JOURNAL GEOLOGICAL SOCIETY OF INDIA
Vol.90, July 2017, pp.77-84

Risk Assessment of Metals from Groundwater in Northeast Rajasthan

Vikas Duggal[1], Asha Rani[2], Rohit Mehra[3] and V. Balaram[4]

[1]Baba Hans Raj Memorial College, Bajakhana, Faridkot – 151 205, Punjab, India
[2]Department of Physics, Dev Samaj College for Women, Ferozpur – 152 002, Punjab, India
[3]Department of Physics, Dr. B.R. Ambedkar National Institute of Technology, Jalandhar - 144 001, India
[4]CSIR-National Geophysical Research Institute (NGRI), Hyderabad - 500 007, India
E-mail: *vikasduggal86@yahoo.in*; ashasachdeva78@gmail.com; mehrar@nitj.ac.in; balaram1951@yahoo.com*

ABSTRACT

The present study was conducted to investigate trace metal (Li, Be, B, Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, As Se, Mo, Cd, Sb, Ba and Pb) concentrations of drinking water samples in northeast Rajasthan, India. Furthermore, the study aimed to ascertain carcinogenic and non-carcinogenic health risks of metals by ingestion and dermal absorption pathways to the local residents. Metal concentrations were analyzed by using high resolution inductively coupled plasma mass spectrometry and compared with permissible limits set by the Bureau of Indian Standards, United States Environmental Protection Agency and World Health Organization. The results indicate that the concentrations of Be, B, Al, Cr, Fe, Cu, Zn, As, Mo, Sb and Ba were lower than their respective permissible limits, whereas the concentrations of Mn, Ni, Se, Cd and Pb in some samples were higher than their permissible limits.The total hazard index (summing the hazard index through ingestion and dermal routes) at all the sampling sites exceeded or nearing unity, indicating the presence of non-carcinogenic health effects from ingestion of water and dermal contact with water. The results indicate that the total excess lifetime cancer risk (considering both ingestion and dermal exposure pathways) of metals exposure was in accordance to the acceptable lifetime risks for carcinogens in drinking water (10^{-6}–10^{-4}). Both carcinogenic and non-carcinogenic risks were mainly attributed to the ingestion pathways.

INTRODUCTION

Groundwater is the major source of drinking water in both urban and rural India. It is also important source of water for the agricultural and the industrial sectors. In recent years, metal contamination in the aquatic environment has attracted global attention owing to its environmental toxicity, abundance and persistence. Anthropogenic inputs such as urban waste, industrial effluents and agriculture activities as well as natural processes such as atmospheric deposition, erosion and mineral weathering, degrade groundwater and surface water and impair their use for agricultural, industrial, drinking or other purposes (Krishna et al. 2009; Li and Zhang, 2010; Iqbal et al. 2013; Islam et al. 2015). The quality of groundwater varies from site to site depending upon the geological formations. The distribution and concentration of trace metals in groundwater vary from one area to another depending on the variables, i.e. pH, geological locations, redox potential, hydro-geometry of aquifers etc. Heavy metals toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, damage the blood composition, lungs, kidneys, liver and other vital organs (Donaldson et al. 2010). To protect human health, the WHO and USEPA have developed guideline values and BIS, India has developed standards for regulating the maximum contamination levels (MCLs) in water for metals.

Risk assessment is defined as a process used to estimate health effects that might result from exposure to non-carcinogenic and carcinogenic chemicals. Risk assessment is typically performed in four steps: Hazard identification, exposure assessment, toxicity (dose-response) assessment and risk characterizations. The main routes for trace metals intake to human body are oral, nasal and dermal. Ingestion and dermal absorption are common for water pathways (USEPA 2004). Hazard identification step is used to establish a link between identification of toxic chemicals and their health effects on habitants in the study region. Exposure assessmentis used to estimate the type and magnitude of exposures from the chemicals of potential concern that are present at or migrating from a site.In order to assess exposure, it is necessary to calculate the chronic daily intake (CDI) of contaminant via the three identified pathways (groundwater, food and soil). Toxicity (dose-response) assessment presents the relationship between the magnitude of exposure and adverse effects. In dose-response assessment for non-carcinogens, reference doses (RfD) are calculated and that for carcinogens, slope factors (SF) are obtained by the Risk Assessment Information System (RAIS) (USDOE 2011). The risk characterization step synthesizes all the information gathered in the three previous steps (Hazard identification, exposure assessment and toxicity assessment) to estimate the likelihood that a hypothetical exposure may adversely impact human health.

Many studies have investigated the occurrence of heavy metals in groundwater and surface water. Giri et al. (2012) have studied heavy metal content in groundwater around two proposed uranium mining areas in Jharkhand, India and results of the study showed that the level of most elements determined was within the Indian and WHO standards for drinking water. Frisbie et al. (2002) have determined the concentrations of arsenic and other toxic elements in drinking water in Bangladesh, and results of the study confirmed that the Bangladesh is contaminated with arsenic and other toxic elements that might affect human health as well as the health of the ecosystem. Kumar et al. (2015) have analyzed different trace metals in drinking water of Jammu & Kashmir, India and results showed that the concentrations of metals in water samples were below the prescribed limits. Muhammad et al. (2011) have investigated heavy metals in drinking water of Kohistan region, northern Pakistan and results showed that majority of heavy metals were found within the permissible limits set by WHO and Pak EPA. Li and Zhang (2010) have studied the concentrations of dissolved trace elements and heavy metals in the surface water of the upper Han river and results showed that arsenic was the most important pollutant causing carcinogenic and non-carcinogenic concerns, particularly for sensitive children.

The main objectives of the present study are to: (1) study the physico-chemical contents in groundwater. (2) quantify the concentrations of trace metals (Li, Be, B, Al, Cr, Mn, Fe, Co, Ni, Cu,

0016-7622/2017-90-1-77/$ 1.00 © GEOL. SOC. INDIA | DOI: 10.1007/s12594-017-0666-z

Zn, As Se, Mo, Cd, Sb, Ba and Pb) in groundwater; (3) compare the observed concentrations of metals with the national and international drinking water quality guidelines; (4) evaluate the carcinogenic and non-carcinogenic health risks associated with selected levels of metals in humans via ingestion of, and dermal contact with water in the study region by children and adults; (5) compare the carcinogenic and non-carcinogenic health hazards results with acceptable values set by the USEPA.

MATERIALS AND METHODS

Study Area

The Sikar district is situated in northeastern part of Rajasthan (Fig.1). The Sikar district is located between 27°21" and 28°12" N latitudes and between 74°44" and 75°25" E longitudes. The total human population of Sikar district is about 27 lakh (2011 census) and has a geographical area of 7,742 km^2. The climate of the district is characterized by a chilly winter season, scanty rainfall and hot summer season. The minimum and maximum temperature is 3°C and 46°C, respectively. The annual mean rainfall is 466 mm.

