

Geochemical distribution and environmental risk assessment of heavy metals in groundwater of an industrial area and its surroundings, Haridwar, India

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Abstract The aim of this study was to assess environmental risk due to heavy metals such as cobalt (Co), chromium (Cr), cadmium (Cd), iron (Fe), nickel (Ni) and zinc (Zn) in the groundwater around integrated industrial estate (IIE) Haridwar. Index of geo-accumulation (I_{geo}) values showed Cr contamination in groundwater of both the industrial areas. The quantification of contamination index showed that anthropogenic causes were source of contamination of all metals. Contamination factor showed that contamination levels in the study area ranged from low contamination to moderate contamination. Pollution linked index (PLI) values were highest in Bahadrabad old industrial area > Shivalik Nagar > commercial area > IIE Haridwar = Aneki > RNP. Ecological risk index (ERI) was highest in Bahadrabad old industrial area > Shivalik Nagar > commercial area > IIE Haridwar > RNP > Aneki rural area. Values of PLI and ERI showed moderate pollution and low ecological risk due to heavy metals in the study area. Study showed that although Rajaji National Park (RNP) is a protected area, it was not free of metal contamination.

Keywords Groundwater · Heavy metals · Industrial area · Enrichment factor · Pollution load index · Ecological risk factor

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1 Introduction

Groundwater conventionally considered a safe reserve of good quality water worldwide is now found to be contaminated with heavy metals in excess of natural background loads due to increasing urbanization and industrialization. In India, groundwater is the major source of drinking water and the industrial sector also relies heavily on groundwater for its processes. Although the industrial sector accounts for only 3 % of the annual groundwater consumption in India, its contribution to water pollution, particularly in urban areas, is considerable. In the absence of effective regulations, about 70 % of the wastewater generated by industries is discharged untreated. As per an estimate, each liter of discharged wastewater further pollutes 5–8 L of water (IDFC 2011). Besides rapidly depleting groundwater table, the country faces another major problem on the water front-groundwater contamination, a problem which has affected as many as 19 states, including Delhi (MoEF 2009). Anthropogenic activities such as industrial production, unsafe disposal of industrial wastes, agricultural wastes and domestic sewage release heavy metals into the environment (Sirajudeen et al. 2014). Water contamination from industrial areas is compounded usually due to the high concentration of industries over a small area. The percolating wastewater picks up a large number of heavy metals and reaches the aquifer system and contaminates groundwater. Health risks of heavy metals include reduced growth and development, cancer, organ damage, nervous system damage and, in extreme cases, death. Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft

tissues (Malassa et al. 2014). Heavy metals such as Cr, Cd and Pb were found to exceed permissible levels in groundwater in the study region and Uttarakhand state, India (Deepali and Joshi 2012; Gaur et al. 2011), whereas Co and Fe were found to be within permissible limits. Several researchers (Mangukiya et al. 2012; Ramesh and Vennila 2012; Ravichandran and Jayaprakash 2011; Sekhar et al. 2007; Sirajudeen et al. 2014; Suman and Srivastava 2011) have reported high levels of metals exceeding permissible limits in urban and industrial areas across the country. While the source of heavy metals can be geogenic, environmental degradation is being catalyzed due to anthropogenic activities. Groundwater contamination may occur from increased population, urbanization, industrial activities, agricultural practices, exploration and exploitation of natural resources (Akinmosin et al. 2009). Metals are the most persistent contaminants in the aquatic environment (Chai et al. 2010; Li et al. 2014). Cr and its salts are used for several industrial processes such as leather tanning, manufacture of catalysts, pigments, paints, fungicides, ceramic and glass, chrome alloy and metal production, and chrome plating. As a result, Cr has become a major factory runoff pollutant (Hu 2002) and the chromium content of surface waters reflects the extent of industrial activity in general (WHO 2003a). Ni, a hard, silvery-white metal, which combines with other metals to form alloys, is used mainly in the production of stainless steels, nonferrous alloys and super alloys. Fe, which is the second most abundant metal in the earth's crust, is a common constituent in soil and groundwater. Iron oxides are used as pigments in paints and plastics and as coagulants in water treatment. The primary anthropogenic sources of Zn in the environment are metal smelters and mining activities. The production and use of Zn in brass, bronze, die-casting metal, alloys, rubbers and paints may also lead to its release to the environment through various waste streams (USEPA 2005). Risk assessment using geostatistical methods is an important tool to assess the anthropogenic impact on the natural environment as the excess contamination over background loads can be determined. The main objectives of the study were to assess the distribution and nature of contamination of groundwater around IIE Haridwar using geostatistical methods.

1.1 Study area

Haridwar district is located in the southwestern part of Uttarakhand state and experiences a moderate subtropical to humid climate with three distinct seasons, viz. summer followed by rainy and winter seasons. The topography of the district is undulating, and the altitude ranges from

869 to 232 m. After the establishment of IIE Haridwar in year 2000, the city known worldwide for its religious significance is fast assuming the garb of an industrial destination. The study area included 18 groundwater sampling locations (L1, L2, L3, ..., L18) spread across five land use areas (Fig. 1). IIE Haridwar (L1, L2, L3) has more than 585 industrial units spread over 8.23 km². The industrial area has several pharmaceutical, plastics and allied, electrical and electronics, metal and fabrication, food and agro, textiles, paper and packaging and chemical industries. Aneki (L4, L5, L6) is a rural/agricultural land use area characterized by unplanned housing with no piped water supply and sewerage facilities. Shivalik Nagar (L7, L8, L9) which has become the most favored residential areas of Haridwar after establishment of IIE Haridwar is a low-density residential colony. It has to its west the Bahadradab old industrial area (L10, L11, L12) which houses electroplating, metal and fabrication, packaging and electrical and electronics units. Rajaji National Park (RNP; L13, L14, L15) is a protected area created in 1983 by the amalgamation of three wildlife sanctuaries and is spread over 820 km² and three districts of Uttarakhand. RNP is densely forested, is home to 23 species of mammals, 315 species of birds and the Asian elephant and has IIE Haridwar on its northern periphery. The railway station arterial road (L16, L17, L18) is the commercial hub of the city and houses the railroad station and state-level bus terminus.

