

Groundwater heavy metal levels and associated human health risk in the North China Plain

Wei Li¹ · Ming-yu Wang¹ · Li-ya Liu² · Hui-fang Wang¹ · Sen Yu¹

Received: 3 November 2014 / Accepted: 25 May 2015 / Published online: 26 June 2015
© Saudi Society for Geosciences 2015

Abstract Heavy metals in domestic water are a serious threat to human health. In this study, 139 groundwater samples were collected from rural wells in the villages of five cities in the middle region of the North China Plain along two transects. Statistical analysis and human health risk assessment were conducted to determine the distribution of heavy metals and the associated human health risk from ingestion and dermal adsorption of local groundwater. The results show that the mean concentrations of heavy metals in local groundwater are in the order: Mn>Zn>Cr>Ni>As>Se>Cu>Pb>Cd; with the exception of some sampling stations of Mn and Ni, concentrations for all metals have not exceeded the drinking water standard. Most of the highest pollution stations are in the middle part of urban areas. Mn–As and Cr–Cu are divided into groups by cluster analysis, indicating either the same source or similar transport behaviors. All of the values of the calculated HI_{total} (the non-carcinogenic risk) range from 1.28×10^{-2} to 5.54×10^{-1} , indicating no or slight chronic risk to residents from heavy metals in groundwater. Average values of $R_{ingestion}$ (carcinogenic risk caused by ingestion) for As, Cr, and Cd are between 1×10^{-6} and 1×10^{-4} , indicating a slight carcinogenic risk from heavy metals in groundwater. Although several policies have already been implemented in the study area to ensure the safety of drinking water for residents, the local administration should continue to direct

significant attention to groundwater pollution from heavy metals.

Keywords Heavy metals · Groundwater · Human health risk · The North China Plain

Introduction

One third of the world's population relies on groundwater supplies (WHO 2006). In arid and semi-arid regions, groundwater is the major source of drinking water to the residents (Rina et al. 2013; Ravenscroft et al. 2013; Mtoni et al. 2013). However, pollution caused by variable anthropogenic activities such as current urbanization, industrial manufacture, and mining developments have been a great threat to groundwater quality currently (Varghese and Jaya 2014; Han et al. 2014). Owing to the toxicity and bio-accumulative nature, a great deal of concern has been expressed over the heavy metal pollution in groundwater, and significant researches have been conducted on this topic (Dwivedi and Vankar 2014; Upadhyaya et al. 2014). Wasserman et al. (2006) pointed out that high manganese contamination in drinking water would affect the intellectual functions of 10-year-old children; nickel-sulfate and nickel-chloride ingestion could cause severe health problems including fatal cardiac arrest (Knight et al. 1997). Study conducted by Liu et al. (2010) at an abandoned tungsten mine in southern China demonstrated that the local water resource had been severely contaminated with arsenic. Furthermore, a number of studies focused on the related topics such as the pollution status and source distribution of heavy metals in groundwater (Nouri et al. 2008; Khalil et al. 2008; Mudiam et al. 2012; Krishna and Mohan 2014), the ecology and health risk associated with groundwater heavy metals pollution (Kim et al. 2005; Lee et al. 2006; Pradhan

✉ Ming-yu Wang
mwang@gucas.ac.cn

¹ College of Resources and Environment, University of Chinese Academy of Sciences, Yuquan Road No.19(jia), Beijing 100049, China

² China Ordnance Industry Survey and Geotechnical Institute, Xibianmen Street No.79, Beijing 100053, China

and Kumar 2014; Ma et al. 2014; Perrodin et al. 2014), natural and anthropogenic factors on groundwater quality (Varghese and Jaya 2014; Khatri and Tyagi 2015), and the mechanism of heavy metals leachate percolation to groundwater (Parameswari and Mudgal 2014).