The rock types in the area belong exclusively to Delhi Supergroup of metasediments which are separated from the older Aravallis by a conspicuous unconformity. The prominent exposures are seen on Neem-ka-Thana hills situated in the eastern and northeastern parts of the area. The Delhi Supergroup rocks are divided into Alwar and Ajabgarh Group. The eastern part is represented by Alwar Group of rocks which comprises of quartzite, marble, schist and gneiss. Among metallic minerals copper and iron ore are the most important deposits. Among non-metallic minerals, apatite, calcite, dolomite, fluorite, limestone, barites and pyrrohotite, mica, quartz are also extracted, radioactive minerals and molybdenite in Khandela-Ghateshwar area are present. The western part is covered with sand dunes. The rocks of Ajabgarh Formation are characterized by large portion of calcareous rocks. The main rock types are marble, calc-gneisses, calc silicates, phyllites and mica schists. The general trend of the rocks is north-east-southwest (NE-SW) with low dips towards west (Kumar et al. 2009). The Ajabgarh Formation represented by quartzites, gneisses and amphibole marble are best exposed south of Kotri Rampura and around Atheaga. The soils of the district are predominantly light textured, weak structured, well drained alluvial and eolian in nature. The study region is bounded on the north by Jhunjhunun district, on the north-west by Churu district, on the southwest by Nagaur district and on the southeast by Jaipur district.

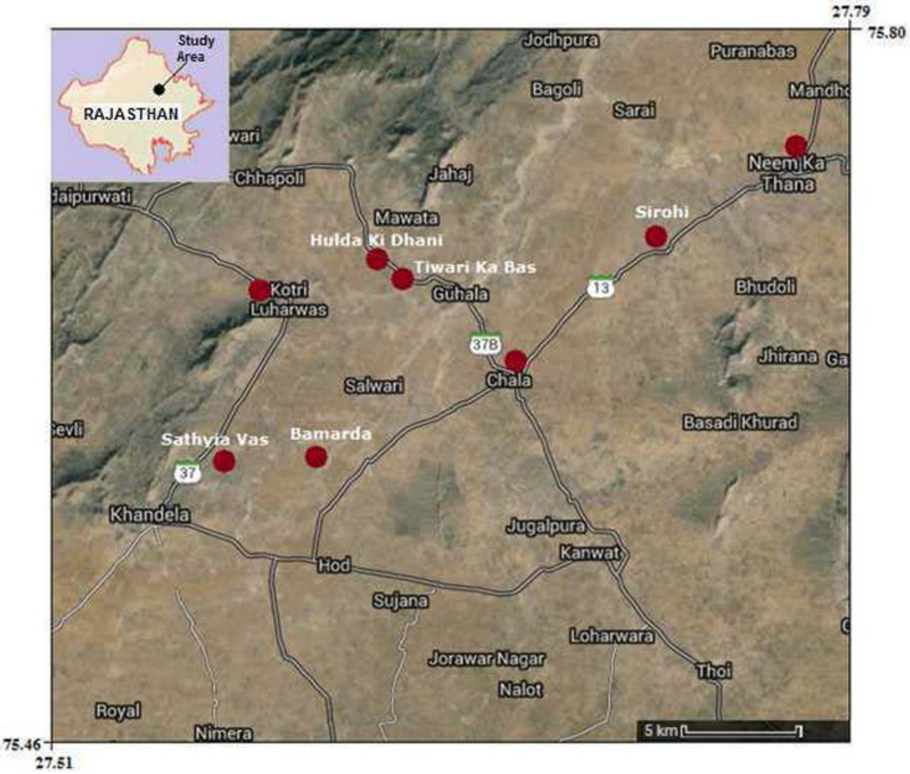

Fig.1. Location map of the study area and major sampling sites.

Water Sampling and Physico-chemical Analysis

Groundwater samples were collected from eight sampling sites namely, Sathyia Vas, Bamarda, Chala, Kotri Luharwas, Tiwari ka bas, Hulda Ki Dhani, Sirohi, Nim Ka Thana in Sikar district of Rajasthan, India. A global positioning system was used to locate the sampling sites. The samples were collected during February and March (winter) from electric motors (EM) and manually operated hand-pumps (HP) of privately owned or from hand-pumps established by Municipal Corporation in residential localities of studied habitations. Prior to collection, the water samples were filtered through pre-washed 0.45 μm millipore nitrocellulose filters (disposable not reusable) to remove suspended matter/sediments and acidified to pH < 2 (0.2% v/v) using supra pure nitric acid (HNO_3) for preservation and then refrigerated in pre-cleaned acid-washed high density polyethylene (HDPE) containers until analysis. On-site observations like location, source and depth of the hand pumps were recorded. Water pH, electrical conductivity (EC), total dissolved solids (TDS), salinity and temperature were analyzed *in situ* with the help of portable micro controller water analysis kit NPC 362D.

Analytical Procedure

Trace elements in water samples were determined from acidified, filtered and diluted solutions after adjusting the total dissolved solids to lower levels (~20-30 mg/l) recommended for high resolution instruments. The clear solutions were analyzed at CSIR-NGRI, Hyderabad, using high resolution inductively coupled plasma mass spectrometer (HR-ICP-MS) (Nu Instruments Attom®, UK) in jump-wiggle mode which permits the analytes of interest (viz., Li, Be, B, Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, As Se, Mo, Cd, Sb, Ba, Pb) to be measured accurately. The samples introduction consisted of a standard Meinhard® nebulizer with a cyclonic spray chamber housed in Peltier cooling system. All quantitative measurements were performed using the instrument software (Attolab v.1), while the data processing was done using Nu Quant®, which uses knowledge-driven routines in combination with numerical calculations (quantitative analysis) to perform an automated/manual interpretation of the spectrum of interest. Instrumental parameters are given in Table 1. Instrument was optimized using 1μg/l tuning solution and the sensitivity of ^{114}In was about 1 million cps. Oxide and oxy-hydroxide ratios were low (< 0.2%) and the double charges ions ratio was < 3%. Mass bias fractionation and several well-known isobaric interferences were addressed by using certified geochemical reference materials. External drift was corrected by repeated analyses of a NIST1640a (NIST, USA). Instrument response was corroborated relative to two analyses of NIST1643e and NIST1640a (NIST, USA). Precision and accuracy are better than RSD 3% for the majority of trace elements.

Table 1. Instrument operating conditions of HR-ICP-MS (Nu Attom)

Plasma control parameters	
Coolant gas flow rate	13 l/min
Auxillary gas flow rate	1.05 l/min
Nebulizer gas pressure	33.3 psi
Forward RF power	1300 W
Peristaltic rate	15 rpm
Peltier cooling temperature	5 °C
Spray chamber	Glass-Cyclonic
Sample uptake rate	0.2 ml/min
Detector	Ion counter and faraday
Sensitivity	1.1×10^6 counts for ^{115}In 2.1×10^6 counts for ^{238}U
Scan type	Magnet jumping with electric scan over a small mass range
Ion lens setting	Optimized for sensitivity and resolution peaks
Data acquisition parameters	
Dwell time per peak	3 ms
Switch delay per peak	200 µs
Number of sweeps	50
Number of cycles	3
Instrument resolution	300
Internal standard	^{103}Rh

Human Health Risk Assessment

Risk assessment is a multi-step procedure including collection and evaluation of data, assessment of exposure, evaluation of toxicity and risk characterization (USEPA 1989; USDOE 2011). Exposure to human being to trace metals could occur through three main routes including direct ingestion, inhalation and dermal absorption through skin, while ingestion and dermal absorption are common routes for water exposure (USEPA 1989; Miguel et al. 2007; Wu et al. 2009). Both carcinogenic and non-carcinogenic risks related to these exposure routes were separately assessed (Ni et al. 2011). The dose received (chronic daily intake, CDI) via two exposure routes was computed using Eqs. (1) to (9) adapted from USDOE Risk Assessment Information System (USDOE 2011) and USEPA (USEPA 1989, 2004; 1996; 1997; 2001)for two sub-population groups of children and adults.