2 Materials and methods

2.1 Sampling and analytical methodology

Heavy metals (Cr, Co, Cd, Ni, Fe and Zn) were sampled monthly at 18 locations for a year from January 2012 to December 2012. Three locations were sampled from each land use adding to a total of 216 (3 samples × 6 locations × 12 months) samples. Sampling was done by grab sampling method in the early morning hours. Groundwater was sampled in 1-L plastic containers after flushing out the initial discharge of water from hand pumps/tube wells for a few minutes. 250 mL of sample was oven-dried at 105 °C overnight until the sample evaporated. 25 mL of 5 % nitric acid solution was added to the beaker after which care was taken to dissolve the evaporated residues from the walls of the container also into the nitric acid. The sample was then filtered through a Whatman filter paper into a 25-mL volumetric flask and made up to volume by adding 5 % HNO₃ solution. Sample blank was also prepared in the same manner as the sample using double-distilled water. Heavy metals were analyzed by aspirating samples in atomic absorption

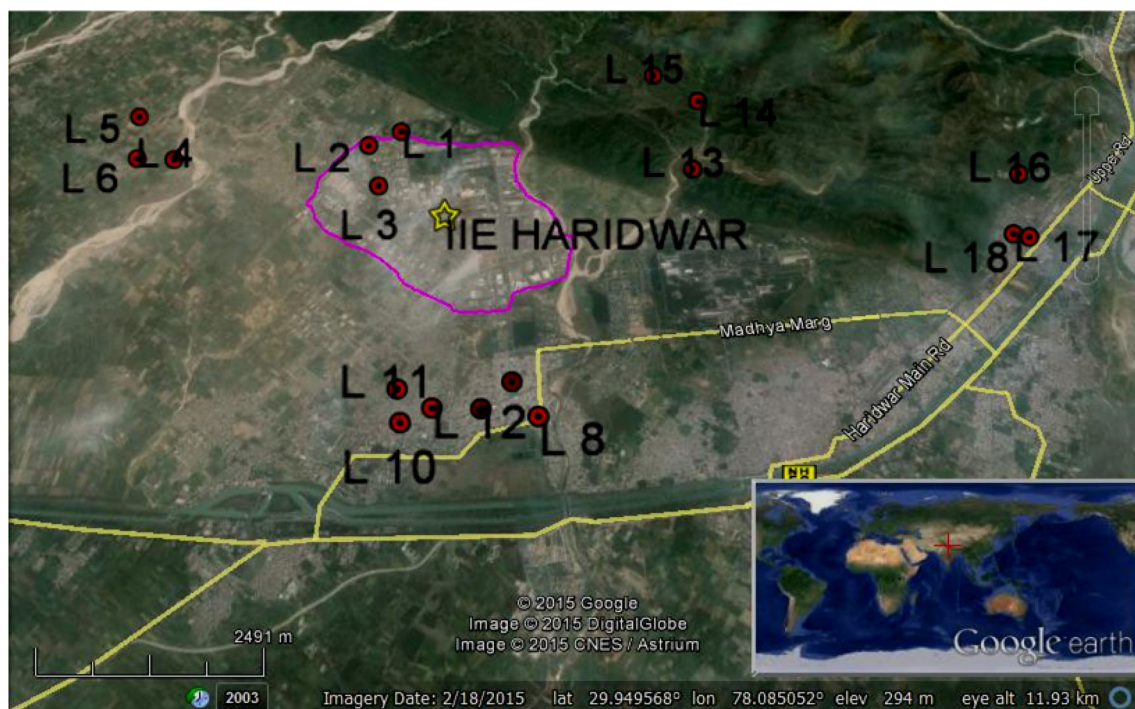


Fig. 1 Location map of study area showing groundwater monitoring locations

spectrophotometer (AAS) at the respective wavelengths for the metals quality control standards were used for the preparation of calibration curves. These curves were used to evaluate data from each set of samples. The procedural blanks and samples were analyzed three times, and the average of these three values was used for data interpretation. The data set was first examined for the presence of non-detect data. As the total number of non-detect data was less than 15 % of the total data, non-detect data were substituted with half of the limit of detection (LOD) of the respective heavy metal. Outliers were substituted with the nearest highest value. All statistical analysis was performed using SPSS 21 (SPSS, version 21) and Microsoft Excel. Surfer 11 was used for mapping and graphing data. Descriptive statistics and Kriging interpolation method were used to assess the distribution of metals in the study area. Annual average values have been used in the analysis.

2.2 Environmental risk assessment methodology

Environmental risk assessment was based on the use of geostatistical methods or indices to ascertain the extent and source of contamination (anthropogenic or geogenic). Environmental indices such as contamination factor (CF), pollution load index (PLI), enrichment factor (EF), index

of geo-accumulation (I_{geo}) and ecological risk index (ERI) were applied in the study. The very basis of environmental risk assessment is to ascertain the extent by which a contaminant exceeds its presence in the natural background. However, as industrial and urban areas are characterized by increased level of contaminants and local variability, consequently it is difficult to identify background groundwater sources with similar hydrogeological setting and water chemistry. Thambavani and Uma Mageswari (2013) have considered the geometric mean as background value for their study, while Monakhov et al. (2015) recommend the use of median. In this study, both geometric mean (BGM) and median (BM) of sampled data were used as background values so that a comparison of variation in results from use of the means could be done. The indices used in the study have been mentioned briefly. Contamination factor (CF) and degree of contamination (CD) suggested by Hakanson (1980) and given by $CF = C_n/B_n$, where C_n is the concentration of metals in the target area and B_n is the metal concentration in the reference area. The following criteria are used to describe the values of the contamination factor: $CF < 1$, low contamination; $1 \leq CF < 3$, moderate contamination; $3 \leq CF < 6$, considerable contamination; and $CF \geq 6$, very high contamination. Contamination degree (CD) is the numeric sum of all contamination factors and gives a measure of the degree of overall

contamination in a particular core or sampling site. Based on Hakanson’s (1980) classification, contamination degree (CD) was grouped into four classes: $CD < 8 =$ low contamination; $8 \leq CD < 16 =$ moderate contamination; $16 \leq CF < 32 =$ considerable contamination; and $CD > 32 =$ very high degree of contamination indicating serious anthropogenic pollution. *Pollution load index* (PLI) provides comprehensive information about the metal toxicity in the respective samples (Tomlinson et al. 1980; Yang et al. 2011) and was determined by formula:

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n},$$

where PLI represents the pollution load index, CF is the contamination factor and n is the number of elements. The pollution load index can be classified as: no pollution ($PLI < 1$), moderate pollution ($1 < PLI < 2$), heavy pollution ($2 < PLI < 3$) and extremely heavy pollution ($3 < PLI$), *Quantification of contamination* represents the lithogenic metal (Asaah et al. 2006) and was calculated by

$$QoC (\%) = ((C_n - B_n)/C_n) \times 100,$$

where QoC is the index of contamination, C_n is the concentration of metal in the sample and B_n is the concentration of metal in the background, and *enrichment factor* (EF) estimates by how much the sediment is impacted (naturally and anthropogenically) with heavy metal concentrations above uncontaminated background levels. Fe was used as the normalized metal as it is an acceptable normalization element to be used in the calculation of enrichment factor (Deely and Fergusson 1994). Fe usually has a relatively high natural concentration and is therefore not expected to be substantially enriched from anthropogenic sources in estuarine sediments. EF is mathematically expressed as:

$$EF = [HM(s)/Fe(s)]/[HM(b)/Fe(b)]$$

where HM(s) stands for concentration of metal in sample, Fe(s) stands for concentration of Fe in sample, HM(b) stands for concentration of the heavy metal in the reference background and Fe(b) is the concentration of Fe in the

Fig. 2 Distribution of metals in the study area and comparison with background levels