Among the researches mentioned above, correlation and hierarchical cluster analysis are widely used to analyze the similarity between metals in soil, surface water, and groundwater and identify reactive processes, transfer behavior, and potential pollution sources (Rahman et al. 2013; Upadhyaya et al. 2014; Yuan et al. 2014; Tang et al. 2014). These analyses provide a valuable tool for reliable management of water resources and rapid solution to pollution problems (Wunderlin et al. 2001; Muhammad et al. 2011). To determine the health risk levels posed by various contaminants, health risk assessment is an effective approach which has been conducted by researchers worldwide (Wu et al. 2010; Yang et al. 2011; Ma et al. 2014; Giri and Singh 2015; Hu et al. 2015).

The North China plain (abbreviated as NCP) is one of global hotspots of groundwater depletion (Alley et al. 2002; Zheng et al. 2010; Cao et al. 2013). More seriously, extensive use of pesticides/fertilizers and disposal of municipal and industrial waste have caused severe pollution to soil, surface water, and groundwater in the NCP (MEP 2011). Being the main drinking water source, groundwater is of great importance to the residents in the NCP, and the evolution of groundwater quality and associated human health risks should be well concerned, while relative studies focused on the heavy metal pollution in groundwater in the NCP are rare.

In the context of current needs, the specific objectives of this study are to (1) determine the concentrations and distribution of heavy metals in groundwater in the central regions of the NCP; (2) analyze the natural or anthropogenic sources of heavy metals in local groundwater by cluster analysis and by aquifer structure and lithology, and (3) identify the potential human health risks from heavy metals in groundwater for domestic supply based on the U.S. EPA risk assessment methods.

Materials and methods

Study area

Locating in the eastern part of China with longitude from 112° 30' to 119° 30' and latitude from 34° 46' to 40° 25', the NCP is the second largest plain and the political and economic center of China (Fig. 1). The NCP is a typical alluvial plain with an average elevation of 100 m, and it is relatively flat and slopes slightly to Bohai Bay in the east. The Quaternary porous aquifer system of the NCP consists of fluvial fans, alluvial fans, and lacustrine deposits, which can be divided into four groups (I–IV, Fig. 2) according to the lithological properties,

geological age, the distribution of aquifers and aquicludes, and hydrodynamic conditions (Chen et al. 2003; Xing et al. 2013). Because of severe shortage of surface water and discontinuously distributing of saltwater in the shallow aquifer (group II), group I and group III are the major groundwater exploitation aquifers to sustain the industrial, agricultural, and domestic use of water for the residents in the NCP (Zhang et al. 2009).

Sample collection and analysis

Groundwater samples in 139 sampling stations in the central region of the NCP were collected during 2010 to 2012. All of the samples were obtained from rural pumping wells along two transects, transect A–A' was from Baoding to Cangzhou and transect B–B' was from Shijiazhuang to Dezhou (Fig. 1). The groundwater samples were collected in high-density polyethylene containers and kept refrigerated during transport to the lab in Beijing. Electrical conductivity (EC) and total dissolved solids (TDS) were tested on-site by a multi-parameter portable meter (YSI pro^{plus}, USA). It should be noted that the TDS was calculated by the test values of EC and temperature which mainly reflected the content of ions in groundwater. In the study area, the major ions were the primary species in groundwater and the contents of other species were relatively negative (Zhang et al. 2009; Xing et al. 2013), and the calculated values of TDS could be considered to reflect the “total dissolved solids” in local groundwater. Manganese [Mn], chromium [Cr], cadmium [Cd], arsenic [As], lead [Pb], selenium [Se], nickel [Ni], copper [Cu], and zinc [Zn] were analyzed by inductively coupled plasma mass spectrometry (ICP-MS, THERMO X-7, UK) using the People's Republic of China Drinking Water Standard Examination Methods (MOH 2006). The ICP-MS settings for the sample analysis were as follows: measurement mode CCT, H₂/He mixture (7.8 %), 5 mL/min; sample promotion speed 0.8 mL/min; cooling gas 13 L/min; and auxiliary gas 0.8 L/min.

Analysis and discussion

Statistical analysis

Table 1 provides the basic information of groundwater samples. The pH of samples range from 6.23 to 8.94, and the average value is 7.76, indicating a slightly alkaline condition of local groundwater. The TDS of groundwater samples range from 230.1 to 1950.0 mg/L, and the average value is 708.9 mg/L. The pH and TDS of the samples exceed the People's Republic of China quality standard for drinking water and groundwater in 17.8 and 17.7 %, respectively (MEP 1993; MOH 2006).