Non-carcinogenic (nc) hazard

$$CDI_{ing-nc} = \frac{C_W \times IRW \times EF \times ED}{BW \times AT} \quad (1)$$

$$CDI_{derm-nc} = \frac{DA_{event} \times SA \times EF \times ED \times EV}{BW \times AT} \quad (2)$$

$$DA_{event} = K_P \times C_W \times ET \times CF \quad (3)$$

Carcinogenic (ca) risk

$$CDI_{ing-ca} = \frac{C_W \times IRW_{adj} \times EF}{AT} \quad (4)$$

$$IRW_{adj} = \frac{ED_C \times IRW_C}{BW_C} + \frac{(ED_a - ED_C) \times IRW_a}{BW_a} \quad (5)$$

$$CDI_{derm-ca} = \frac{DA_{event} \times SA_{adj} \times EF}{AT} \quad (6)$$

$$SA_{adj} = \frac{ED_C \times SA_C \times EV_C}{BW_C} + \frac{(ED_a - ED_C) \times SA_a \times EV_a}{BW_a} \quad (7)$$

$$DA_{event} = K_P \times C_W \times ET_{adj} \times CF \quad (8)$$

$$ET_{adj} = \frac{(ET_C \times ED_C) + ((ED_a - ED_C) \times ET_a)}{ED_a} \quad (9)$$

The description and values of the different parameters used for health risk assessment are summarized in Table 2(USEPA 2004; USDOE 2011; Rani et al. 2013; Harries and Harper 2004; Duggal et al. 2013).

Non-carcinogenic risks are assessed by estimating the hazard quotient (HQ). To yield the HQ, the estimated CDIs for each metal are divided by corresponding reference dose (RfD) (Eqs. 10-12):

$$HQ_{ing} = \frac{CD_{ing-nc}}{RfD_{ing}} \quad (10)$$

$$HQ_{derm} = \frac{CD_{derm-nc}}{RfD_{derm}} \quad (11)$$

$$RfD_{derm} = RfD_{ing} \times GIABS \quad (12)$$

RfD is the maximum permissible concentration of a metal that will not pose any deleterious effects on human health. In present investigation, RfD_{ing} for water ingestion and RfD_{derm} for dermal absorption are taken into account. The reference doses for dermal absorption were calculated by multiplying the water ingestion reference doses with gastrointestinal absorption (GIABS) factors as suggested by USDOE-RAIS (Eq. 12) (USDOE 2011). Combination of non-carcinogenic risks on human across different exposure routes can be obtained by summing the HQ value of each exposure route for each metal to produce the screening level hazard index (HI) (Eqs. 13, 14):

$$HQ_{ing/derm} = \Sigma\ HQ_{ing/derm} \quad (13)$$

$$HQ_{total} = HQ_{ing} + HI_{derm} \quad (14)$$

If the HI value is less than unity, non-carcinogenic risks are not expected to occur from any chemical. If HI exceeds 1, there may be concern for potential non-carcinogenic effects (USEPA 1989).

The potential excess lifetime cancer risks (ELCRs) for water ingestion of Pb and As were calculated by multiplying the chronic daily intake values with the corresponding cancer slope factors (CSFs) of 8.5×10^{-3} and 1.5 mg/kg/day, respectively recommended by USDOE-RAIS (Eq. 15)(USDOE 2011). However, the ELCRs for dermal absorption are calculated by multiplying the CDI values with CSFs and divided by GIABS factors suggested by USDOE-RAIS(Eq. 16) (USDOE 2011). The estimated value of carcinogenic risk is the probability of an individual developing any type of cancer from lifetime exposure to carcinogenic hazards. Finally, the total excess lifetime cancer risks ($ELCR_{total}$) was calculated by adding the ELCRs through ingestion and dermal absorption pathways ($ELCR_{ing}$ and $ELCR_{derm}$) (Eqs. 17,18). In general, the ELCRs lower than 10^{-6} (a probability of 1 chance in 1000000 of an individual developing cancer) are considered to be negligible, while ELCRs above 10^{-4} are considered unsafe by most of the international regulatory agencies (USEPA 1989; Rodriguez-Proteau and Grant 2005).

$$ELCR_{ing} = CDI_{ing-nc} \times CSF_{ing} \quad (15)$$

$$ELCR_{derm} = CDI_{derm} \times (CSF_{ing} / GIABS) \quad (16)$$

$$ELCR_{ing/derm} = \Sigma\ ELCR_{ing/derm} \quad (17)$$

$$ELCR_{total} = ELCR_{ing} + ELCR_{derm} \quad (18)$$

RESULTS AND DISCUSSION

Physico-chemical Characteristics of Water Samples

The parameters of water samples, including water temperature,

Table 2. Summary of exposure assumptions used to calculate drinking water intake for Sikar district, Rajasthan

Exposure Route/Exposure Factor	Symbol	Value	Units	Reference/Source
Water ingestion rate-adult	IRW_a	2	L/day	(Rani et al. 2013; Harries and Harper 2004)
Water ingestion rate-child	IRW_c	1	L/day	(Harries and Harper 2004)
Age-adjusted water ingestion rate	IRW_{adj}	2.229	L-year/kg-day	Equation 5
Contaminant concentration in groundwater	C_w	COPC-specific	µg/l	
Exposure frequency	EF	365	days/year	(Duggal et al. 2013)
Exposure duration-adult	ED_a	70	Year	(Harries and Harper 2004)
Exposure duration-child	ED_c	6	Year	(Harries and Harper 2004)
Body weight-adult	BW_a	70	Kg	(Rani et al. 2013; Harries and Harper 2004)
Body weight-child	BW_c	15	Kg	(Harries and Harper 2004)
Average time-adult	AT_a	25550	Days	AT = EF × ED
Average time-child	AT_c	2190	Days	AT = EF × ED
Absorbed dose per event	DA_{event}	Calculated value	mg/cm^2-event	Equation 3
Exposure time-adult	ET_a	0.58	hours/day	(USEPA 2004)
Exposure time-child	ET_c	1	hours/day	(USEPA 2004)
Age-adjusted exposure time	ET_{adj}	0.616	hours/day	Equation 9
Event frequency-adult	EV_a	1	event/day	(USEPA 2004)
Event frequency-child	EV_c	1	event/day	(USEPA 2004)
Skin surface area-adult	SA_a	18000	cm^2	(USEPA 2004)
Skin surface area-child	SA_c	6600	cm^2	(USEPA 2004)
Age-adjusted skin surface area	SA_{adj}	19097	cm^2-yr/kg-day	Equation 7
Conversion factor	CF	0.001	L/cm^3	1L = 1000 cm^3
Dermal permeability coefficient	K_p	Contaminant of potential concern (COPC)-specific	cm/hour	(USDOE 2011)
Gastrointestinal absorption factor	GIABS	COPC-specific	Unitless	(USDOE 2011)
Reference dose-ingestion/dermal	$RfD_{ing/derm}$	COPC-specific	mg/kg/day	(USDOE 2011), Equation 12
Cancer slope factor-ingestion	CSF_o	COPC-specific	(mg/kg/day)$^{-1}$	(USDOE 2011)
Chronic daily intake-non-carcinogenic ingestion	CDI_{ing-nc}	Calculated value	mg/kg/day	Equation 1
Chronic daily intake-non-carcinogenic dermal	$CDI_{derm-nc}$	Calculated value	mg/kg/day	Equation 2
Chronic daily intake-carcinogenic ingestion	CDI_{ing-ca}	Calculated value	mg/kg/day	Equation 4
Chronic daily intake-carcinogenic dermal	$CDI_{derm-ca}$	Calculated value	mg/kg/day	Equation 6