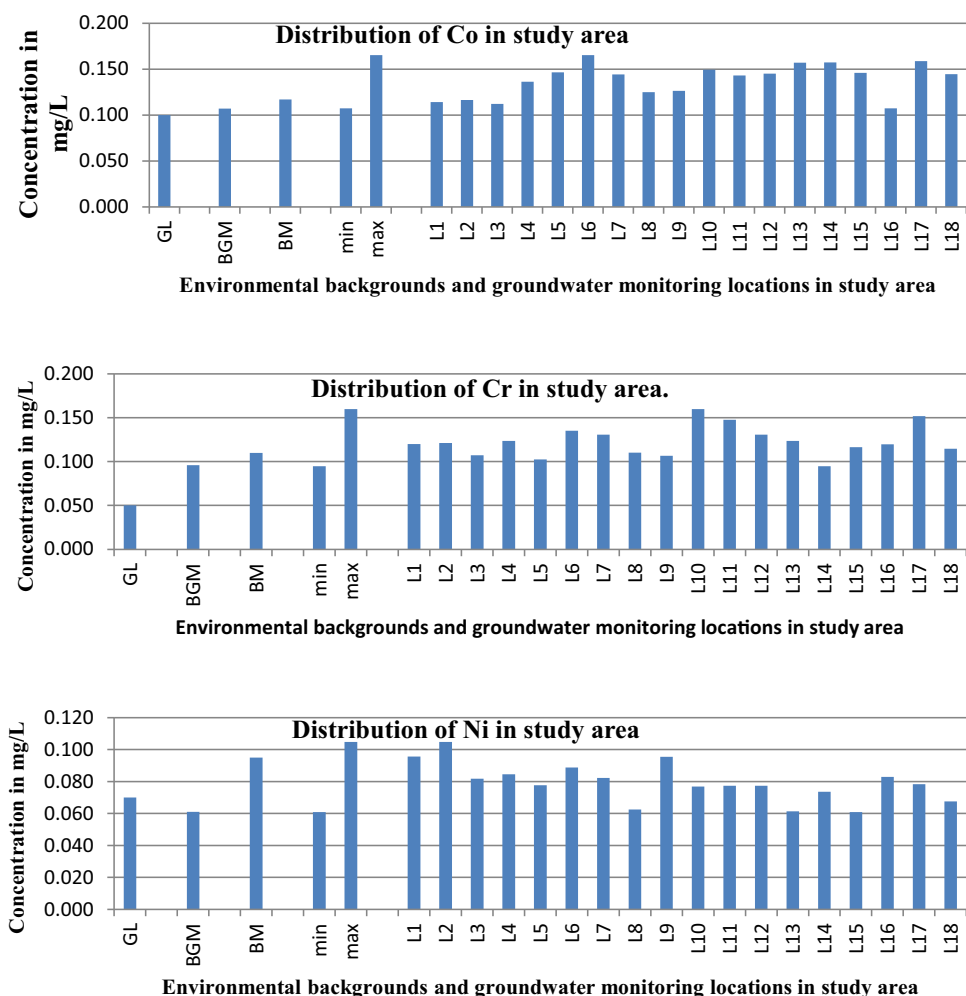
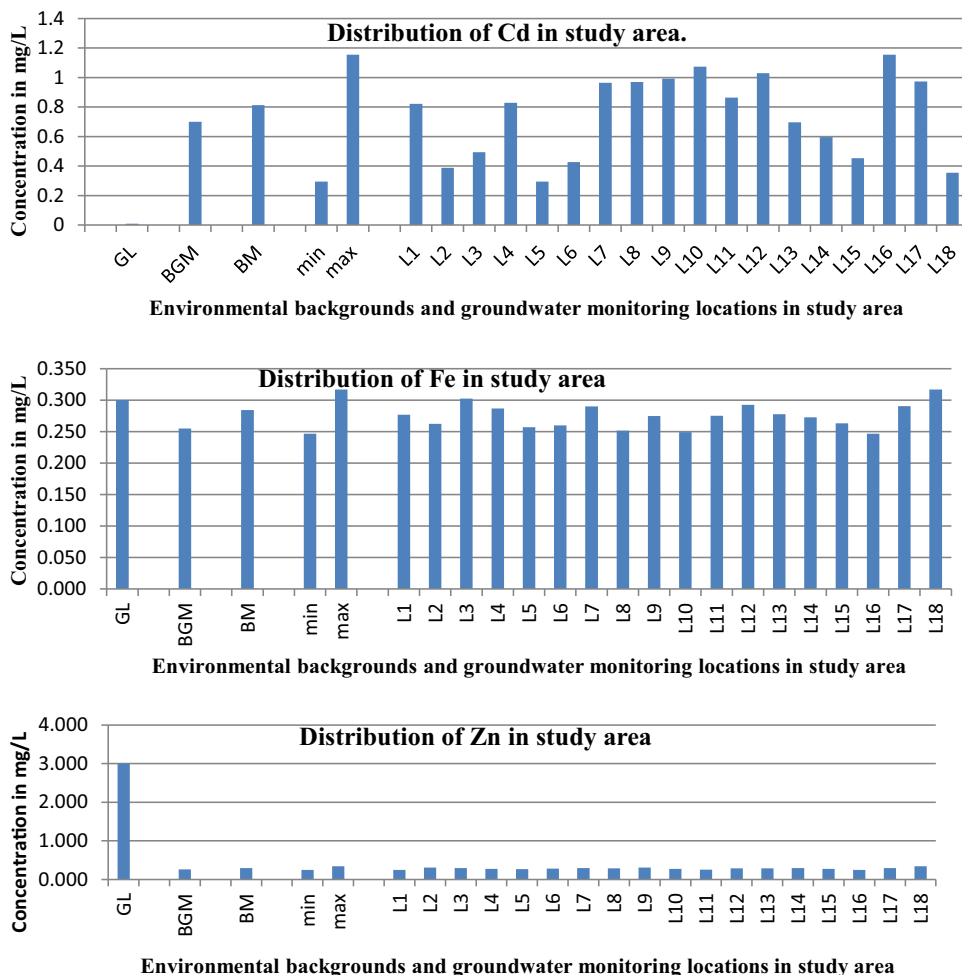


Fig. 2 continued



earth’s crust or reference background. On the basis of enrichment factor, six degrees are recognized (Sutherland 2000). If the enrichment factor (EF) is ≤ 1 , it is considered as background rank, 1–2 as minimal enrichment, 2–5 as moderate enrichment, 5–20 as significant enrichment and 20–40 as a very high enrichment, while the EF above 40 was considered as extremely high enrichment, and *geo-accumulation index* (I_{geo}) to quantify the degree of anthropogenic or geogenic accumulated pollutant loads is given by:

$$I_{geo} = \log_2[HM(s)/(1.5 \times HM(b))],$$

where HM(s) is the measured concentration of metal in sample, HM(b) is the background value for the metal and the factor 1.5 is used because of possible variations of the background data due to lithological variations. Muller (1969) classified I_{geo} as: uncontaminated ($I_{geo} \leq 0$); uncontaminated to moderately contaminated ($0 < I_{geo} \leq 1$); moderately contaminated ($1 < I_{geo} \leq 2$); moderately to heavily contaminated ($2 < I_{geo} \leq 3$); heavily contaminated ($3 < I_{geo} \leq 4$); heavily to extremely contaminated

