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Quantification and health risk assessment due to heavy metals in potable water to the population living in the vicinity of a proposed nuclear power project site in Haryana, India

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ABSTRACT

This study reports heavy metals' concentrations in groundwater in the proximity of proposed nuclear power project site in Fatehabad district of Haryana, India. Heavy metals' quantification was done using flame atomic absorption spectrometer. The average concentration of metals was: Zn ($0.20 \pm 0.72\,mg\,L^{-1}$), Cu ($0.13 \pm 0.11\,mg\,L^{-1}$), Ni ($0.20 \pm 0.05\,mg\,L^{-1}$), Fe ($0.16 \pm 0.10\,mg\,L^{-1}$), Cr ($0.13 \pm 0.05\,mg\,L^{-1}$), Cd ($0.02 \pm 0.004\,mg\,L^{-1}$) and Co ($0.07 \pm 0.02\,mg\,L^{-1}$). Ni, Cr and Cd concentrations were higher than WHO and Indian Standards (IS: 10500). Multivariate statistical techniques, viz. inter-metal correlation, cluster analysis (CA) and principal component analysis were applied for the interpretation of data. Significantly, positive correlations were observed between Fe and Cr ($r = 0.341$; $p < 0.01$) and Co and Cr ($r = 0.441$; $p < 0.01$). The results of inter-metal correlation were further supported by CA as primary cluster pairs were found for Cr–Co, Fe–Cr and Ni–Cd in groundwater. Potential non-carcinogenic health risks of heavy metals were calculated using Hazard Quotient (HQ) and Hazard Index (HI) methods. For non-cancer risks, HQ values were in the following order: Cd (2.16 ± 0.53) > Ni (0.67 ± 0.19) > Cu (0.21 ± 0.18) > Zn (0.04 ± 0.13) > Fe (0.02 ± 0.01) > Cr (0.01 ± 0.003) for inhabitants of the study area. HI results indicate non-carcinogenic risk to general public of this area through consumption of groundwater.

Keywords: Heavy metal; Groundwater pollution; Chronic daily intake; Health risk index; Atomic absorption spectrophotometer

1. Introduction

Potable water is the basic requirement of every individual for survival. The potable water is either obtained from surface water sources including rivers, lakes and streams or groundwater sources. Groundwater is the largest reserve of potable water and has played an important role in the development of human civilization. It is an important water source in rural areas, particularly in developing nations [1]. Groundwater characteristics in any area depend on various geological, environmental and anthropogenic activities. In India, about 80% of potable water

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requirements in rural areas and 50% in urban areas are attained by groundwater and it is under severe threat from natural and anthropogenic pollutants, i.e. heavy metals, pesticides, fluoride, nitrate etc. [2]. Anthropogenic activities such as poor sanitation practices, haphazard industrialization, intensive agriculture, excessive use of agrochemicals and unsustainable irrigation practices are the decisive determinants to the quality of groundwater [2,3].

The heavy metals are globally distributed pollutants and their presence has been detected in different environmental matrices. Some of the metals, viz. copper, zinc, iron etc. play irreplaceable roles in life functioning systems. Whereas some other metals such as lead, chromium, arsenic, cobalt, mercury, cadmium etc. are toxic for the humans even at low level of ingestion, tend to accumulate in living organisms and cause health problems. In addition to this, some metals are known as xenobiotics also.

Heavy metals are deposited in soil due to continuous land disposal of municipal, industrial wastes, extensive applications of agrochemicals and natural fallout [4]. With sufficient surface water infiltration heavy metals through leaching find their way to underlying aquifers. Further, permeable soils underlain by unconfined aquifers with shallow water tables are especially vulnerable to these contaminants. About 80% of incidence of diseases in Indian population is due to unsanitary conditions and poor drinking water quality [5,6].

Heavy metal intake by drinking water can be critical in human health risk assessment as ingestion is the major route of exposure [7]. In the study area, no work has been undertaken on quantification and health risks due to heavy metals in potable water. Keeping this in view, the objectives of this study were quantification of heavy metals in groundwater and non-carcinogenic health risk assessment associated with the ingestion of heavy metals in different villages located in the vicinity of proposed nuclear power project in Fatehabad district, Haryana, India. The proposed site of Gorakhpur Atomic Power project is situated at the village Gorakhpur in Fatehabad district of Haryana, India. At this site, four reactors of 700 MWe would be established by Nuclear Power Corporation India Ltd., Mumbai.

2. Material and methods

2.1. Study area

The study area is situated between the latitude from N29°29′04.4″to N29°23′58.3′′ and longitude E75° 34′51.2′′ to E75°41′10.8′′ in Fatehabad district of Haryana, India (Fig. 1). There is no perennial or seasonal river. Groundwater is main source of drinking water in the study area. There is a canal and its water is used by some household for their domestic needs. The climate is tropical type with wide variation in temperature ranging from 47°C in summer to 2°C in winter. The area receives an annual rainfall of 395.6 mm. About 71% of the annual rainfall is received during the short south-west monsoon period, July to September. The study area is an alluvial plain of Indo-Gangetic basin with sandy, sandy loam and clay soil types. As a whole topography of the region is flat plain with an average elevation of 215 m, gently sloping from north-east to south-west. A total of 63 sampling locations were established, based on the wind pattern and location of the proposed nuclear power project site, in seven villages.