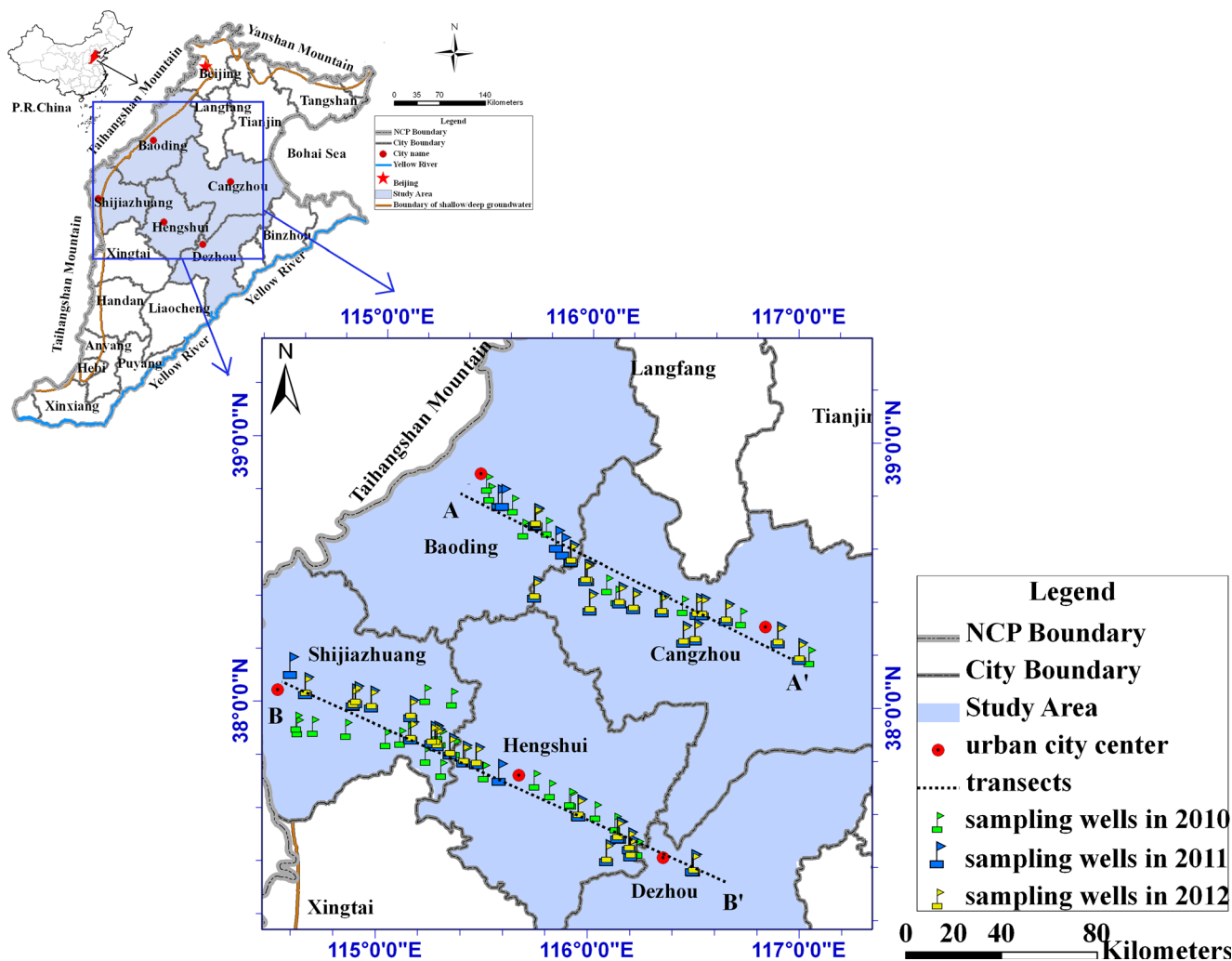


Fig. 1 Geographical location of the NCP and sampling stations and transects

Concentrations of heavy metals in groundwater samples are presented in Fig. 3 and Table 2. Fifty-eight, forty-eight, and thirty-three samples were collected in 2010, 2011, and 2012, respectively. The concentration values of heavy metals are combined and separated yearly for statistical analysis. The mean concentrations of heavy metals decreased in the following order: Mn>Zn>Cr>Ni>As>Se>Cu>Pb>Cd. With the exception of some sampling stations of Mn and Ni, the mean metal concentrations are within the standard thresholds. Concentrations of Mn and Ni are higher than the People’s Republic of China Quality Standard for Groundwater/Drinking Water (MEP 1993; MOH 2006) in 3.25 and 4.11 % of samples, respectively; concentration of Mn exceeds the Drinking Water Standards and Health Advisories (EPA 2012) in 7.32 % of samples. Compared with the concentrations of heavy metals in groundwater from other regions, for instance, studies carried out in Heilongjiang, China (Ma et al. 2014), Unnao, India (Dwivedi and Vankar 2014), and Shibganj, Bangladesh (Saha and Zaman 2011), the concentrations of groundwater heavy metals in the study area are relatively low, indicating that the

local groundwater is either unpolluted or suffering slight pollution from heavy metals. Besides, the yearly concentration distribution for most of the detected heavy metals is mainly the same which varies within small ranges except for Cr and Cu, of which the mean concentrations increase from 2010 to 2012. Though both of the maximal concentrations of Cr and Cu are below the standard thresholds, the potential deterioration trend of local groundwater quality should be well concerned.

The central part of the NCP consists of five cities named Baoding, Cangzhou, Shijiazhuang, Hengshui, and Dezhou (Figs. 1 and 2). Groundwater samples were collected from the rural pumping wells of the villages that belonged to these five cities. Field investigations indicate that domestic use (drinking and washing, etc.), irrigation, and mixed use (for both domestic use and irrigation) are the major use types of local groundwater; the depth and exploited horizon of the irrigation and domestic wells are roughly the same.

The groundwater heavy metal distribution of the two transects is mainly the same, indicating that these areas have