($4 < I_{geo} \leq 5$); and extremely contaminated ($I_{geo} \geq 5$). ERI evaluates the ecological risk degrees for toxins and heavy metals in soils (Hakanson 1980) which could be toxic for biological species (Yisa et al. 2012) determined by $Er = Tr \times CF$, where Er is the potential ecological risk factor/index, Tr represents the toxic response factor and CF represents the contamination factor. The potential ecological risk (Er) and its grading are summarized as follows: If Er is < 40 , it is ranked as low risk for the environment, if $40 \leq Er < 80$, it may cause moderate risk, if the values are found between $80 \leq Er < 160$, it may cause considerable risk, and if $160 \leq Er < 320$, it may cause high risk, while $Er \geq 320$ is ranked as a very high risk for the environment. The toxic response values (Tr) for some of the toxic and trace elements suggested by Hakanson (1980) are Cr = 2, Cd = 30, Ni = 5 and Zn = 1. The sum of the individual potential risks (Er) is the potential risk of the water body, $ERI = \sum Er = \sum (Tr \times CF)$. In keeping with Hakanson (1980), RI value < 50 represents low ecological risk, while $RI > 600$ is an indicator of very high ecological risk of the water body.

3 Results and discussion

3.1 Elemental concentration and spatial distribution in study area

Figure 2 shows the location wise distribution of metals in the study area compared with respective background levels (BGM and BM), standard guidelines for drinking water quality (GL) and range (min–max) in the study area. Cr, Cd and Co concentrations were found to exceed permissible limits for drinking water quality at all locations. Fe concentrations were within permissible limits at 17 (95 %) out of 18 locations, while Zn was found to be within limits at all locations. Ni concentrations exceeded permissible limits at 15 (83 %) out of 18 locations. The incidence of Cr was highest at L10, Bahadrabad old industrial area, and lowest at L14, RNP. Co levels were maximum at L6 in rural area and minimum at L16 in commercial area. Ni levels were maximum at L1 in IIE Haridwar and minimum at L13 and L15 in RNP. Fe and Zn levels were highest and lowest at L18 and L16 in commercial area. The maximum concentration of Cd was at L16 in commercial area and minimum at L5 in rural area.

3.2 Contamination levels in the study area

Contamination factor (CF) for metals in the study area is given in Table 1. Results showed that contamination ranged between low contamination and moderate contamination at all the locations. Contamination level due to Cr was low at L14 in the RNP and moderate contamination at all other locations. Contamination due to Co and Ni was moderate at all locations, while contamination levels due to Fe were moderate at 15 (83 %) out of 18 locations and low at L8, L10 and L16. PLI at all locations showed moderate pollution indicating anthropogenic sources to be source of pollution (Sekabira et al. 2010). The results of PLI varied for both background scenarios. PLI showed moderate contamination for 17 (95 %) out of 18 locations and 7 (39 %) out of 18 locations with BGM and BM as background, respectively. Figure 3 depicts the spatial variation of pollution in the study area based on the PLI of metals in groundwater.

The I_{geo} values for metals are listed in Table 2. The values of I_{geo} indicated uncontaminated levels for metals Fe and Zn at all locations. I_{geo} for Cr showed that 15 (83 %) out of 18 locations were not polluted. I_{geo} values show low contamination due to Cr at L10 and L11 (Ba-

Table 1 Contamination factor (CF) and pollution load index (PLI) of metals in groundwater of study area

Location	Geometric mean (BGM) as background							Median (BM) as background						
	Contamination factor (CF)						PLI	Contamination factor (CF)						PLI
	Cr	Co	Fe	Ni	Zn	Cd		Cr	Co	Fe	Ni	Zn	Cd	
L1	1.25	1.07	1.09	1.57	0.96	1.22	1.22	1.09	0.97	0.97	1.01	0.84	1.03	0.98
L2	1.26	1.09	1.03	1.72	1.19	0.58	1.11	1.10	0.99	0.92	1.10	1.04	0.49	0.89
L3	1.12	1.05	1.19	1.34	1.14	0.74	1.09	0.98	0.96	1.06	0.86	1.00	0.62	0.88
L4	1.29	1.27	1.12	1.39	1.06	1.24	1.27	1.12	1.16	1.01	0.89	0.93	1.03	1.02
L5	1.07	1.37	1.01	1.27	1.02	0.44	0.97	0.93	1.25	0.90	0.82	0.90	0.37	0.78
L6	1.41	1.54	1.02	1.45	1.09	0.64	1.17	1.23	1.41	0.91	0.94	0.96	0.53	0.95
L7	1.36	1.35	1.14	1.35	1.14	1.44	1.36	1.19	1.23	1.02	0.87	1.00	1.21	1.09
L8	1.15	1.17	0.99	1.03	1.10	1.45	1.17	1.00	1.06	0.89	0.66	0.96	1.21	0.94
L9	1.11	1.18	1.08	1.56	1.18	1.48	1.31	0.97	1.08	0.97	1.01	1.04	1.24	1.06
L10	1.66	1.40	0.98	1.26	1.06	1.60	1.37	1.45	1.27	0.88	0.81	0.93	1.34	1.10
L11	1.54	1.34	1.08	1.27	0.97	1.29	1.29	1.34	1.22	0.97	0.81	0.85	1.08	1.04
L12	1.36	1.36	1.15	1.27	1.12	1.54	1.36	1.19	1.24	1.03	0.82	0.98	1.29	1.09
L13	1.29	1.47	1.09	1.01	1.10	1.04	1.19	1.12	1.34	0.98	0.65	0.96	0.87	0.96
L14	0.99	1.47	1.07	1.21	1.13	0.89	1.13	0.86	1.34	0.96	0.78	0.99	0.74	0.91
L15	1.21	1.36	1.03	1.00	1.06	0.68	1.04	1.06	1.24	0.93	0.64	0.93	0.57	0.84
L16	1.25	1.00	0.97	1.36	0.95	1.72	1.22	1.09	0.91	0.87	0.87	0.83	1.44	0.98
L17	1.58	1.48	1.14	1.28	1.14	1.45	1.41	1.38	1.35	1.02	0.83	1.00	1.22	1.14
L18	1.20	1.35	1.24	1.11	1.30	0.53	1.09	1.05	1.23	1.12	0.71	1.14	0.44	0.88

CF < 1, low contamination; 1 ≤ CF < 3, moderate contamination; 3 ≤ CF < 6, considerable contamination; and CF ≥ 6, very high contamination

PLI < 1, no pollution; 1 < PLI < 2, moderate pollution; 2 < PLI < 3, heavy pollution; 3 < PLI, extremely heavy pollution

Fig. 3 Spatial variation of pollution in the study area based on PLI of heavy metals