2.2. Sampling and analysis

The water samples were extracted from the manually operated handpumps after running them for 10–15 min to avoid any contamination. The sampling stations were decided on the basis of the frequency of the use. Samples were collected in pre-conditioned plastic containers of 1 L capacity. The samples were brought to the laboratory within 2 h and kept at 4°C for further analysis. Prior to analysis, the water samples were filtered through 0.45-μm Whatmann filter paper. All Working standard used for the analysis were of AAS grade (certified purity > 99.9%). Double distilled water was used for rinsing glassware and preparation of standards. Filtered samples were acidified using 2–3 drops of concentrated HNO_3 and were analysed with in 48 h after receiving in the laboratory.

Heavy metal quantification was done by atomic absorption spectrophotometer (Model GBC SensAA). Acetylene gas was used as fuel and air as support. An oxidising flame was used in all the cases except chromium, where reducing nitrous oxide flame was used for metal quantification. Detailed instrumental analytical conditions for the analysis of selected heavy metals are given in Table 1. To ensure the reliability of results, standards of respective metal were analyzed after each set of 15 samples. Collected water samples were analysed for eight metals, viz. Fe, Cu, Cr, Co, Cd, Pb, Ni and Zn. Being a regulatory factor for metal solubility, pH of all the collected samples was also determined using pH meter.

2.3. Health risk from the intake of heavy metals through ingestion: hazard quotient

Wayne [8] has reported that concentrations of heavy metals in environmental samples are better

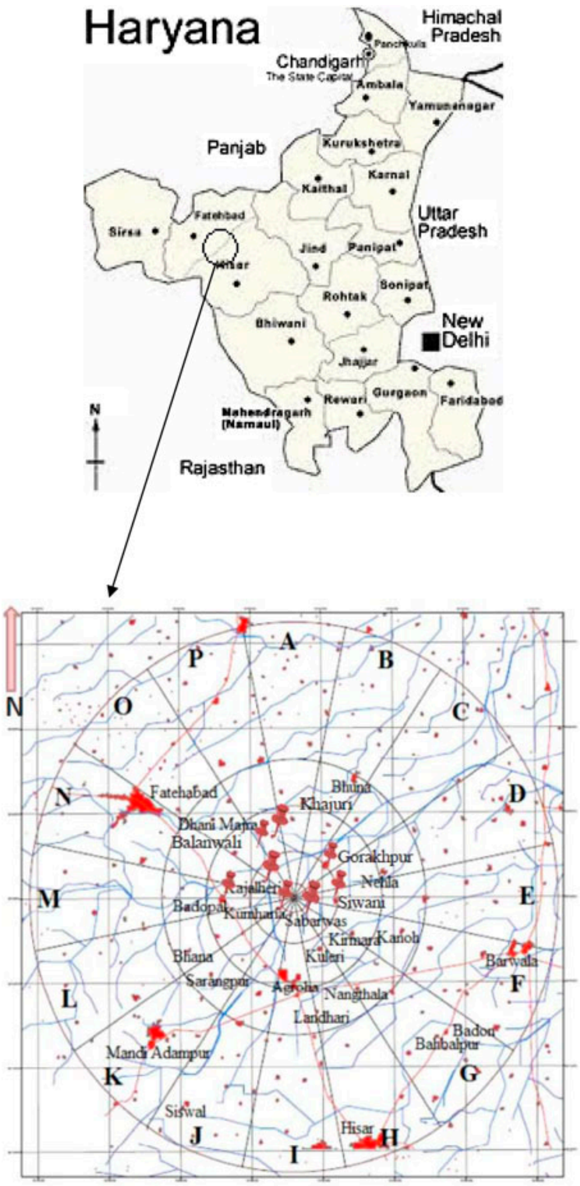

Fig. 1. Base Map of the study area showing sampling locations.

represented by the log-normal distribution and central tendency. So, these should be given as geometric average. The main routes of heavy metal intake to human body are oral, dermal and nasal but oral intake is most important [9]. Chronic Daily Intake (CDI) is the exposure expressed as the mass of a substance per unit body weight per unit time, averaged over lifetime. CDI ($\mathrm{mg\,kg^{-1}\,day^{-1}}$) through water consumption was calculated according to equation given by USEPA [10].

$$\mathrm{CDI} = \frac{[\mathrm{CF} \times \mathrm{IR} \times \mathrm{EF} \times \mathrm{ED}]}{[\mathrm{BW} \times \mathrm{AT}]} \tag{1}$$

where CF is the concentration of a heavy metal in water ($\mathrm{mg\,L^{-1}}$); IR is the water ingestion rate ($4.05\,\mathrm{L\,day^{-1}}$) of water for an adult Indian [11]; EF is the exposure frequency ($365\,\mathrm{days\,year^{-1}}$); ED is the exposure duration (70 years for adults); BW is the average body weight (60 kg for Indian adults) [12,13]; and AT is the average exposure time for non-carcinogenic effects ($\mathrm{ED} \times 365\,\mathrm{days\,year^{-1}}$).