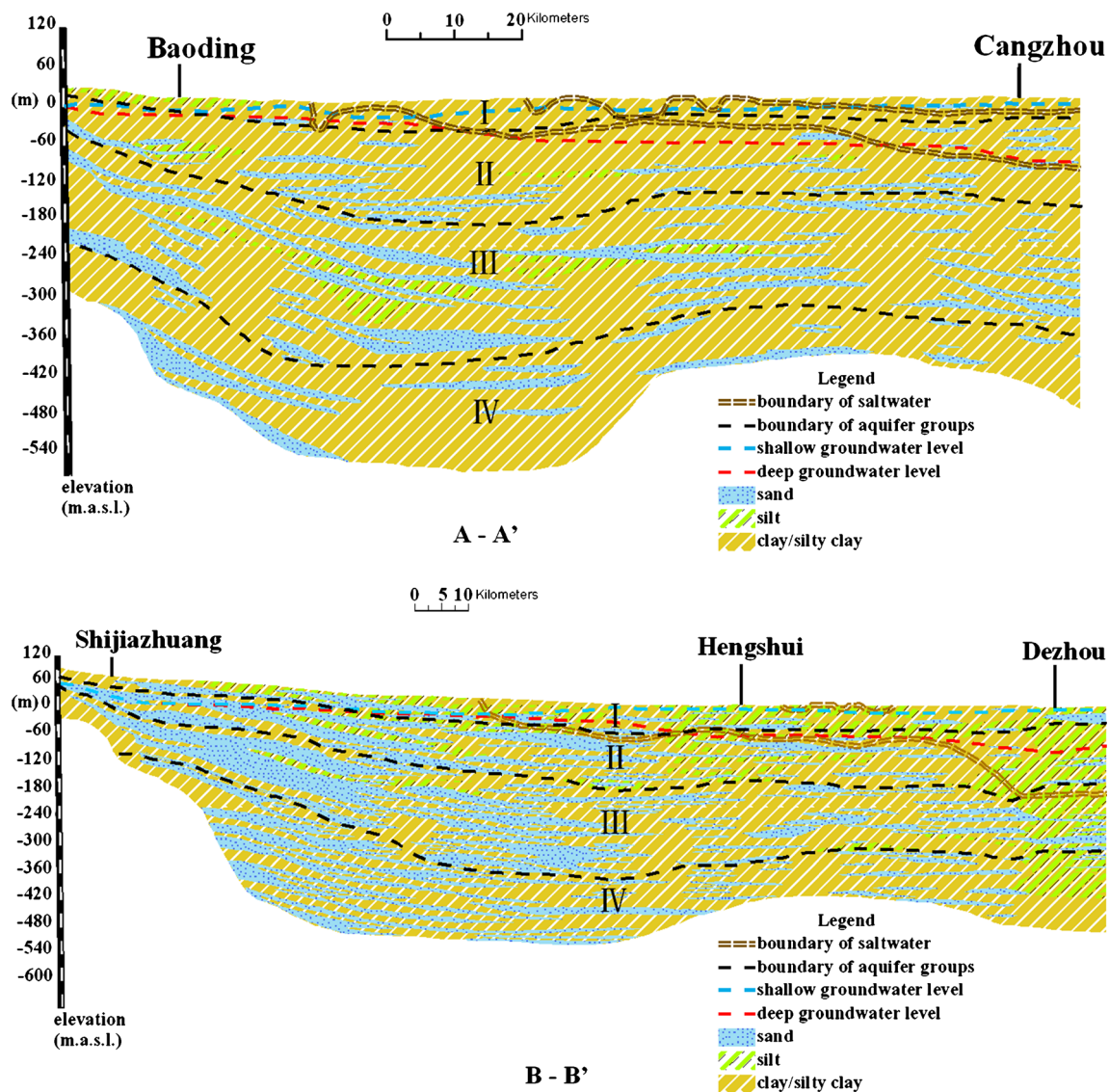


Fig. 2 Aquifer structures and lithology of transect A–A' and B–B' in the study area (Modified from Zhang and Fei 2009)

similar pollution trends. Most of the sampling sites with high concentrations are detected surround the urban centers, especially for Shijiazhuang and Baoding, suggesting a higher pollution level in these two cities than the others. Field investigations show that there are dozens of gasoline stations, chemical factories, landfills, and breeding farms around the cities which can be considered as potential groundwater pollution sources,

and a pollution tendency that spreads from the cities to the countryside is demonstrated. Additionally, the different structure and lithological character of aquifers may influence the distribution of heavy metal concentrations in groundwater. Shijiazhuang and Baoding are located in the piedmont alluvial plain, and the multi-layered sand aquifer (Fig. 2) is more permeable and therefore can facilitate pollutant migration. The size of aquifer particles decreases from west to east, and the lithology changes from gravel, sand to clay. Clay minerals have a strong heavy metal adsorption ability (Sparks 2003; Gu et al. 2010), which may inhibit the migration of heavy metals in the vadose zone. In addition, the thickness of the vadose zone in the middle and east of the study area roughly exceeds 100 m, while heavy metals migrate downwards during infiltration or irrigation, the concentrations of heavy metals in soil pore water may decrease owing to precipitation/adsorption, resulting in low heavy metal concentrations

Table 1 Basic sampling test results

	Min	Max	Mean	Median
Depth of wells (m)	30	430	219.89	240
Depth for pumping (m)	12	300	106.14	100
pH	6.23	8.94	7.76	7.89
TDS(mg/L)	230.1	1950.0	708.9	624.0
EC(mS/cm)	0.20	2.53	0.87	0.69