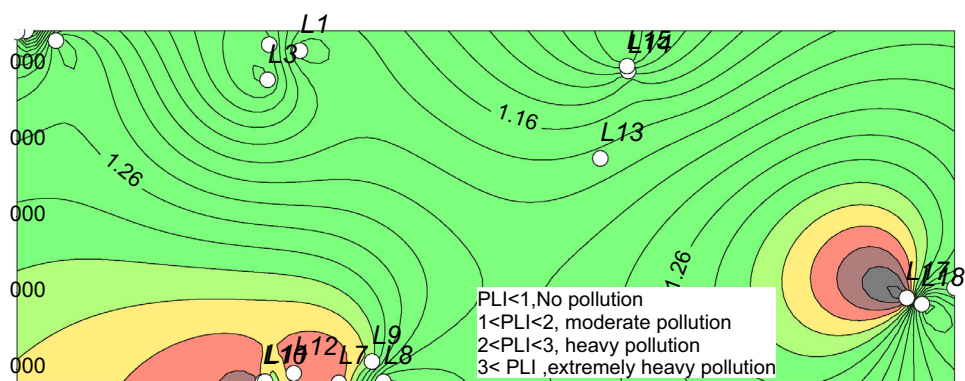


Table 2 Index of geo-contamination (I_{geo}) of metals in groundwater of study area

Location	Geometric mean (BGM) as background						Median (BM) as background					
	Cr	Co	Fe	Ni	Zn	Cd	Cr	Co	Fe	Ni	Zn	Cd
L1	-0.26	-0.49	-0.47	0.06	-0.64	-0.29	-0.46	-0.62	-0.62	-0.57	-0.83	-0.55
L2	-0.25	-0.46	-0.54	0.19	-0.34	-1.37	-0.44	-0.60	-0.70	-0.44	-0.53	-1.63
L3	-0.43	-0.52	-0.34	-0.16	-0.40	-1.03	-0.62	-0.65	-0.50	-0.80	-0.59	-1.28
L4	-0.22	-0.24	-0.42	-0.11	-0.50	-0.28	-0.42	-0.37	-0.57	-0.75	-0.69	-0.54
L5	-0.49	-0.13	-0.57	-0.24	-0.55	-1.77	-0.68	-0.27	-0.73	-0.87	-0.74	-2.03
L6	-0.09	0.04	-0.56	-0.05	-0.46	-1.24	-0.28	-0.09	-0.71	-0.68	-0.65	-1.49
L7	-0.14	-0.15	-0.40	-0.15	-0.40	-0.06	-0.34	-0.29	-0.56	-0.79	-0.59	-0.32
L8	-0.38	-0.36	-0.60	-0.55	-0.45	-0.05	-0.58	-0.49	-0.76	-1.18	-0.64	-0.31
L9	-0.43	-0.35	-0.48	0.06	-0.34	-0.02	-0.63	-0.48	-0.63	-0.58	-0.53	-0.27
L10	0.15	-0.10	-0.62	-0.25	-0.50	0.09	-0.04	-0.24	-0.78	-0.89	-0.69	-0.16
L11	0.04	-0.17	-0.48	-0.24	-0.63	-0.22	-0.16	-0.30	-0.63	-0.88	-0.82	-0.47
L12	-0.14	-0.15	-0.39	-0.24	-0.43	0.03	-0.34	-0.28	-0.54	-0.88	-0.62	-0.22
L13	-0.22	-0.03	-0.46	-0.58	-0.45	-0.53	-0.42	-0.17	-0.62	-1.21	-0.64	-0.79
L14	-0.61	-0.03	-0.49	-0.31	-0.41	-0.75	-0.80	-0.16	-0.65	-0.95	-0.60	-1.01
L15	-0.31	-0.14	-0.54	-0.59	-0.50	-1.15	-0.50	-0.27	-0.70	-1.22	-0.69	-1.40
L16	-0.27	-0.58	-0.63	-0.14	-0.66	0.20	-0.46	-0.71	-0.79	-0.78	-0.85	-0.06
L17	0.07	-0.02	-0.40	-0.23	-0.39	-0.05	-0.12	-0.15	-0.55	-0.86	-0.58	-0.30
L18	-0.33	-0.15	-0.27	-0.44	-0.21	-1.50	-0.52	-0.28	-0.43	-1.07	-0.40	-1.76

$I_{geo} \leq 0$, uncontaminated; $0 < I_{geo} \leq 1$, uncontaminated to moderately contaminated; $1 < I_{geo} \leq 2$, moderately contaminated; $2 < I_{geo} \leq 3$, moderately to heavily contaminated; $3 < I_{geo} \leq 4$, heavily contaminated; $4 < I_{geo} \leq 5$, heavily to extremely contaminated; $I_{geo} \geq 5$, extremely contaminated

hadhrabad old industrial area) and L17 (commercial land use). I_{geo} results showed that 15 (83 %) out of 18 locations were free from Ni contamination. I_{geo} values for Cd showed that 17 (95 %) out of 18 locations did not have Cd contamination. I_{geo} values vary considerably for the two background scenarios. When BM was used as background, I_{geo} values showed uncontaminated levels at all locations in the study area. Figure 3 shows the spatial extent of pollution in the study area based on PLI.

3.3 Identification of source of contamination

The results of enrichment factor (EF) and the quantification of contamination index (QoC) are presented in Tables 3

and 4, respectively. EF analysis showed minimal enrichment due to Cr at 15 (83 %) out of 18 locations. Cr enrichment was maximum in the Bahadrabad old industrial area followed by commercial area and IIE Haridwar respectively. Co enrichment was found at 16 (89 %) out of 18 locations, maximum enrichment being at L6 in the rural area and minimum being at L3 in IIE Haridwar. Ni was found to be minimally enriched at 15 (83 %) out of 18 locations with maximum value at L2 in IIE Haridwar and minimum value at L18 in the commercial area. Eleven (61 %) out of 18 locations showed minimal enrichment for Zn. Zn enrichment was maximum at L2, IIE Haridwar followed by L9, Shivalik Nagar. Ten (56 %) out of 18 locations showed minimal enrichment due to Cd. Cd