Non-carcinogenic risk for individual heavy metals has been expressed in terms of Hazard Quotient (HQ) and computed as the ratio of the CDI ($\mathrm{mg\,kg^{-1}\,day^{-1}}$) of the heavy metal to its reference dose ($\mathrm{mg\,kg^{-1}\,day^{-1}}$). Reference oral dose (RfDo) is the

Table 1
AAS analytical condition for heavy metals analysis

Heavy metal	Flame type	Wavelength (nm)	Slit width (nm)	Working range	Lamp current (Ma)	Detection limits (mg/L)
Zn	Air-acetylene	213.9	0.5	0.4–1.5	5	0.008
Cu	Air-acetylene	327.4	0.5	2.5–10	3	0.05
Pb	Air-acetylene	217	1.0	2.5–20	5	0.06
Ni	Air-acetylene	232	0.2	1.8–8	4	0.04
Fe	Air-acetylene	248.3	0.2	2–9	7	0.05
Cr	Nitrous oxide–acetylene	357.9	0.2	2.0–15	6	0.05
Cd	Air-acetylene	228.8	0.5	0.2–1.8	3	0.009
Co	Air-acetylene	240.7	0.2	2.5–9	6	0.05

estimation of daily exposure to a specific metal to which the human population is likely to be exposed without any appreciable risk of deleterious effects during a lifetime.

$$HQ = \frac{CDI}{RfDo} \quad (2)$$

According to USEPA Guidelines [14], oral dose toxicity values (RfDo) are 3.0E−01, 5.0E−04, 1.5, 3.7E−02, 2.0E−02, 3.6E−02 and 7E−01 mg kg^{-1} $day^{-1}$for Zn, Cd, Cr, Cu, Ni, Pb and Fe respectively.

2.4. Hazard Index

Overall potential for non-carcinogenic risk posed by heavy metals is assessed in terms of Hazard Index (HI) approach. HI is the sum of the HQs due to individual heavy metals. There may be a concern when it exceeds unity potential non-cancer effects may be a concern. The equation used to calculate HI is given below:

$$HI = \sum HQ = \frac{CDI_1}{RfDo_1} + \frac{CDI_2}{RfDo_2} + \ldots + \frac{CDI_i}{RfDo_i} \quad (3)$$

2.5. Statistical analysis

In the present study, understanding of groundwater chemistry was appraised with the use of statistical applications. The bivariate correlation analysis with the Pearson's correlation coefficient (r) at two-tailed significance level (p), principal component analysis (PCA) and cluster analysis (CA) dendrogram was done using SPSS software package (version 16.0).

3. Results and discussion

3.1. Heavy metals analysis

The heavy metals' concentration range, their geometric means and standard deviations along with pH in groundwater samples are encapsulated in Table 2. Metal ions' solubility in water is dependent on its pH. Heavy metals tend to be more toxic at lower pH since they are more soluble at acidic pH values. Minimum solubility for most of the heavy metals is observed between pH 9 and 11. [15]. The pH of groundwater in the study area varied from 7.5 to 8.7.

Box plots for the studied heavy metals are given in Fig. 2(a)–(g). The data showed that different sampling locations contributed differently to groundwater contamination (Table 2). Nickel, Iron, Chromium and Cadmium concentrations in the study area ranged 0.07–0.34, <0.05–0.45, <0.05–0.30 and 0.01–0.02 mg L^{-1} respectively. Lead concentration was BDL (<0.05 mg L^{-1}) in all the water samples from the study area. Cobalt was BDL in most of the water samples from the study area and ranged from <0.05 to 0.12 mg L^{-1}. Zinc concentrations in water samples ranged from 0.01 to 4.4 mg L^{-1}. It is clear from Fig. 2(a) that highest Zn concentration (4.4 mg L^{-1}) was observed in water sample No. 5 from *Balanwali* village. Cu was found BDL (<0.05 mg L^{-1}) in most of the water samples and the highest concentration (0.33 mg L^{-1}) was observed from *Gorakhpur* village from location No. 5 ((Fig. 2(b)). The Highest Cr (0.30 mg L^{-1}) concentration was recorded at *Gorakhpur* village from location No. 4 (Fig. 2(c)). Ni (0.34 mg L^{-1}) and Cd (0.24 mg L^{-1}) concentrations were highest at locations No. 12 and 9 (Fig. 2(d) and 2(e)) at village *Khajuri*, respectively. Acute doses (10–30 mg kg^{-1} day^{-1}) of Cadmium can cause severe gastro intestinal irritation, vomiting, diarrhoea and excessive

Table 2
Heavy metal concentration (mg L^{-1}) in water samples collected from study area