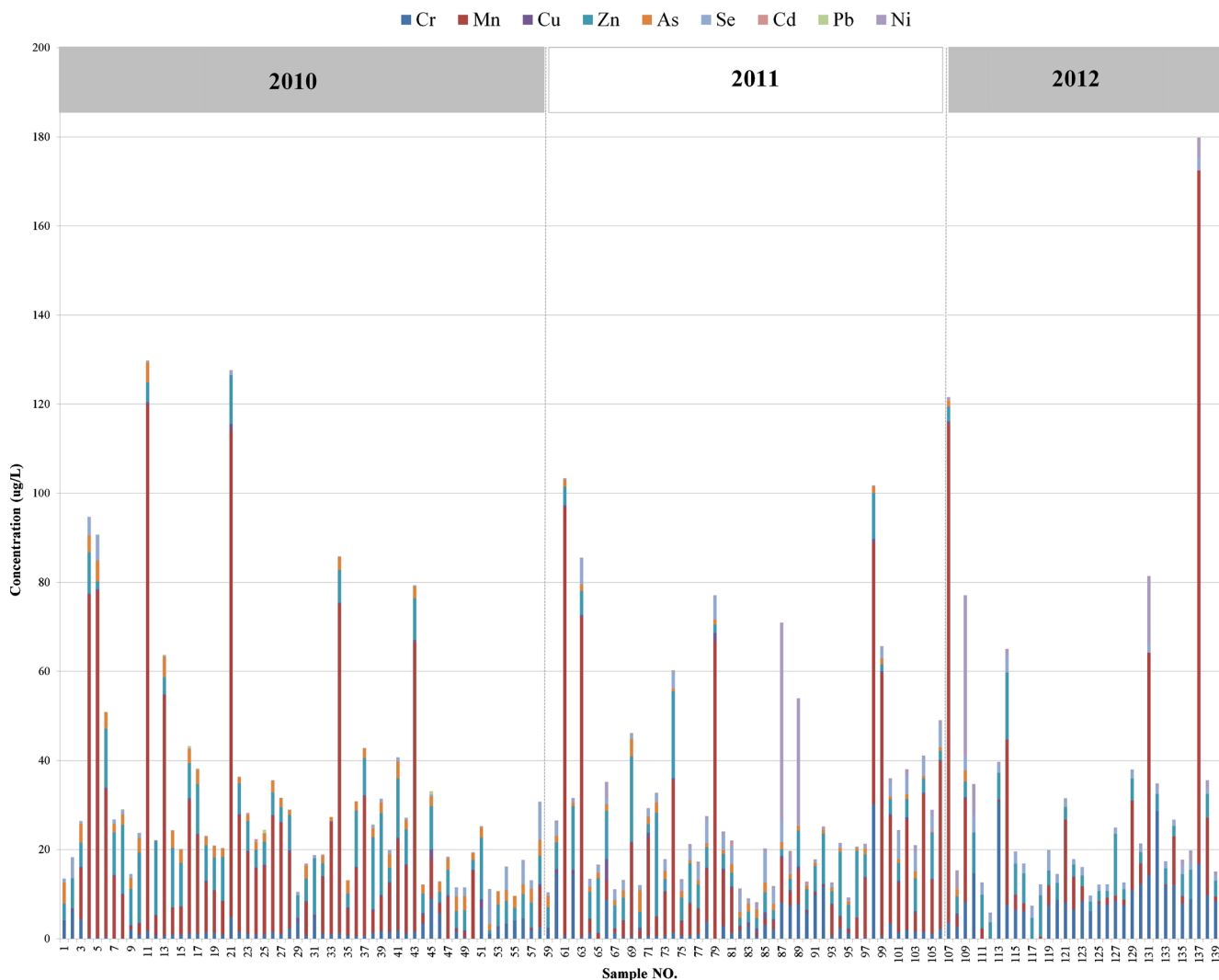


Fig. 3 Cumulative heavy metal concentrations at groundwater sampling sites

in local groundwater. With the exception of few sites at which the heavy metal concentrations are high, the test results show relatively low concentrations of heavy metals in local groundwater at most of the sampling stations (Fig. 4).