Table 3. Basic parameters of samples

Sr. No.	Sample Location	Latitude (N)	Longitude (E)	Altitude (m)	Source	Type	Depth (m)	Temp (ºC)	pH	TDS (mg/l)	EC (µS/cm)	Salinity (ppt)
1	Sathiya Vas	27º37'25º	75º31'26º	464	HP	Public	105	25	7.0	652	1309	0.7
2	Bamarda	27º37'32º	75º34'5º	446	HP	Public	90	24	8.2	380	760	0.3
3	Chala	27º39'22º	75º39'35º	436	EM	Public	185	22	7.6	399	796	0.3
4	Kotri Luharwas	27º41'17º	75º33'46º	442	HP	Public	85	23	7.3	417	839	0.3
5	Tiwari Ka Bas	27º42'4º	75º36'26º	429	EM	Public	185	20	7.1	378	787	0.3
6	Hulda Ki Dhani	27º42'21º	75º36'5º	429	EM	Public	140	20	7.2	314	629	0.2
7	Sirohi	27º42'30º	75º43'41º	439	HP	Public	100	24	8.0	367	752	0.3
8	Nim Ka Thana	27º44'20º	75º46'58º	453	HP	Private	90	23	7.4	262	525	0.1

Table 4. Concentration of dissolved metals (µg/l) in thedrinking water

Element	1 Sathiya-vas	2 Bamarda	3 Chala	4 Kotri Luharwas	5 TiwariKa Bas	6 Hulda Ki Dhani	7 Sirohi	8 Nim Ka Thana	Range	Mean	SD
Li	0.97	0.69	0.79	0.72	0.65	0.64	0.75	0.67	0.64–0.97	0.74	0.10
Be	0.03	0.04	0.63	0.13	0.03	0.03	0.03	0.02	0.02–0.63	0.12	0.20
B	284.96	213.51	259.61	341.78	153.00	139.90	327.56	231.16	139.90–341.78	243.94	69.53
Al	65.18	81.12	14.98	47.72	14.98	22.81	55.63	36.62	14.98–81.12	42.38	22.76
Cr	2.79	3.48	2.45	3.45	2.04	2.24	3.08	2.46	2.04–3.48	2.75	0.51
Mn	21.63	9.95	26.98	16.65	4.38	4.11	72.08	31.84	4.11–72.08	23.45	20.67
Fe	121.66	132.64	49.99	128.03	46.49	44.95	97.96	151.47	44.95–151.47	96.65	40.74
Co	0.51	0.35	0.74	0.27	0.15	0.25	1.22	0.85	0.15–1.22	0.54	0.34
Ni	4.99	11.27	1.19	4.86	1.50	2.56	101.57	4.00	1.19–101.57	16.49	32.29
Cu	2.44	8.85	1.82	2.84	1.35	1.61	10.34	3.69	1.35–10.34	4.12	3.26
Zn	2328.96	539.40	65.27	464.23	49.93	28.42	705.77	686.04	28.42–2328.96	608.50	702.20
As	1.20	0.80	1.60	0.67	1.45	0.79	0.93	0.62	0.62–1.60	1.01	0.34
Se	16.50	4.87	4.90	8.52	4.78	12.31	4.70	3.25	3.25–16.50	7.48	4.36
Mo	12.12	6.06	16.49	14.30	6.05	7.29	6.07	8.04	6.05–16.49	9.55	3.89
Cd	2.55	0.36	0.09	0.13	0.39	5.62	0.60	1.00	0.09–5.62	1.34	1.78
Sb	0.51	2.73	1.24	1.58	0.86	2.08	1.89	4.37	0.51–4.37	1.91	1.14
Ba	105.74	135.26	70.22	81.95	33.56	43.05	35.26	132.57	33.56–135.26	79.70	38.89
Pb	13.98	4.19	1.25	1.86	4.95	49.50	7.58	7.91	1.25–49.50	11.40	14.89

pH, TDS, EC, salinity and sampling depth were summarized in Table 3. Water pH is considered as one of the most significant water quality parameters in the aquatic system. The solubility of metal ions in groundwater depends on its pH. At low pH value, the heavy metals tend to be more toxic due to more solubility in acidic water. WHO suggested that water pH has no direct effects on human health (WHO 2011). However, low and high pH values attribute sour and bitter taste to drinking water, respectively. The pH value in the study region was slightly alkaline and varied marginally between 7.0 and 8.2. All the samples have pH values within permissible limits set by the WHO (2011), USEPA (2011) and BIS (2012). The lowest pH value (7.0) was recorded in the groundwater of Sathyia Vas, while the highest pH value (8.2) in Bamarda. The TDS, EC and salinity of the groundwater samples ranged from 262 to 652 mg/l, 525 to 1309 µS/cm and 0.1 to 0.7 ppt with averages of 396 mg/l, 800 µS/cm and 0.3 ppt, respectively. The salinity in groundwater was mainly controlled by fresh water influx, evaporation rate and rainfall (Sridhar et al. 2006). The highest TDS, EC and salinity values were observed in the groundwater of Sathyia Vas, may indicate the possibility of high rate of withdrawal of groundwater. The lowest TDS, EC and salinity values in the groundwater of Nim Ka Thana site indicate the availability of fresh groundwater aquifer system. TDS and EC values at each of the location were within the permissible limits. Results showed that water temperature in the study region varied between 20°C and 25°C. The depth of the groundwater levels from the surface ranged from 85 to 185 m (average 122.5 ± 39 m).

Concentration of Metals in Water

The concentrations of 18 elements (Li, Be, B, Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Ba and Pb) in groundwater were summarized in Table 4. The concentration of Li, Be, B, Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, As Se, Mo, Cd, Sb, Ba and Pb in water samples ranged as follows: 0.64–0.97, 0.02–0.63, 139.90–341.78, 14.98–81.12, 2.04–3.48, 4.11–72.08, 44.95–151.47, 0.15–1.22, 1.19–101.57, 1.35–10.34, 28.42–2328.96, 0.62–1.60, 3.25–16.50, 6.05–16.49, 0.09–5.62, 0.51–4.37, 33.56–135.26 and 1.25–49.50µg/l, respectively. Metal concentrations were compared with water quality standards (or guidelines) for drinking water regulated by WHO (2011, 2008 2004), USEPA (2011) and BIS (1993, 2012) (Table 5). The concentrations of Be, B, Al, Cr, Fe, Cu, Zn, As, Mo, Sb and Ba at all sites were below the maximum permitted concentration for drinking water quality guidelines. However, the concentrations of Mn, Ni, Se, Cd and Pb exceeded the permissible limits at some sampling sites.