Heavy metal	Statistics	Gorakhpur $n^a = 10$	Kumharia $n = 10$	Kajalheri $n = 10$	Sabarwas $n = 3$	Khajuri $n = 12$	Siwani $n = 10$	Balanwali $n = 8$	IS:10,500 limit	WHO limit
pH	Range	8.0–8.5	8.2–8.5	8.4–8.5	8.3–8.6	7.6–8.6	7.8–8.7	7.5–7.7	6.5–8.5	6.5–8.5
Zn	Range	0.01–2.28	0.04–0.93	0.06–0.37	0.06–0.09	0.05–0.78	0.09–2.55	0.15–4.4	5	3
	Mean	0.15	0.30	0.12	0.07	0.15	0.34	0.44		
	Std[b]	0.71	0.29	0.09	0.02	0.23	0.93	1.46		
Cu	Range	<0.05–0.33	<0.05–0.51	<0.05–0.47	<0.05	<0.05	<0.05–0.18	<0.05–0.21	0.05	2
	Mean	–	–	–	–	–	–	–		
	Std[b]	–	–	–	–	–	–	–		
Pb	Range	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	0.01	0.01
	Mean	–	–	–	–	–	–	–		
	Std[b]	–	–	–	–	–	–	–		
Ni	Range	0.13–0.25	0.12–0.27	0.07–0.28	0.22–0.29	0.11–0.34	0.16–0.28	0.13–0.27	0.02	0.07
	Mean	0.19	0.19	0.17	0.24	0.21	0.22	0.22		
	Std[b]	0.04	0.05	0.07	0.04	0.06	0.03	0.06		
Fe	Range	0.09–0.37	0.08–0.45	0.13–0.36	0.12–0.17	0.1–0.4	<0.05–0 .16	<0.05–0.23	0.3	0.3
	Mean	0.18	0.19	0.21	0.14	0.17	0.08	0.12		
	Std[b]	0.11	0.12	0.08	0.03	0.11	0.03	0.06		
Cr	Range	<0.05–0.30	<0.05–0.20	0.055–0.25	<0.05–0.13	<0.05–0.12	<0.05	<0.05	0.05	0.05
	Mean	0.13	0.14	0.14	0.12	0.11	–	–		
	Std[b]	0.07	0.05	0.06	0.01	0.01	–	–		
Cd	Range	0.01–0.02	0.01–0.02	0.01–0.02	0.02–0.02	0.02–0.02	0.01–0.02	0.02–0 .02	0.003	0.003
	Mean	0.01	0.01	0.01	0.02	0.02	0.02	0.02		
	Std[b]	0.003	0.002	0.002	0.001	0.003	0.003	0.002		
Co	Range	<0.05	<0.05–0.62	<0.05–0.12	<0.05	<0.05	<0.05–0.48	<0.05		
	Mean	–	–	0.0.73	–	–	–	–		
	Std[b]	–	–	0.025	–	–	–	–		

Notes: [a] = Number of samples. [b] = Standard deviation.

salivation, and doses of 25 mg of Cd kg^{-1} body weight can cause death. Low-level chronic exposure to Cd may also cause gastrointestinal, haematological, musculoskeletal, renal, neurological and reproductive effects on humans. The main target organ for cadmium following chronic oral exposure is kidney [16]. Hyper intake of nickel may lead to hypoglycemia, asthma, nausea and headache. The permissible safe limit of Ni is 3.0–7.0 mg day^{-1} in man [17]. Highest Fe (0.45 mg L^{-1}) and Co (0.12 mg L^{-1}) concentrations were recorded at locations No. 4 and 1 (Fig. 2(f) and 2(g)) of village *Kumharia* and *Kajalheri*, respectively. Deficiency of Cobalt in diet results into pernicious anaemia, severe fatigue, shortness of breath and hypothyroidism, while overdose may lead to angina, asthma, cardiomyopathy, polyeythemia and dermatitis. The safety limit for human consumption of Cobalt is 0.05–1.0 mg day^{-1} [18].

The groundwater quality was assessed for its potability based on the IS:10,500 [19] and WHO [20] standards (Table 2). All the studied groundwater locations had higher concentrations of Ni, Cr and Cd than their permissible limits. About 19% of the water samples exceeded threshold set for Fe. Copper concentrations of all the samples were within WHO permissible limits but 4.7% of water samples exceeded permissible limits set by IS:10,500 [19]. Zn concentrations were within thresholds limits given by IS:10,500 [19] and only one sample crossed WHO [20] permissible limit.

