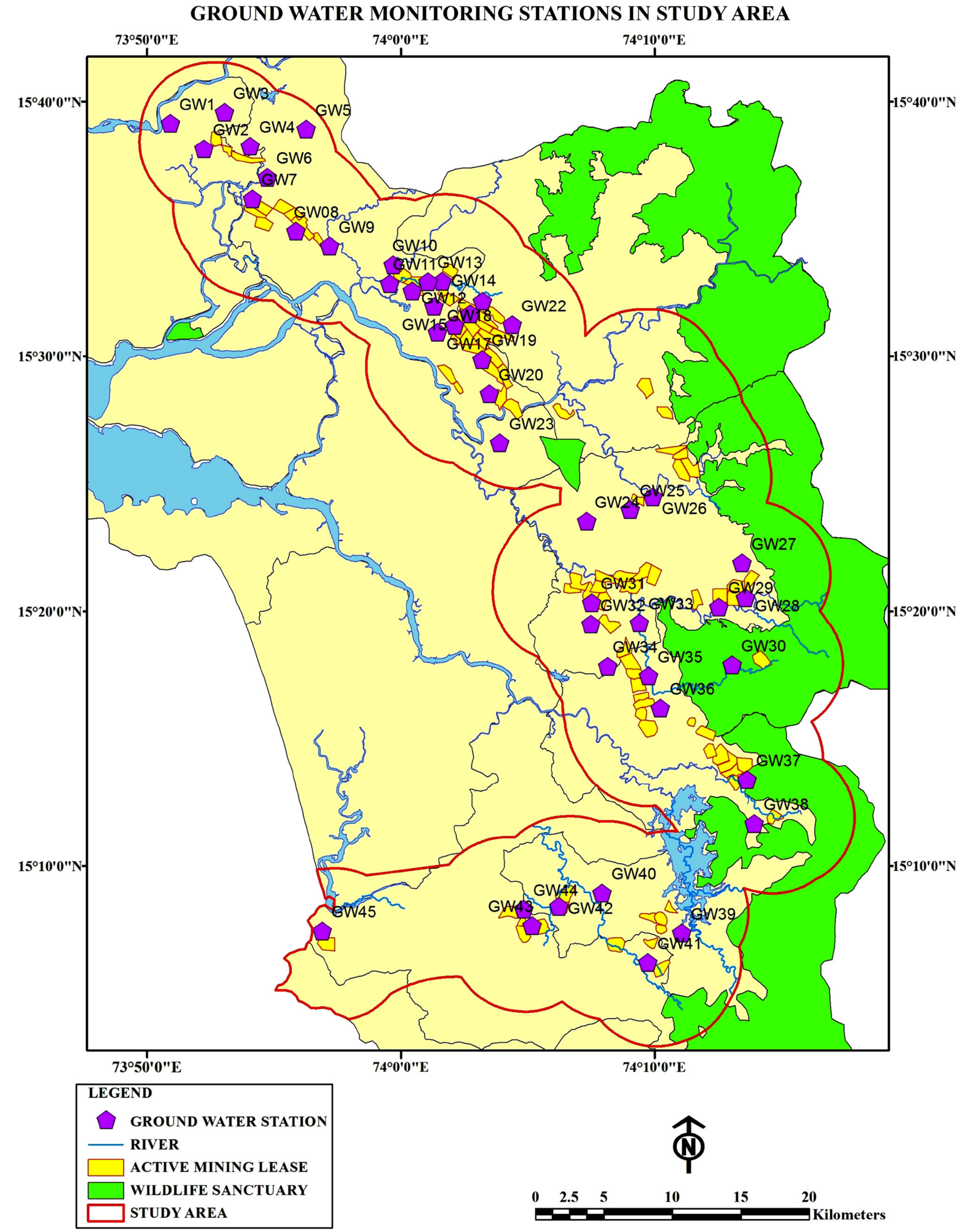

Fig. 2 Map showing water sampling points in the study area

Table 1 Heavy metal pollution calculation for ground water during the monsoon and post-monsoon seasons

Heavy metals	Mean concentration (V_i) (µg/L)		Highest permitted values for water (S_i) (µg/L)	Unit weightage (W_i)	Sub index (Q_i)		$W_i \times Q_i$	
	Monsoon	Post-monsoon			Monsoon	Post-monsoon	Monsoon	Post-monsoon
Pb	8.080	4.710	50	0.020	16.160	9.400	0.323	0.188
Cu	1.890	8.701	1500	0.001	3.318	2.848	0.002	0.002
Mn	50.550	15.710	300	0.003	24.725	42.150	0.082	0.141
Zn	14.600	22.310	15000	0.0001	49.854	49.777	0.003	0.003
Cd	0.900	1.100	10	0.100	9.000	11.000	0.900	1.100
Fe	75.314	30.651	1000	0.001	32.143	35.456	0.032	0.039
Cr	2.821	14.700	50	0.020	5.600	29.400	0.112	0.588