The local geology, atmospheric sources, fertilizers factories, chemical factories and cement factories are the major sources of Mn, Ni, Se, Cd and Pb in drinking water in the study region. Rodell et al. (2009) have concluded that withdrawal for irrigation and other uses also depleting the groundwater reserves of Rajasthan. Mn at Sirohi site exceeded USEPA drinking water quality guidelines. The high level of Mn in drinking water may cause neurological damage (WHO 2011). Ni at Sirohi site was above the WHO, USEPA and BIS guidelines. Ni is a “probable carcinogen to humans” (ATSDR 2005). Ni level above permissible limit may cause decrease in body weight, liver and heart damage (USEPA 2011). The Se and Pb at Sathiya Vas and Hulda Ki Dhani sites were found to exceed BIS and WHO drinking water quality guidelines, respectively. The high intake of Se in drinking water is associated with hair or nail loss, decayed teeth and gastrointestinal diseases (WHO 2011). Pb toxicity causes many non-carcinogenic disorders in humans. Pb is a “possible carcinogen to humans” (WHO 1996). Pb toxicity causes anaemia, respiratory disorders, gastroenteritis, vomiting and nausea. Fetuses, infants and young children are most vulnerable to Pb poisoning (WHO 2004). Cd at Hulda Ki Dhani site exceeded WHO and USEPA guidelines. Cd is a “probable human carcinogen”. The brain, bones, lungs, kidneys and liver are the main target organ for Cd toxicity(ATSDR 2012). Se, Cd and Pb metals at Hulda Ki Dhani site exceeded the permissible limits may be due to the site belongs to Khetri copper belt, where younger rocks belonging to Ajabgarh Group and older rocks to Alwar Group are exposed.

Table 5. Risk-based drinking water criteria and the percentage of samples exceeding these criteria

Parameters	Risk-based drinking water criteria (mg/l)			% of samples exceeding criteria		
	WHO	U.S. EPA	BIS (Indian) IS: 10500	WHO	U.S. EPA	BIS (Indian) IS: 10500
Li	None	None	None	NA	NA	NA
Be	None	0.004	None	NA	0	NA
B	2.4	None	5	0	NA	0
Al	0.2	0.2	0.2	0	0	0
Cr	0.05	0.1	0.05	0	0	0
Mn	0.4	0.05	0.5	0	12.5	0
Fe	None	0.3	1.0	NA	0	0
Co	None	None	None	NA	NA	NA
Ni	0.07	0.100	0.02	12.5	12.5	12.5
Cu	2.0	1.3	1.5	0	0	0
Zn	3	5	10	0	0	0
As	0.01	0.01	0.05	0	0	0
Se	0.04	0.05	0.01	0	0	25
Mo	0.07	None	0.07	0	NA	0
Cd	0.003	0.005	0.01	12.5	12.5	0
Sb	0.02	0.006	None	0	0	NA
Ba	0.7	2.0	0.7	0	0	0
Pb	0.01	0.015	0.1	25	12.5	0
pH	6.5–8.5	6.5–8.5	6.5–9.2	0	0	0
TDS	<600	500	2000	12.5	12.5	0
EC	1500	None	None	0	NA	NA
Salinity	None	None	None	NA	NA	NA

Inter-metal Relationship

Table 6 summarizes the inter-metals correlation coefficient in groundwater. The inter-metal relationships provide valuable information on metal sources and pathways (Frisbie et al. 2002). The correlation analysis showed strong positive correlations (r > 0.7) in some heavy metal pairs, such as,Li–Zn (r = 0.85), Li–TDS (r = 0.91), Li–EC (r = 0.90), Li–salinity (r = 0.89), Zn–TDS (r = 0.80), Zn–EC (r = 0.79), Zn–salinity (r = 0.81), TDS–EC (r = 1.0), TDS–salinity (r = 0.99), EC-salinity (r = 0.99), Be–Mo (r = 0.75), Al–Cr (r = 0.83), Al–Fe (r = 0.74), Mn–Co (r = 0.95), Mn–Ni (r = 0.88), Co–Ni (r = 0.74), Fe–Ba (r = 0.81), Ni–Cu (r = 0.78), Cu–pH (r = 0.88), As–depth (r = 0.84), Se–TDS (r = 0.71), Se–EC (r = 0.70), Se–salinity (r = 0.70), Cd–Pb (r = 0.98) and strong negative correlations, such as, Al–depth (r = -0.80), Cr–depth (r = -0.75), Fe–depth (r = -0.90), As–Sb (r = -0.70), Sb–TDS (r = -0.72), Sb–EC (r = -0.74), Sb–salinity (r = -0.73). A strong positive correlation was found among Mn, Co and Ni, indicating that these three metals have similar pollution source. pH showed strong positive correlation with copper. Muhammad et al. (2011) have also reported a significant positive correlation between pH and Cu in drinking water of Kohistan region, northern Pakistan. Cd and Pb may be from the same pollution source due to the strong positive correlation between them. Cadmium occurs naturally with lead in sulphide ores (WHO 2011), present in Khetri copper belt. The results showed that Ni was positively and significantly correlated with Cu. Nickel-rich pyrrohotite has been found along with the copper ores in the Khetri copper belt.

It is evident from Tables 4 and 5, if a sample exceeded the WHO permissible limit for Mn, then the sample also exceeded the permissible limit for Ni (r = 0.88). Similarly, if a sample exceeded the WHO permissible limit for Cd, then the sample also exceeded the permissible limit for Pb (r = 0.98). The strong positive correlation between As and

Table 6. Correlation among trace metals, and between trace metals and physico-chemical parameters