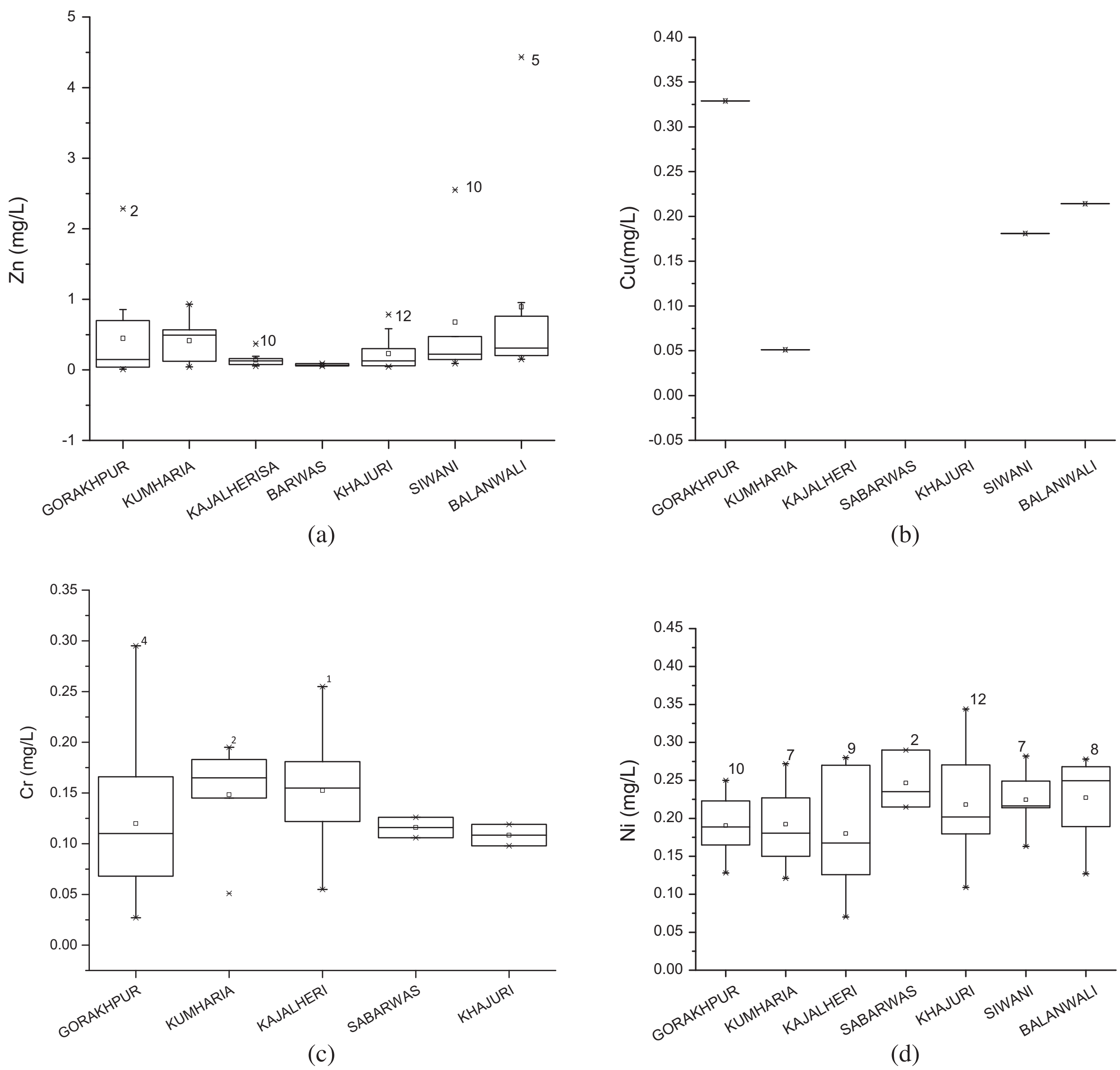

Fig. 2. (a–g) Box plots of selected heavy metals.

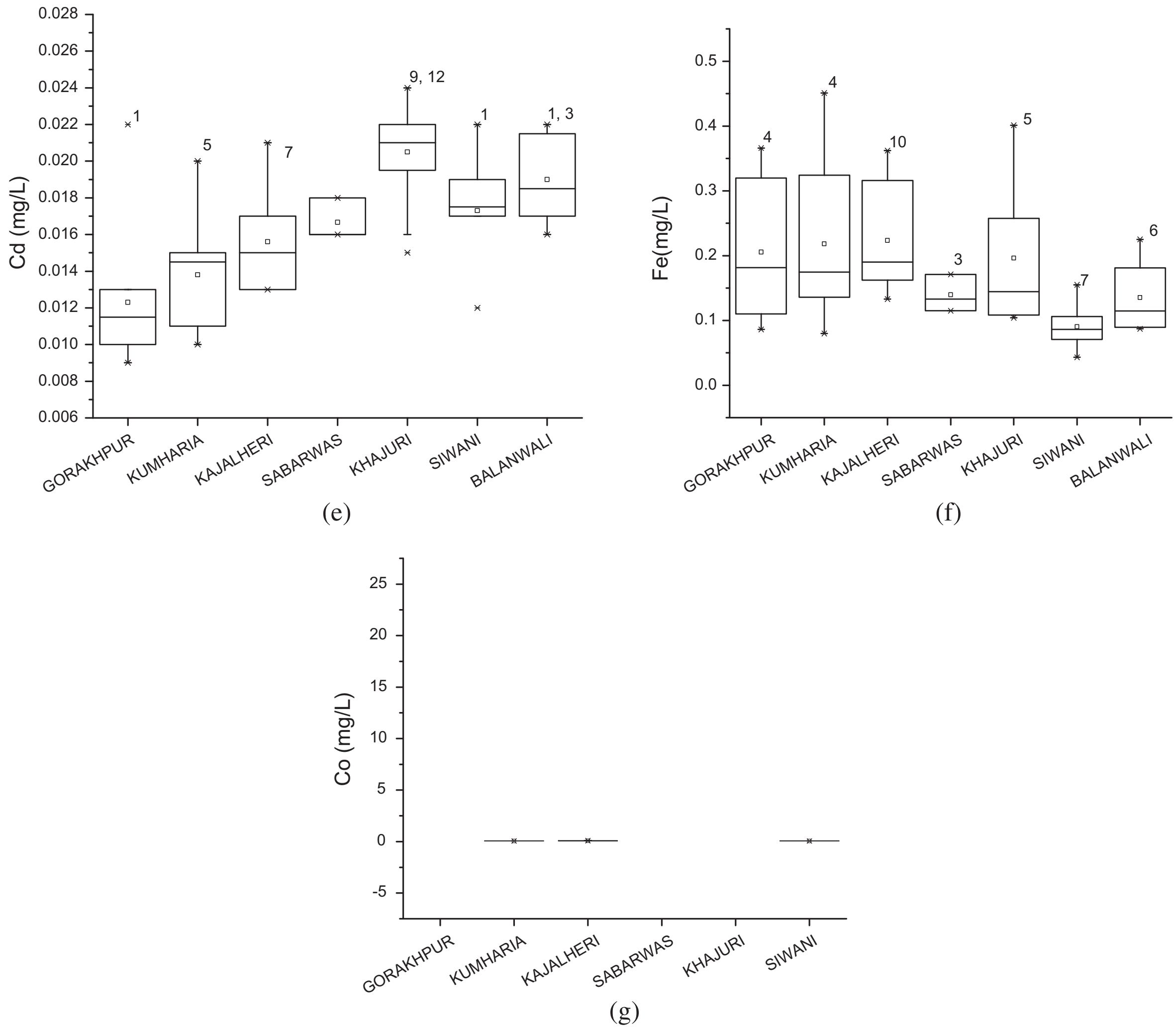

Fig. 2. (a–g) (*Continued*)