Table 3 Enrichment factor (EF) for metals in groundwater of study area

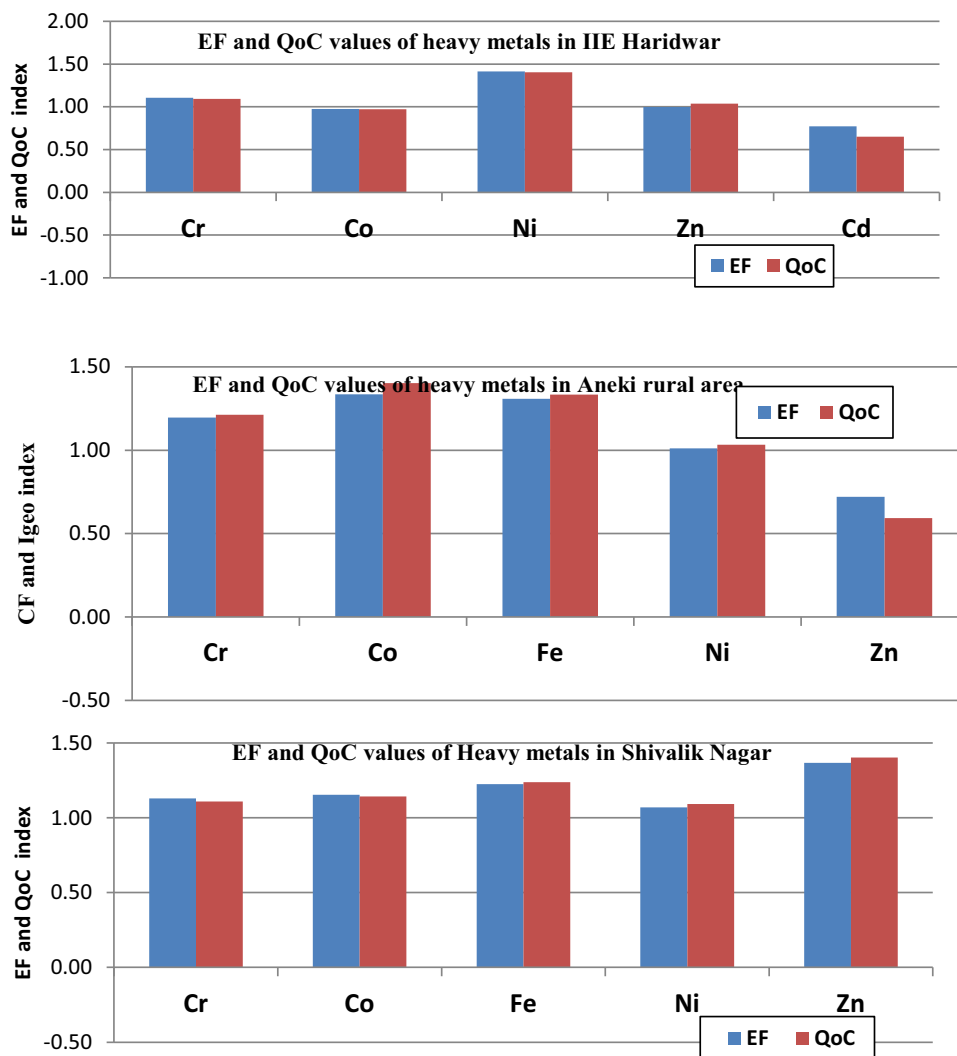
Location	Geometric mean (BGM) as background					Median (BM) as background				
	Cr	Co	Ni	Zn	Cd	Cr	Co	Ni	Zn	Cd
L1	1.15	0.98	1.44	0.88	1.13	1.12	1.00	1.04	0.86	1.05
L2	1.23	1.06	1.67	1.15	0.56	1.20	1.07	1.20	1.13	0.53
L3	0.94	0.88	1.13	0.96	0.62	0.92	0.90	0.81	0.94	0.58
L4	1.14	1.13	1.23	0.95	1.10	1.12	1.15	0.88	0.92	1.03
L5	1.06	1.36	1.26	1.02	0.44	1.03	1.38	0.91	0.99	0.41
L6	1.38	1.52	1.43	1.07	0.62	1.35	1.54	1.02	1.05	0.58
L7	1.20	1.18	1.19	1.00	1.26	1.16	1.20	0.85	0.98	1.18
L8	1.16	1.18	1.04	1.11	1.47	1.13	1.20	0.74	1.09	1.37
L9	1.03	1.10	1.45	1.10	1.37	1.01	1.11	1.04	1.07	1.28
L10	1.70	1.43	1.29	1.09	1.64	1.66	1.45	0.93	1.06	1.53
L11	1.43	1.24	1.17	0.90	1.20	1.39	1.26	0.84	0.88	1.12
L12	1.19	1.18	1.10	0.97	1.34	1.16	1.20	0.79	0.95	1.25
L13	1.18	1.35	0.92	1.01	0.95	1.15	1.37	0.66	0.99	0.89
L14	0.92	1.37	1.13	1.06	0.83	0.90	1.40	0.81	1.03	0.78
L15	1.17	1.32	0.97	1.03	0.66	1.14	1.34	0.69	1.01	0.61
L16	1.29	1.04	1.41	0.98	1.78	1.26	1.05	1.01	0.96	1.66
L17	1.39	1.30	1.13	1.00	1.28	1.35	1.32	0.81	0.98	1.19
L18	0.96	1.09	0.89	1.05	0.43	0.94	1.10	0.64	1.02	0.40

EF \leq 1, background rank; 1 < EF < 2, minimal enrichment; 2 < EF < 5, moderate enrichment; 5 < EF < 20, significant enrichment; 20 < EF < 40, very high enrichment; EF > 40, extremely high enrichment

Table 4 QOC (%) values of metals in groundwater of study area

Location	Geometric mean (BGM) as background						Median (BM) as background					
	Cr	Co	Fe	Ni	Zn	Cd	Cr	Co	Fe	Ni	Zn	Cd
L1	20.00	6.23	7.83	36.16	-4.22	18.34	8.50	-2.80	-2.72	0.78	-18.85	2.50
L2	20.78	8.02	2.75	41.75	15.62	-72.64	9.39	-0.83	-8.39	9.48	3.77	-106.14
L3	10.34	4.66	15.68	25.41	11.97	-35.93	-2.55	-4.52	6.03	-15.93	-0.39	-62.30
L4	22.21	21.40	10.98	27.84	5.93	19.05	11.03	13.83	0.79	-12.15	-7.28	3.34
L5	6.32	26.89	0.75	21.50	2.29	-127.25	-7.15	19.85	-10.61	-21.99	-11.43	-171.34
L6	29.00	35.27	1.85	31.22	8.42	-57.25	18.80	29.03	-9.38	-6.90	-4.43	-87.76
L7	26.45	25.78	12.09	25.84	11.99	30.50	15.87	18.64	2.02	-15.25	-0.37	17.02
L8	12.94	14.30	-1.28	2.49	8.93	30.89	0.43	6.05	-12.88	-51.54	-3.86	17.48
L9	10.02	15.25	7.15	36.05	15.46	32.47	-2.91	7.10	-3.48	0.62	3.59	19.37
L10	39.87	28.39	-2.38	20.69	5.91	37.58	31.23	21.49	-14.10	-23.25	-7.30	25.47
L11	34.96	25.22	7.24	21.04	-3.08	22.47	25.61	18.02	-3.38	-22.71	-17.55	7.43
L12	26.44	26.25	12.79	21.07	10.38	34.93	15.87	19.15	2.80	-22.67	-2.21	22.30
L13	22.19	31.82	8.12	0.61	9.00	3.70	11.00	25.25	-2.41	-54.46	-3.78	-14.98
L14	-1.40	31.92	6.42	17.07	11.37	-12.46	-15.98	25.37	-4.30	-28.88	-1.07	-34.28
L15	17.41	26.65	3.05	-0.18	5.75	-47.74	5.54	19.59	-8.05	-55.69	-7.48	-76.41
L16	19.82	0.26	-3.46	26.39	-5.56	41.97	8.30	-9.35	-15.31	-14.40	-20.38	30.71
L17	36.70	32.52	12.17	22.05	12.40	31.16	27.60	26.02	2.11	-21.14	0.10	17.80
L18	16.33	25.95	19.53	9.70	23.10	-88.82	4.31	18.82	10.31	-40.34	12.31	-125.46

Fig. 4 EF and QoC of heavy metals by land use in the study area



contamination was maximum at L16 and minimum at L18 in commercial area. EF results were comparable for both background scenarios.