	Li	Be	B	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Mo	Cd	Sb	Ba	Pb	pH	TDS	EC	Salinity	Depth
Li	1	0.20	0.54	0.37	0.20	0.25	0.21	0.24	0.06	-0.05	**0.85**	0.36	0.59	0.52	-0.03	-0.53	0.20	-0.20	-0.20	**0.91**	**0.90**	**0.89**	-0.12
Be		1	0.17	-0.43	-0.12	0.04	-0.39	0.16	-0.20	-0.28	-0.31	0.60	-0.21	**0.75**	-0.31	-0.25	-0.09	-0.30	0.10	0.03	0.01	-0.03	0.54
B			1	0.44	0.68	0.65	0.51	0.52	0.47	0.37	0.43	-0.15	0.03	0.49	-0.48	-0.13	0.14	-0.53	0.23	0.38	0.37	0.33	-0.52
Al				1	**0.83**	0.21	**0.74**	0.14	0.30	0.69	0.61	-0.45	0.19	-0.20	-0.15	0.13	0.58	-0.22	0.49	0.40	0.38	0.42	**-0.80**
Cr					1	0.25	0.66	0.12	0.32	0.65	0.27	-0.48	-0.02	0.11	-0.39	0.10	0.43	-0.39	0.58	0.22	0.21	0.19	**-0.75**
Mn						1	0.23	**0.95**	**0.88**	0.63	0.21	-0.08	-0.29	-0.06	-0.30	0.15	-0.15	-0.29	0.45	-0.06	-0.05	-0.02	-0.30
Fe							1	0.24	0.07	0.42	0.54	-0.65	-0.05	-0.02	-0.31	0.52	**0.81**	-0.38	0.25	0.12	0.10	0.08	**-0.90**
Co								1	**0.74**	0.55	0.19	-0.04	-0.34	-0.01	-0.26	0.30	0.01	-0.25	0.46	-0.13	-0.14	-0.10	-0.24
Ni									1	**0.78**	0.08	-0.13	-0.24	-0.36	-0.17	0.02	-0.37	-0.11	0.55	-0.09	-0.07	-0.02	-0.28
Cu										1	0.10	-0.36	-0.38	-0.48	-0.32	0.32	0.16	-0.27	**0.88**	-0.15	-0.14	-0.08	-0.55
Zn											1	-0.04	0.61	0.14	0.10	-0.22	0.42	-0.09	-0.22	**0.80**	**0.79**	**0.81**	-0.48
As												1	0.001	0.33	-0.22	**-0.70**	-0.40	-0.25	-0.20	0.38	0.39	0.40	**0.84**
Se													1	0.25	0.68	-0.51	-0.03	0.55	-0.58	**0.71**	**0.70**	**0.70**	-0.11
Mo														1	-0.20	-0.37	0.11	-0.28	-0.28	0.41	0.39	0.31	0.16
Cd															1	-0.02	-0.20	**0.98**	-0.42	0.02	0.01	0.05	0.04
Sb																1	0.53	0.04	0.38	**-0.72**	**-0.74**	**-0.73**	-0.48
Ba																	1	-0.30	0.21	0.11	0.08	0.07	-0.59
Pb																		1	-0.33	-0.15	-0.16	-0.11	0.08
pH																			1	-0.33	-0.33	-0.28	-0.30
TDS																				1	**1.00**	**0.99**	-0.06
EC																					1	**0.99**	-0.05
Salinity																						1	-0.04
Depth																							1

Table 7. Non-carcinogenic health risks of metals by ingestion and dermal pathways

Element	RfD_{ing} (mg/kg/day)	Gastrointestinal Absorption Factor (GIABS)	HQ_{ing}		HQ_{derm}		HI = ©HQs	
			Adult	Child	Adult	Child	Adult	Child
Li	2.00E-03	1.00E+00	1.05E-02	2.45E-02	5.48E-05	1.62E-04	1.06E-02	2.47E-02
Be	2.00E-03	7.00E-03	1.68E-03	3.92E-03	1.25E-03	3.69E-03	2.93E-03	7.61E-03
B	2.00E-01	1.00E+00	3.49E-02	8.13E-02	1.82E-04	5.37E-04	3.51E-02	8.18E-02
Al	1.00E+00	1.00E+00	1.21E-03	2.83E-03	6.32E-06	1.86E-05	1.22E-03	2.85E-03
Cr	1.50E+00	1.30E-02	5.24E-05	1.22E-04	2.10E-05	6.20E-05	7.34E-05	1.84E-04
Mn	4.60E-02	4.00E-02	1.46E-02	3.39E-02	1.90E-03	5.60E-03	1.65E-02	3.95E-02
Fe	7.00E-01	1.00E+00	3.95E-03	9.20E-03	2.06E-05	6.08E-05	3.97E-03	9.26E-03
Co	3.00E-04	1.00E+00	5.17E-02	1.20E-01	1.08E-04	3.18E-04	5.18E-02	1.20E-01
Ni	2.00E-02	4.00E-02	2.35E-02	5.50E-02	6.15E-04	1.82E-03	2.41E-02	5.68E-02
Cu	4.00E-02	1.00E+00	2.94E-03	6.86E-03	1.54E-05	2.10E-03	2.96E-03	8.96E-03
Zn	3.00E-01	1.00E+00	5.80E-02	1.35E-01	1.82E-04	5.36E-04	5.82E-02	1.36E-01
As	3.00E-04	1.00E+00	9.59E-02	2.24E-01	5.01E-04	1.48E-03	9.64E-02	2.25E-01
Se	5.00E-03	1.00E+00	4.27E-02	9.97E-02	2.23E-04	6.58E-04	4.29E-02	1.00E-01
Mo	5.00E-03	1.00E+00	5.46E-02	1.27E-01	2.85E-04	8.41E-04	5.49E-02	1.28E-01
Cd	5.00E-04	5.00E-02	7.67E-02	1.79E-01	8.01E-03	2.36E-02	8.47E-02	2.03E-01
Sb	4.00E-04	1.50E-01	1.36E-01	3.18E-01	4.75E-03	1.40E-02	1.41E-01	3.32E-01
Ba	2.00E-01	7.00E-02	1.14E-02	2.66E-02	8.49E-04	2.51E-03	1.22E-02	2.91E-02
Pb	3.50E-03	1.00E+00	9.31E-02	2.17E-01	4.86E-05	1.43E-04	9.31E-02	2.17E-01

Table 8. Total hazard index and excess lifetime cancer risk due to ingestion and dermal pathways

Sample Location	Adult			Child			Excess lifetime cancer risk		
	HI_{ing}	HI_{derm}	HI_{total}	HI_{ing}	HI_{derm}	HI_{total}	$ELCR_{ing}$	$ELCR_{derm}$	$ELCR_{total}$
Sathiya vas	9.44E-01	2.25E-02	9.67E-01	2.20E+00	6.65E-02	2.27E+00	6.11E-05	3.04E-07	6.14E-05
Bamarda	5.70E-01	1.33E-02	5.83E-01	1.33E+00	4.40E-02	1.37E+00	3.93E-05	2.02E-07	3.95E-05
Chala	5.45E-01	1.52E-02	5.60E-01	1.27E+00	4.58E-02	1.32E+00	7.68E-05	4.04E-07	7.72E-05
Kotri Luharwas	4.98E-01	1.01E-02	5.08E-01	1.16E+00	3.13E-02	1.19E+00	3.25E-05	1.69E-07	3.27E-05
Tiwari Ka Bas	3.88E-01	6.86E-03	3.95E-01	9.04E-01	2.10E-02	9.25E-01	7.06E-05	3.66E-07	7.10E-05
Hulda ki dhani	1.13E+00	4.13E-02	1.17E+00	2.64E+00	1.23E-01	2.76E+00	5.11E-05	2.06E-07	5.13E-05
Sirohi	8.30E-01	2.03E-02	8.50E-01	1.94E+00	6.54E-02	2.01E+00	4.65E-05	2.36E-07	4.67E-05
Nim Ka Thana	8.01E-01	2.26E-02	8.24E-01	1.87E+00	6.84E-02	1.94E+00	3.18E-05	1.57E-07	3.19E-05
Range	3.88E-01 – 1.13E+00	6.86E-03 – 4.13E-02	3.95E-01 – 1.17E+00	9.04E-01 – 2.64E+00	2.10E-02 – 1.23E-01	9.25E-01 – 2.76E+00	3.18E-05 – 7.68E-05	1.57E-07 – 4.04E-07	3.19E-05 – 7.72E-05
Mean	7.13E-01	1.90E-02	7.32E-01	1.66E+00	5.82E-02	1.72E+00	5.12E-05	2.56E-07	5.15E-05

depth (r = 0.84), indicating that drilling deeper hand-pumps/ electric motors can assess groundwater with significantly higher As concentrations. The strong negative correlations between Cr and depth (r = -0.75), and Fe and depth (r = -0.90), indicates that Cr and Fe concentrations decreases with depth.