3.2. Health risk assessment

3.2.1. CDI of metals through consumption of water

CDI values for studied heavy metals' for different sampling locations are given in Table 3. The mean CDI of metals, for the residents who consume ground water is 0.13 ± 0.04, 0.008 ± 0 .007,0.013 ± 0.004, 0.011 ± 0.007, 0.008 ± 0.004, 0.001 ± 2E–04 and 0.005 ± 0.002 mg $kg^{-1}day^{-1}$ for Zn, Cu, Ni, Fe, Cr, Cd and Co, respectively (Table 3). The Pb was below detectable limits in all the water samples, so CDI values could not be calculated. According to Indian Standards [19], permissible CDI for Zn, Cu, Ni, Fe, Cr, and Cd is 0.338, 0.003, 0.001, 0.020, 0.003 and 2E-04 mg $kg^{-1}day^{-1}$, respectively. Results of the present study revealed that mean CDI of Cu, Ni, Cr and Cd was higher than the threshold CDI values given by Indian Standards. It has been reported by Giri et al. [21] that mean CDI of Cu and Ni was higher in ground water of the proposed Bagjata and Banduhurang uranium mining site in India. Shah et al. [22] have also reported that mean CDI of heavy metals in sub-surface water of Northern Pakistan was higher than permissible limits.

3.2.2. Hazard quotient and hazard index

HQ is used to assess potential non-cancer risks associated with the consumption of individual heavy metals. The HQs of Zn, Cu, Ni, Fe, Cr, Cd and Co through oral route of exposure are given in Table 4. All the studied metals in the area except Ni and Cd had HQ values lesser than unity. For inhabitants of the study area, mean HQ values showed the following

Table 3
CDI (mg kg^{-1} day^{-1})of heavy metals in the study area through oral intake of water

Heavy metal	Statistics	Gorakhpur $n^{a}=10$	Kumharia $n=10$	Kajalheri $n=10$	Sabarwas $n=3$	Khajuri $n=12$	Siwani $n=10$	Balanwali $n=8$
Zn	Range	6.0E-04–0.16	3.0E-03–0.06	4.0E-03–0.03	4.0E-03–0.01	3.0E-03–0.05	0.01–0.17	0.01–0.30
	Mean	50.01	0.02	8.0E–03	5.0E–03	1.0E–02	0.02	0.03
	Std[b]	0.05	0.02	6.0E–03	1.0E–03	1.5E–02	0.06	0.09
Cu	Range	0.02	3.0E–03	3.0E–03	BDL[c]	BDL	1.2E–02	1.4E–02
	Mean	–	–	–	–	–	–	–
	Std	–	–	–	–	–	–	–
Pb	Range	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Mean	–	–	–	–	–	–	–
	Std	–	–	–	–	–	–	–
Ni	Range	0.01–0.02	0.01–0.02	5.0E-03–0.02	1.5E-02–0.02	0.01–0.02	0.01–0.02	0.01–0.02
	Mean	1.3E–02	1.3E–02	1.1E–02	2.0E—02	1.4E–02	1.5E–02	1.5E–02
	Std	3.0E–03	3.0E–03	5.0E–03	2.0E–03	4.0E–03	2.0E–03	3.0E–03
Fe	Range	0.01–0.03	0.01–0.03	0.01–0.02	8.0E-03–1.2E-02	0.01–0.03	3.0E-03–0.01	0.01–0.02
	Mean	1.2E–02	1.3E–02	1.4E–02	9.0E–03	1.2E–02	6.0E–03	8.0E–03
	Std	7.0E-03	8.0E-03	5.0E-03	2.0E-03	7.0E-03	2.0E-03	4.0E-03
Cr	Range	2.0E-03–0.02	3.0E-03–0.01	4.0E-03–0.02	7.0E-03–9.0E-03	7.0E-03–8.0E-03	BDL	BDL
	Mean	7.0E–03	0.01	0.01	4.0E–03	4.0E–03	–	–
	Std	5.0E–03	3.0E–03	4.0E–03	3.0E–03	3.0E–03	–	–
Cd	Range	6.0E-04–1.5E-03	7.0E-04–1.4E-04	9.0E-04–1.4E-04	1.1E-04–1.2E-04	1.0E-03–2.0E-03	8.0E-04–1.5E-03	1.1E-03–1.5E-03
	Mean	8.0E–04	9.0E–04	1.0E–03	1.1E–03	1.0E—03	1.2E–03	1.3E–03
	Std	2.0E–04	2.0E–04	2.0E–04	1.0E–04	2.0E–04	2.0E–04	2.0E–04
Co	Range	BDL	3.0E-03–4.0E-03	3.0E-03–0.01	BDL	BDL	3.0E-03	BDL
	Mean	–	4.0E–03	5.0E–03	–	–	–	–
	Std	–	4.0E–04	2.0E–03	–	–	–	–

Notes: [a] = Number of samples. [b] = Standard deviation. [c] = (BDL) Below detectable limits.