QoC values for Co were positive at all locations, indicating that Co contamination was anthropogenic in nature at all locations. For Cr and Ni, QoC values were positive at 17 (95 %) out of 18 locations. QoC values were positive at 15 (83 %) out of 18 locations for Zn and at 11 (61 %) out of 18 locations for Cd. Results indicate that anthropogenic activities are the causes of contamination at majority locations in the study area. QoC values varied for all metals in both background scenarios. Table 4 shows QoC values in the study area for both background scenarios, and Fig. 4 shows the average EF and QoC for different land uses in the study area.

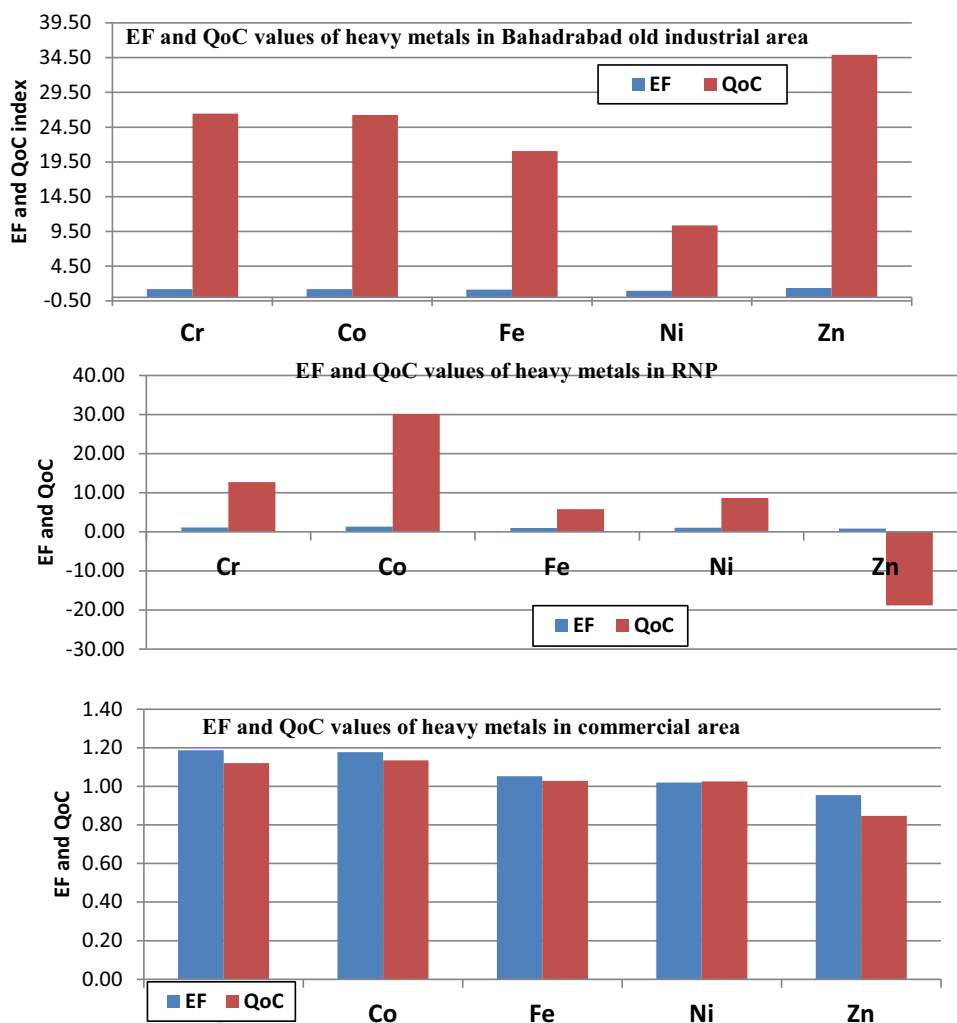
3.4 Ecological risk index (ERI)

Results show that Er values were maximum for Cd followed by Ni and Cr. Location L16 in commercial area had

highest ERI, while L5 in rural area had lowest ERI. Er, and ERI due to all metals at all locations was low when BGM was used as background. When BM was considered as the background, the risk index due to the cumulative impact of metals exceeded 50 at locations L9 and L16. However, maximum–minimum ERI for locations was same for both background scenarios. Table 5 depicts the ecological risk (Er) due to individual metals and ERI by location, while Fig. 5 shows spatial variation of ecological risk due to heavy metals in the study area.

Average ERI was highest in Bahadrabad old industrial area > Shivalik Nagar > commercial area > IIE Haridwar > RNP > Aneki rural area. PLI values were also highest in Bahadrabad old industrial area > Shivalik Nagar > commercial area > IIE Haridwar = Aneki > RNP. Values of PLI and ERI showed moderate pollution and low ecological risk due to heavy metals in the study area. In Bahadrabad old industrial area, I_{geo} values indicated Cr and Cd contamination, while EF values show maximum enrichment for Cr > Cd > Co > Ni > Zn in the industrial area. Cr and its

Fig. 4 continued



compound are primarily used in the manufacture of steel and other alloys, chrome plating and pigment production and have been reported by many researchers in industrial areas (Qu et al. 2012; Zarei et al. 2014). Cd enrichment at all locations in Bahadrabad old industrial area was supported by high positive QoC values. Cadmium metal is used as an anticorrosive, electroplated on steel; cadmium sulfide and selenide are commonly used as pigments in plastics, in batteries and in various electronic components (Gupta et al. 2014). The industrial area is characterized by activities such as electroplating, dyeing and pigment manufacturing. Additionally, industrial and sewage runoff coupled with indiscriminate dumping of solid waste in the area was significant in Bahadrabad old industrial area as compared to other land use areas. Highest ERI and PLI values in Bahadrabad old industrial area indicated that its groundwater was most polluted in the study area. I_{geo} values showed low contamination levels due to Ni at IIE, Haridwar. EF analysis and CF showed minimal contamination due to all metals in the industrial area. QoC values