Human Health Risk Assessment

The concentrations of metals in water samples are used to assess human exposure through ingestion and dermal absorption pathways. Two population groups are considered: adults and children. Table 7 and 8 present the HQ and HI values estimated for local residents based on the ingestion and dermal absorption of water. The calculated mean levels of HQ_{ing} and HQ_{derm} in the study region were observed in the order of Sb>As>Pb>Cd>Zn>Mo>Co> Se>B>Ni>Mn> Ba>Li> Fe>Cu>Be>Al>Cr and Cd>Sb>Mn>Be>Ba>Ni>As>Mo>Se>Zn> B>Co>Li>Pb>Cr>Fe>Cu>Al, respectively for both the adult and child. Hazard quotients (HQ_{ing} and HQ_{derm}) of all the metals calculated through ingestion and dermal absorption pathways for adults and children were found to be lower than unity, indicating that the metals would not pose any adverse effect and non-carcinogenic health risk to the habitants. The results indicated that Sb, As, Pb and Cd were the major contributors to the ingestion exposure to the inhabitants, while Cr, Al and Be were the least participants. In case of dermal exposure, Cd, Sb and Mn were the largest, while Al, Cu and Fe were the least contributors.

HI_{ing} (hazard index via ingestion) and HI_{derm} (hazard index via dermal absorption) were estimated for each sampling site to assess the overall non-carcinogenic risk posed by trace metals through ingestion and dermal absorption routes. Finally, the HI_{total} was computed for each sampling site by adding the HIs via ingestion and dermal absorption pathways (HI_{ing} and HI_{derm}, respectively) (Table 8). For adults, the HI_{ing}, HI_{derm} and HI_{total} values were ranged from 3.88E-01–1.13E+00, 6.86E-03–4.13E-02 and 3.95E-01–1.17E+00 with mean values of 7.13E-01, 1.90E-02 and 7.32E-01, respectively.HI_{total} at Hulda Ki Dhani site (1.17) was higher than unity and Sathyia Vas (9.67E-01), Sirohi (8.50E-01) and Nim Ka Thana (8.24E-01) sites were nearing unity, implying that trace metals may cause adverse health effects and non-carcinogenic health risks to the local residents. At Hulda Ki Dhani site, Pb posed serious health concern through ingestion, while other metals through ingestion and all the elements via dermal absorption had little or no health threat.

HI_{ing}, HI_{derm} and HI_{total} values for children were varied from 9.04E-01–2.64E+00, 2.10E-02–1.23E-01 and 9.25E-01–2.76E+00 with averages of 1.66E+00, 5.82E-02 and 1.72E+00, respectively. HI_{total} values at all the sampling sites except Tiwari Ka Bas site were found to be higher than unity and Tiwari Ka Bas (9.25E-01) site was nearing unity, indicating that the metals posed serious health concerns to the inhabitants. The mean levels of HI_{derm} at all the sampling sites were below unity, indicating that the metals would not pose any health risk to the consumers through dermal absorption. The result revealed that the HI_{total} mainly attributed to the ingestion pathway (Table 8). The non-carcinogenic risk assessment indicated that Sb, As, Pb and Cd are the important pollutants in the study region.

Carcinogenic risks were evaluated for As and Pb via ingestion and dermal absorption pathways (Table 8). The cancer slope factors (CSFs) were not available for the other trace metals. The cancer risk of As was higher than that of Pb for both ingestion and dermal absorption pathways. The results revealed that the $ELCR_{ing}$ was more than 2-3 orders of magnitude higher than the $ELCR_{derm}$. The ingestion route contributed more notably to the total excess lifetime cancer risk ($ELCR_{total}$) than the dermal absorption. Considering both exposure pathways, the $ELCR_{total}$ was calculated in the range 3.19E-05–7.72E-05 with a mean value of5.15E-05, depending on the sampling site. Therefore, the $ELCR_{total}$ of metals exposure in the study region was in accordance to the acceptable lifetime risks for carcinogens in drinking water (10^{-6}–10^{-4}).

However, there existed uncertainties for risk characterization, which was emphasized by the USEPA, RAIS and other documents (USEPA 2004; Wu et al. 2009; Li and Zhang, 2010; USDOE 2011). Uncertainties in some methodological aspects such as permeability constant (K_p), varied exposure condition due to different age and receptor, temporal and spatial variations in contaminant concentrations could not be quantified. In addition, exposure parameters employed in the study were from the RAIS, USEPA and WHO, which might not be specific to Indian conditions. However, daily water intake rate and body weight were considered from Indian reference for better estimation of the risk. Therefore, further precise risk characterization should be defined and risk assessment approaches may be modified through the investigation on the risk levels in the study region.

CONCLUSIONS

The physico-chemical parameters of water from all sampling sites were found within the national/international drinking water quality guidelines. Majority of trace metals (Be, B, Al, Cr, Fe, Cu, Zn, As, Mo, Sb and Ba) were found within the permissible limits prescribed by WHO, USEPA and BIS, India. However, the concentrations of Mn, Ni, Se, Cd and Pb were higher than their respective permissible limits at some sampling sites. The results revealed that the major contributing sources towards the drinking water contamination are local geology, atmospheric sources, fertilizers factories, chemical factories and cement factories. In this study, both non-carcinogenic and carcinogenic health risks of trace metals in groundwater via ingestion and dermal absorption pathways were evaluated.For children, the HI_{ing} (risk via ingestion) at all the sampling sites exceeded or nearing unity, suggesting that trace metals posed serious health concerns to the residents. Risk characterization showed that Sb, As, Pb and Cd were the major contributors to non-cancer health risks through ingestion pathway. The non-carcinogenic risks values indicate that the adverse effect of the metals on children's organs and systems is double to that of adults. The estimated total carcinogenic risk was found within the USEPA's acceptable cancer risk range of 10^{-6} to 10^{-4}. Both carcinogenic and non-carcinogenichealth risks were mainly attributed to the ingestion pathway.

References

Agency for Toxic Substances and Disease Registry (ATSDR) (2012) Toxicological Profile for Cadmium, Atlanta, GA: U.S. Department of Public Health and Human Services, Public Health Service.

Agency for Toxic Substances and Disease Registry (ATSDR) (2005) Toxicological Profile for Nickel, Atlanta, GA: U.S. Department of Public Health and Human Services, Public Health Service.

BIS, IS: 10500(1993) Standards for Drinking water, Bureau of Indian Standards, New Delhi.

BIS (2012) Drinking Water – Specification, Second Revision, Bureau of Indian Standards, New Delhi.