Table 2 Statistical variation of the groundwater parameters compared to Indian Standards (IS: 10500) for domestic purposes

Parameters	Monsoon season		Post-monsoon season		BIS (2003) IS:10500	
	Range	Mean	Range	Mean	Maximum desirable	Highest permissible
pH	4.5–7.1	5.9	5.5–8.2	6.0	6.5–8.5	8.5–9.2
TDS	452–768	480	542–658	540	500	2000
Pb	<6–20	8.08	<2–9.8	4.7	50	No relaxation
Cu	<0.2–2.1	1.9	<0.3–19.3	8.7	50	1500
Mn	<8–264	50.5	<1–29.0	15.7	100	300
Zn	<0.24–45.2	14.6	<0.30–65.2	22.3	5,000	15,000
Cd	<0.2–1.7	0.9	<0.3–2.3	1.1	3.0	10
Fe	<12–500	75	<8–65.6	30.6	300	1000
Cr	<0.5–11.8	2.8	<3.0–30	14.7	50	No relaxation

All units in µg/L, except TDS (mg/L) and pH

carbonates of calcium and magnesium in water (Begum et al. 2009). High pH of the groundwater may result in the reduction of heavy metal toxicity (Aktar et al. 2010). To our attention to total dissolved solids (TDS), there was a considerable amount of dissolved ions in all the sampling locations. It was in the range of 452–768 and 542–652 mg/L in the monsoon and post-monsoon seasons, respectively.

Seasonal variation

Concentrations of Pb, Cu, Mn, Zn, Fe, Cd, and Cr were found within limit except for Fe content during the monsoon season in two sampling locations which is above desirable limit, i.e., 300 µg/L as per Indian drinking water standard (BIS 2003). Excess Fe is an endemic water quality problem in many part of India (Singh et al. 2013c). Iron and manganese are common metallic elements found in the earth's crust (Kumar et al. 2010). The Fe concentration can be attributed due to the earth's crust and the geological formation of the area (Dang et al. 2002; Senapaty and Behera 2012). Mine tailings and other mining-related operations are a major source of contaminants, mainly of heavy metals in water (Younger 2001; Vanek et al. 2005; Vanderlinden et al. 2006; Conesa et al. 2007; Tiwari et al. 2015a; 2016a). The observed high values of Fe in the monsoon season might be associated with the phenomenon of leaching due to heavy precipitation from the overburden dumps and tailing ponds. The previous studies by Ratha et al. 1994, Yellishetty et al. 2009 and Tiwari et al. 2016a indicate that mine waste and tailings were found to contain several heavy metals, such as iron and manganese.

Heavy metal pollution index

The HPI is very useful tool in evaluating over all pollution of water bodies with respect to heavy metals (Prasad and Kumari 2008). Details of the calculations of HPI with unit weightage (Wi) and standard permissible value (Si) as obtained in the presented study are shown in Table 1. To calculate the HPI of the water, the mean concentration value of the selected metals (Pb, Cu, Mn, Zn, Fe, Cd, Fe, and Cr) has been taken into account (Prasad and Mondal 2008). The mean of heavy metal pollution index values is 1.5 and 2.1 in the monsoon and post-monsoon seasons, respectively. The critical pollution index value, above which the overall pollution level should be considered unacceptable, is 100 (Prasad and Kumari 2008). The HPI values were below the critical pollution index value of 100 in both the seasons. However, considering the classes of HPI, all of the locations fall under the low class (HPI < 15) in the monsoon season, while only one sample fall under medium class (HPI 15–30) in the post-monsoon season.

Conclusions

The present study reveals that most of the groundwater samples during the monsoon and post-monsoon seasons were found less polluted with respect to heavy metals contamination. The concentrations of Pb, Cu, Mn, Zn, Fe, Cd, and Cr were found within limit except for Fe content during the monsoon season in few locations which is above desirable limit recommended for drinking water by the Bureau of Indian Standard (BIS 2003). It is attributed to the concentration of various mines and associated industries along with the nearby wells. The HPI values of Goa mining region groundwater falls under the low-to-medium class. However, it was well below the maximum threshold value of 100. This indicates the groundwater is not critically polluted with respect to heavy metals in Goa mining region.

Acknowledgments The authors are thankful to MoEF (Ministry of Environment and Forests), Government of India for sponsoring this study. Authors are also grateful to professor D.C Panigrahi Director, Indian School of Mines, Dhanbad, India to providing research facilities. We are thankful to the Editor-in-Chief and anonymous reviewer for his valuable suggestions to improve the quality of paper.

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