Table 4
HQ of heavy metals in the study area through oral intake of water

Heavy metal	Statistics	Gorakhpur $n^a = 10$	Kumharia $n = 10$	Kajalheri $n = 10$	Sabarwas $n = 3$	Khajuri $n = 12$	Siwani $n = 10$	Balanwali $n = 8$
Zn	Range	2.0E-03–0.51	0.01–0.21	0.01–0.08	0.01–0.02	0.01–0.18	0.02–0.57	0.03–1.00
	Mean	0.03	0.07	0.03	0.02	0.03	0.08	0.10
	Std[b]	0.15	0.06	0.02	0.003	0.05	0.20	0.31
Cu	Range	0.56	0.09	0.08	BDL[c]	BDL	0.31	0.36
	Mean	–	–	–	–	–	–	–
	Std	–	–	–	–	–	–	–
Pb	Range	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Mean	–	–	–	–	–	–	–
	Std	–	–	–	–	–	–	–
Ni	Range	0.43–0.84	0.41–0.92	0.24–0.95	0.73–0.98	0.37–1.16	0.55–0.95	0.43–0.94
	Mean	0.63	0.63	0.56	0.83	0.71	0.75	0.74
	Std	0.13	0.17	0.23	0.11	0.21	0.10	0.17
Fe	Range	0.01–0.04	0.01–0.04	0.01–0.04	0.01–0.02	0.01–0.04	4.0E-03–0.02	0.01–0.02
	Mean	0.02	0.02	0.02	0.01	0.02	0.01	0.01
	Std	0.01	0.01	0.01	2.0E-03	0.01	3.0E-03	0.01
Cr	Range	1.0E-03–0.013	2.0E-03–0.01	2.0E-03–0.01	5.0E-03–6.0E-03	4.0E-03–0.01	BDL	BDL
	Mean	4.0E-03	0.01	0.01	0.01	0.01		
	Std	3.0E-03	2.0E-03	2.0E-03	5.0E-04	5.0E-04		
Cd	Range	1.22–2.97	1.35–2.70	1.76–2.84	2.16–2.43	2.03–3.24	1.62–2.97	2.16–2.97
	Mean	1.61	1.82	2.08	2.25	2.74	2.30	2.55
	Std	0.47	0.40	0.34	0.13	0.36	0.38	0.30

Notes: [a] = Number of samples. [b] = Standard deviation. [c] = (BDL) Below detectable limits.

decreasing order of non-cancer risks: Cd (2.16 ± 0.53) > Ni (0.67 ± 0.19) > Cu (0.21 ± 0.18) > Zn (0.04 ± 0.13) > Fe (0.02 ± 0.01) > Cr (0.01 ± 0.003). No HQ values for Co could be determined as no RfDo value available for the element. Also as the Pb in all the water samples was BDL, so HQ could not be calculated for this metal. HQ for Cu and Ni was higher than those reported by Giri et al. [21] in the groundwater of Jharkhand, India. HQ of all the heavy metals in this study is higher than reported for Northern Pakistan by Shah et al. [22]. The HQ of Cr, Cu, Cd and Ni tends to be on higher side when compared with groundwater at Kohistan region, Pakistan [23], Korea [24] and surface water in Turkey [25].

HI of different water samples is shown in Fig. 3. The results indicate that all the studied sampling areas are experiencing significant non-carcinogenic risk through consumption of water from these water sources. The HI values indicated that the highest non-cancer risks were from consuming water from *Khajuri–12* (4.6) and least from consuming water from *Gorakhpur–8* (1.9).

3.3. Inter-metal relationship and cluster analysis

The correlation matrix describing the inter-metal relationship among various heavy metals is given in Table 5. The results showed that Fe was positively and significantly correlated with Cr ($r = 0.341^{**}$; $p < 0.01$). Also Cr showed a high degree of positive correlation with Co ($r = 0.441^{**}$; $p < 0.01$) but correlated negatively with Cd ($r = -0.519^{**}$; $p < 0.01$). Results of correlation matrix suggested that some metals have strong correlation and due to which they form primary cluster pairs. Further CA dendrogram supported the observed inter-metal relationship in groundwater (Fig. 4). In the present analysis, the primary clusters were found for Cr–Co, Fe–Cr and Ni–Cd in groundwater (Fig. 4).

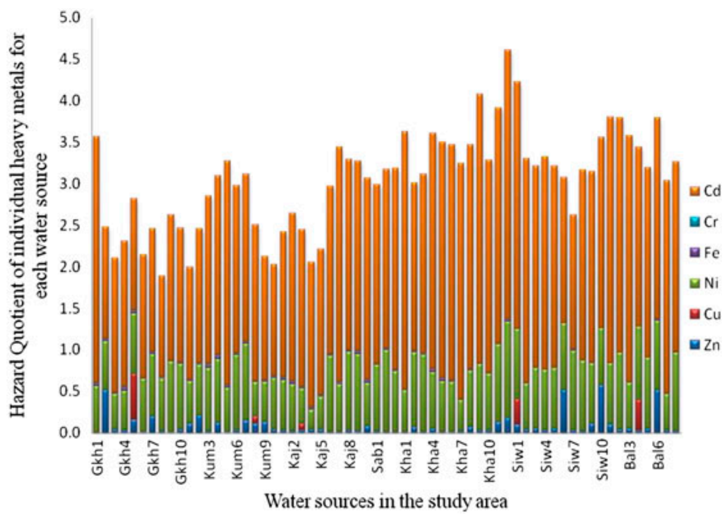

Fig. 3. HI for aggregate non-cancer risks through oral intake of water from study area.