Donaldson, S.G., Van Oostdam, J., Tikhonov, C., Feeley, M., Armsstrong, B., Ayotte, P., Boucher, O., Bowers, W., Chan, L., Dallaire, F., Dallaire, R., Dewailly,É., Edwards, J., Egeland, G.M., Fontaine, J., Furgal, C., Leech, T., Loring, E., Muckle, G., Nancarrow, T., Pereg, D., Plusquellec, P., Potyrala, M., Receveur, O. and Shearer, R.G. (2010) Environmental contaminants and human health in the Canadian Arctic. Sci. Total Environ., v.408, pp.5165-5234.

Duggal, V., Mehra, R. and Rani, A. (2013) Determination of ^{222}RN level in groundwater using a RAD7 detector in the Bathinda district of Punjab, India. Radiat. Prot. Dosim., v.156, pp.239-245.

Frisbie, S.H., Ortega, R., Maynard, D.M. and Sarkar, B. (2002) The concentrations of arsenic and other toxic elements in Bangladesh's drinking water. Environ. Health Prespect., v.110, pp.1147-1153.

Giri, S., Mahato, M.K., Singh, G. and Jha, V.N. (2012) Risk assessment due to intake of heavy metals through the ingestion of groundwater around two proposed uranium mining areas in Jharkhand, India. Environ. Monit. Assess.,v.184,pp.1351-1358.

Harries, S., and Harper, B. (2004) Exposure Scenario for CTUIR traditional Subsistence Lifeways, Confederated Tribes of the Umatilla Indian Reservation, Department of Science and Engineering, Pendleton, Oregon.

Iqbal, J., Shah, M.H. and Akhter, G. (2013) Characterization, source apportionment and health risk assessment of trace metals in freshwater Rawal Lake, Pakistan. Jour. Geochem. Explor., v.125,pp.94-101.

Islam, Md.S., Ahmed, Md.K., Raknuzzaman, M., Habibullah-Al-Mamun, Md. and Islam, M.K.(2015) Heavy metal pollution in surface water and sediment: A preliminary assessment of an urban river in a developing country. Ecol. Indic., v.48, pp.282-291.

Krishna, A.K.,Satyanarayanan, M. andGovil, P.K.(2009)Assessment of heavy metal pollution in water using multivariate statistical techniques in an industrial area: a case study from Patancheru, Medak District, Andhra Pradesh, India. Jour. Hazard. Material, v.167, pp.366-373.

Kumar, A., Vij, R., Gupta, M., Sharma, S. and Singh, S. (2015) Risk assessment of exposure to radon concentration and heavy metal analysis in drinking water samples in some areas of Jammu & Kashmir, India. Jour. Radioanal. Nucl. Chem., v.304, pp.1009-1016.

Kumar, T.B.P., Tiwary, A. and Fahmi, S. (2009) Nature of uranium mineralization in the Kerpura-Tiwari-ka-Bas Area, Sikar district, Rajasthan. Jour. Geol. Soc. India, v.73, pp.220-228.

Li, S. and Zhang, Q. (2010) Risk assessment and seasonal variations of dissolved trace elements and heavy metals in the Upper Han River, China. Jour. Hazard. Material, v.181, pp.1051-1058.

Miguel, E.De.,Iribarren, I., Chacon, E., Ordonez, A. and Charlesworth, S. (2007) Risk-Based evaluation of the exposure of children to trace elements in playgrounds in Madrid (Spain). Chemosphere, v.66, pp.505-513.

Muhammad, S.,Tahir Shah, M. and Khan, S. (2011) Health risk assessment of heavy metals and their source apportionment in drinking water of Kohistan region, northern Pakistan. Microchem. Jour., v.98, pp.334-343.

Ni, T., Diao, W., Xu, J. and Liu, N.(2011) Non-carcinogenic risk assessment of eight metals in the sourcegroundwater of Shaying River Basin. Ecotoxicology, v.20, pp.1117-1123.

Rani, A.,Mehra, R., Duggal, V. and Balaram, V. (2013) Analysis of uranium concentration in drinking water samples using ICPMS. Health Phys., v.104, pp.251-255.

Rodell, M., Velicogna, I. and Famiglietti, J.S. (2009) Satellite-based estimates of groundwater depletion in India. Nature, v.460, pp.999-1002.

Rodriguez-Proteau, R. and Grant, R.L. (2005) Toxicity evaluation and human health risk assessment of surface and ground water contaminated by recycled hazardous waste materials. Handbook Environ. Chem., v.2, pp.133-189.

Sridhar, R., Thangaradjou, T., Sentnil, S.K. and Kannan L. (2006) Water quality and phytoplankton characteristics in the Palk Bay, Southeast coast of India. Jour. Environ. Biol., v.27, pp.561-566.

USDOE(2011) The Risk Assessment Information System (RAIS), U.S. Department of Energy's Oak Ridge Operations Office (ORO), Washington, DC, USA.

US EPA (1989) Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual (Part A) Interim Final. EPA/540/1-89/002. U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Washington, DC, USA.

US EPA (1996) Quantitative Uncertainty Analysis of Superfund Residential Risk Pathway Models for Soil and Groundwater: White Paper. Office of Health and Environmental Assessment, Oak Ridge, TN, USA.

US EPA(1997) Exposure factors handbook. Office of research and development. EPA/600/P-95/002Fa. U.S. Environmental Protection Agency, Washington, DC.

US EPA (2001) Risk Assessment Guidance for Superfund: Volume III: Part A, process for conducting probabilistic risk assessment. EPA 540-R-02-002. Office of Emergency and Remedial Response. U.S. Environmental Protection Agency, Washington, DC.

US EPA(2004) Risk Assessment Guidance for Superfund Volume 1: Human health Evaluation Manual (Part E, Supplemental Guidance for Dermal Risk Assessment) Final. EPA/540/R/99/005 OSWER 9285.7-02EP PB99-963312 July 2004, Office of Superfund Remediation and Technology Innovation U.S. Environmental Protection Agency Washington, DC.

US EPA(2011) Edition of the Drinking Water Standards and Health Advisories, EPA 820-R-11-002, Office of Water, U.S. Environmental Protection Agency Washington, DC.

WHO (1996) Guidelines for Drinking-water Quality, vol. 2, Health Criteria and Other Supporting Information, Second ed., Geneva, Switzerland.

WHO (2004) Guidelines for Drinking-water Quality, Third ed., Recommendations, vol.1, World Health Organization, Geneva, Switzerland.

WHO (2008) Guidelines for Drinking-water Quality, Third ed., Incorporating the first and second addenda, Recommendations, vol.1, World Health Organization, Geneva, Switzerland.

WHO (2011) Guidelines for Drinking-water Quality, Fourth ed., Recommendations, vol.1, World Health Organization, Geneva, Switzerland.

Wu, B., Zhao, D., Jia, H., Zhang, Y., Zhang, X. and Cheng, S. (2009) Preliminary risk assessment of trace metal pollution in surface water from Yangtze River in Nanjing Section, China. Bull. Environ. Contam. Toxicol. v.82, pp.405-409.

(Received: 24 October 2016; Revised form accepted: 8 December 2016)