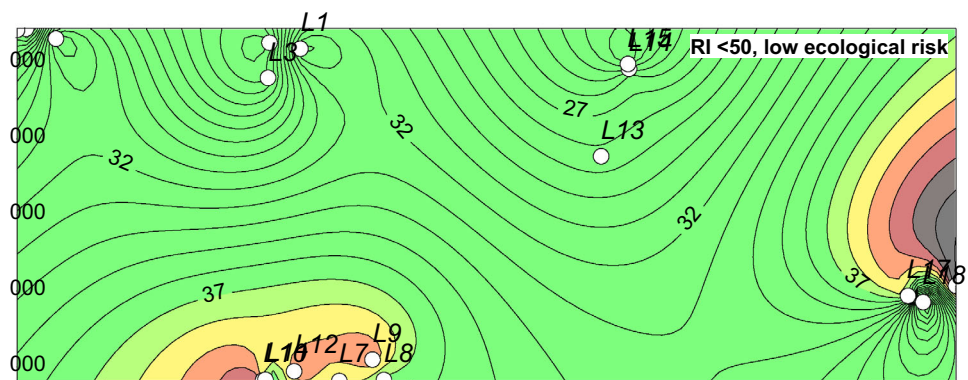
were positive for Cr, Co and Ni indicating anthropogenic sources of pollution. IIE Haridwar has several industries involved in nickel plating, electroplating, welding, color ceramics and battery making which were likely to cause Ni contamination. Negative QoC and I_{geo} values for Cd contradicted positive values of CF and EF at L1 and L2 in the industrial area. Similarly, I_{geo} for Co showed contamination at only one location in the study area, while EF analysis showed that 16 (89 %) out of 18 locations had Co enrichment over background levels for Co and CF also showed moderate contamination due to Co at all locations. Negative I_{geo} values and positive CF values suggest that the metal was imported by human activities, but did not reach the boundary of pollution due to dilution by coarse sediments (Oliveira et al. 2011) or may be due to relatively low levels of contamination of some metals in some cores and the background variability factor (1.5) in the I_{geo} equation (Abraham and Parker 2008). At Shivalik Nagar, I_{geo} values showed contamination levels due to Ni. The high level of nickel may be due to mixing of variety

Table 5 Ecological risk index (ERI) of groundwater in study area

Location	Geometric mean (BGM) as background				ERI	Median (BM) as background				ERI
	Cr	Cd	Ni	Zn		Cr	Cd	Ni	Zn	
L1	1.25	24.62	7.83	0.96	34.66	1.09	30.77	5.04	0.84	38.75
L2	1.26	11.64	8.58	1.19	22.67	1.10	14.55	5.52	1.04	24.80
L3	1.12	14.79	6.70	1.14	23.74	0.98	18.48	4.31	1.00	24.54
L4	1.29	24.83	6.93	1.06	34.11	1.12	31.04	4.46	0.93	37.17
L5	1.07	8.85	6.37	1.02	17.31	0.93	11.06	4.10	0.90	16.85
L6	1.41	12.78	7.27	1.09	22.55	1.23	15.98	4.68	0.96	22.65
L7	1.36	28.92	6.74	1.14	38.16	1.19	36.15	4.34	1.00	47.25
L8	1.15	29.08	5.13	1.10	36.46	1.00	36.35	3.30	0.96	44.18
L9	1.11	29.77	7.82	1.18	39.88	0.97	37.21	5.03	1.04	53.67
L10	1.66	32.20	6.30	1.06	41.23	1.45	40.25	4.06	0.93	46.96
L11	1.54	25.93	6.33	0.97	34.77	1.34	32.41	4.07	0.85	38.28
L12	1.36	30.89	6.33	1.12	39.70	1.19	38.61	4.08	0.98	44.38
L13	1.29	20.87	5.03	1.10	28.29	1.12	26.09	3.24	0.96	31.09
L14	0.99	17.87	6.03	1.13	26.02	0.86	22.34	3.88	0.99	27.80
L15	1.21	13.61	4.99	1.06	20.87	1.06	17.01	3.21	0.93	22.00
L16	1.25	34.64	6.79	0.95	43.62	1.09	43.29	4.37	0.83	53.91
L17	1.58	29.20	6.41	1.14	38.33	1.38	36.50	4.13	1.00	42.56
L18	1.20	10.65	5.54	1.30	18.68	1.05	13.31	3.56	1.14	18.89

Er < 40, low risk; Er 40 ≤ Er < 80, moderate risk; 80 ≤ Er < 160, considerable risk; 160 ≤ Er < 320, high risk; Er ≥ 320, very high risk/RI < 50, low ecological risk; RI > 600, very high ecological risk

Fig. 5 Ecological risk in study area due to heavy metal contamination of groundwater



of wastes including automobiles repair shops, electroplating unit and sewage runoff (Sirajudeen et al. 2014). EF showed minimal enrichment of all metals, while CF showed moderate contamination due to all metals in the urban residential area. QoC gave high positive values for all metals (except Fe at L8), which indicated anthropogenic nature of contamination. Urban residential area of Shivalik Nagar is characterized by sewage and urban runoff, open dumping of garbage and minor commercial activities which could be sources of heavy metal contamination. CF and EF values showed contamination and enrichment above background levels for all metals in the commercial area. In commercial land use area, I_{geo} showed contamination due to Cd at L17, while QoC indicated anthropogenic causes of contamination of all metals. Aneki

agricultural area (L4, L5, L6) is characterized by unplanned informal housing, lack of sewerage facilities, agricultural activities and electroplating/welding activities. The area showed minimal enrichment for Cr, Co and Ni, while QoC index showed that the source of contamination at these locations was anthropogenic. Co enrichment was found to be maximum at L6, and the I_{geo} suggested that Co contamination was anthropogenic. Mining and processing activities, production of alloys and chemicals, sewage effluents, urban runoff and agricultural runoff are major anthropogenic contributors of Co to the aquatic environment. Average ERI and PLI values of RNP closely matched ERI of IIE Haridwar and Aneki rural area. All locations in RNP showed minimal enrichment for Co and Zn, which was also supported by QoC

index and showed the anthropogenic nature of pollution at these locations. Results indicate that although RNP is a protected area, its groundwater was being contaminated due to urban and industrial activities of IIE Haridwar and adjoining areas. Use of BGM and BM as environmental backgrounds gave comparable results with minor variations for all indices except in case of I_{geo} and QoC. I_{geo} using GM showed contaminated levels for some metals at some locations, which was supported by the result of other indices. However, I_{geo} calculated using BM showed uncontaminated levels for all metals at all locations, which did not seem plausible given the result of other indices and actual concentrations of metals in groundwater of study area.

4 Conclusions

The incidence of metals was in order $Cd > Zn > Fe > Co > Cr > Ni$. Cr, Cd and Co levels exceeded standard guideline limits for metals in drinking water at 18 (100 %) out of 18 locations, while Zn concentrations were within the guideline limits at all locations. Fe and Ni concentrations were within permissible limits at 17 (95 %) out of 18 locations and 15 (83 %) out of 18 locations, respectively. Environmental risk assessment indices show that groundwater in the study area was contaminated with metals in varying degrees due to anthropogenic activities. EF results demonstrated that metals in the study area were enriched above background loads. ERI showed low ecological risk due to metal contamination and was supported by PLI values. Environmental risk in the study area was higher due to high concentrations of metals Cd, Ni and Cr as compared to Fe and Zn. Risk assessment showed that metal contamination was maximum in Bahadradabad old industrial area followed by Shivalik Nagar. This clearly showed that both industrial and urban activities were causes of environmental contamination. Study showed that, although RNP is a protected area, it was not free of metal contamination. In the study, use of BGM as environmental background was felt to be more appropriate than BM.

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Compliance with ethical standards

Conflict of interest The authors declare they have no conflict of interest.

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