Table 5
Correlation among different heavy metals in ground water of study area

Parameters	Zn	Cu	Ni	Fe	Cr	Cd	Co
Zn	1.000						
Cu	0.031	1.000					
Ni	0.107	0.082	1.000				
Fe	−0.127	0.110	−0.120	1.000			
Cr	−0.156	−0.146	−0.230	**0.341****	1.000		
Cd	−0.135	−0.122	0.149	−0.028	**−0.519****	1.000	
Co	−0.149	−0.053	−0.231	0.190	**0.441****	−0.203	1.000

Notes: **Correlation is significant at the 0.01 level (2-tailed).

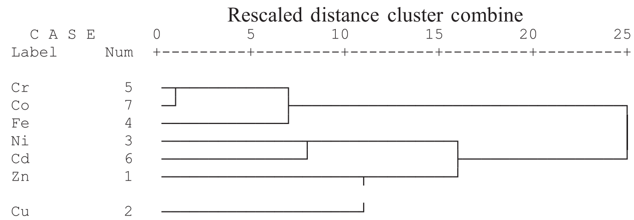

Fig. 4. Dendrogram of selected heavy metals in groundwater samples using Complete Linkage.

Table 6
Factor analysis for selected heavy metals in study area ($n^a = 63$)

Heavy metals	Factor 1	Factor 2	Factor 3
Zn	−0.247	**0.708**	−0.266
Cu	−0.075	**0.438**	**0.788**
Ni	−0.484	0.188	**0.197**
Fe	**0.481**	−0.181	**0.575**
Cr	**0.861**	0.080	−0.097
Cd	−0.585	−0.656	**0.131**
Co	**0.697**	−0.097	−0.040
Eigen value	2.100	1.207	1.090
% of variance	30.003	17.245	15.577
Cumulative%	30.003	47.248	62.825

Notes: [a] = Number of water samples. [b] = Values of dominant heavy metals in each factor are indicated bold.

Also, the primary clusters were found in groundwater for EC-TDS and Cr–Ni at Mohmand agency, Northern Pakistan [22] and Pb–Cd, Cu–Co at Kohistan region, Northern Pakistan [23].

3.4. Principal component analysis

PCA is a multivariate technique designed to analyse the inter-dependencies within a set of variables. For easy interpretation of complex data with the help of statistics, factors are constructed to reduce the complexity. PCA was applied for the qualitative evaluation of clustering behaviour and the results are given in Table 6. Three factors having a total variance of 62.825% were obtained. Factor-1 contributed 30.003% to the total variance with a high loading on Cr ($r = 0.861$), Co ($r = 0.697$) and Fe ($r = 0.481$). Thus, Factor-1 supported purely two primary cluster pairs i.e. Cr–Co and Cr–Fe. Factor-2 contributed 17.245% to the total variance with a high loading on Zn ($r = 0.708$) and Cu ($r = 0.438$), supporting Zn–Cu cluster pair. Factor-3 contributed 15.577% to the total variance with a high loading on Cu ($r = 0.788$), Fe ($r = 0.575$), Ni ($r = 0.197$) and Cd ($r = 0.131$), further supporting third cluster pair i.e. Ni–Cd.

4. Conclusion

In the study area, Ni, Cr and Cd concentrations in groundwater were higher than WHO and Indian Standards for drinking water which can pose health risks to the local inhabitants. Pb concentration in all the water samples was below detectable limits. The mean CDI of heavy metals was in the following order: Zn ($0.13 \pm 0.04\,mg\,kg^{-1}\,day^{-1}$) > Ni ($0.013 \pm 0.004\,mg\,kg^{-1}\,day^{-1}$) > Fe ($0.011 \pm 0.007\,mg\,kg^{-1}\,day^{-1}$) > Cu ($0.008 \pm 0.007\,mg\,kg^{-1}\,day^{-1}$) = Cr ($0.008 \pm 0.004\,mg\,kg^{-1}\,day^{-1}$) > Co ($0.005 \pm 0.002\,mg\,kg^{-1}\,day^{-1}$) > Cd ($0.001 \pm 2E\text{–}04\,mg\,kg^{-1}\,day^{-1}$). The mean CDI of heavy metals was higher than the threshold CDI values givenby IS:10,500. Mean HQ values showed the following decreasing order of non-cancer risks: Cd (2.16 ± 0.53) > Ni (0.67 ± 0.19) > Cu (0.21 ± 0.18) > Zn (0.04 ± 0.13) > Fe (0.02 ± 0.01) > Cr (0.01 ± 0.003). HI results indicated significant non-carcinogenic risk to the general public through the consumption of water from these water sources. Therefore, residents should look up for alternative potable water sources in the study area.

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