Correlation and cluster analysis

In this study, the Pearson’s correlation test and cluster analysis (Ward method) are used to determine the correlation results of heavy metals and their potential sources. Ni and Pb are excluded from the analysis because of insufficient results are detected above the detection limits. Analytical results indicate that Cr–Cu ($r=0.307, p<0.01$) and Mn–As ($r=0.309, p<0.01$) are positively correlated, suggesting that they may have a similar source or transport pathway (Bhuiyan et al. 2010; Prasanna et al. 2012); in contrast, Zn–Se are negatively correlated ($r=-0.246, p<0.05$). Besides, there are no correlations between Cd and the other metals, which indicate that Cd may have a different source from the other metals. Cluster analysis

(Fig. 5) shows that there are two obvious groups: Mn–As and Cu–Cr, which coincide with the correlation analysis results. However, most of the metals cannot be divided into close groups, and the correlations between them are weak, suggesting complex origins or mixed sources of heavy metals in the local groundwater. Furthermore, different reactive processes and deposition behaviors will also affect the concentration distributions of heavy metals in local groundwater.

Human health risks assessment

There are various pathways through which humans are exposed to pollutants, for instance, ingestion (drinking), inhalation (breathing), and dermal absorption (washing and cleaning) (EPA 2001; De Miguel et al. 2007; Ma et al. 2014). Ingestion and dermal absorption are the major pathways for water (Ni et al. 2011; Ma et al. 2014). In this study, the intake dose through ingestion and dermal absorption ($\mu\text{g}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$) is calculated using the US EPA human health risk

Table 2 Heavy metals concentration distribution in groundwater samples

C(ug/L)	Min				Max				Mean			
	2010	2011	2012	total	2010	2011	2012	total	2010	2011	2012	total
Cd	0.01	0.01	0.00	0	0.65	0.69	0.16	0.69	0.09	0.10	0.03	0.08
Cr	0.00	0.18	6.17	0	8.92	30.17	30.84	30.84	2.05	3.66	10.83	4.45
Cu	0.07	0.11	-	0.07	2.04	4.76	-	4.76	0.40	0.57	-	0.46
Mn	0.02	0.10	0.29	0.02	118.20	112.10	155.70	155.7	21.80	16.75	15.35	18.53
Ni	-	0.10	0.03	0.03	-	44.44	15.40	44.44	-	2.94	1.49	2.44
Se	0.01	0.16	1.24	0.01	8.50	7.08	4.47	8.5	1.20	2.58	2.06	1.9
Zn	0.76	1.52	1.49	0.76	18.43	23.14	15.10	23.14	7.61	6.34	5.14	6.61
As	0.85	0.25	-	0.25	4.69	4.80	-	4.8	2.65	1.36	-	2.03
Pb	0.00	-	-	0	0.77	-	-	0.77	0.14	-	-	0.14

C(ug/L)	Median (total)	Standard deviation (total)	Quality Standard for Groundwater-Level III (MEP, 1993)	Quality Standard for Drinking water (MOH, 2006)	Drinking water Standards and Health Adisories (EPA, 2012)
Cd	0.04	0.13	10	5	5
Cr	2.01	5.5	50(Cr ⁶⁺)	50(Cr ⁶⁺)	100(total)
Cu	0.35	0.54	1000	1000	—
Mn	9.06	27.53	100	100	50
Ni	0.39	7.73	50	20	100
Se	1.36	1.85	10	10	50
Zn	5.08	4.47	1000	1000	5000
As	1.89	1.07	50	10	10
Pb	0.56	0.21	50	10	15

assessment methods (EPA 2004); the calculating equations are as follows:

$$Intake_{ingestion} = \frac{C_{water} \times IR_{ingestion} \times EF \times ED}{BW \times AT} \quad (1)$$

$$Intake_{dermal} = \frac{C_{water} \times K_p \times t \times CF \times EV \times SA \times EF \times ED}{BW \times AT} \quad (2)$$

Health risk assessment is generally based on a quantification of the risk level in relation to two types of adverse effects: chronic (non-carcinogenic) and carcinogenic (Krishna and Mohan 2014). According to the list of carcinogen classifications provided by the monographs of the International Agency for Research on Cancer (IARC 2014) and the substances listed in the Integrated Risk Information System of U.S. EPA, As, Cd, Cr, Pb, and Ni are classified as carcinogenic substances, while Cu, Mn, Se, and Zn are classified as non-carcinogenic

Fig. 4 Box plot diagram of heavy metals in groundwater samples

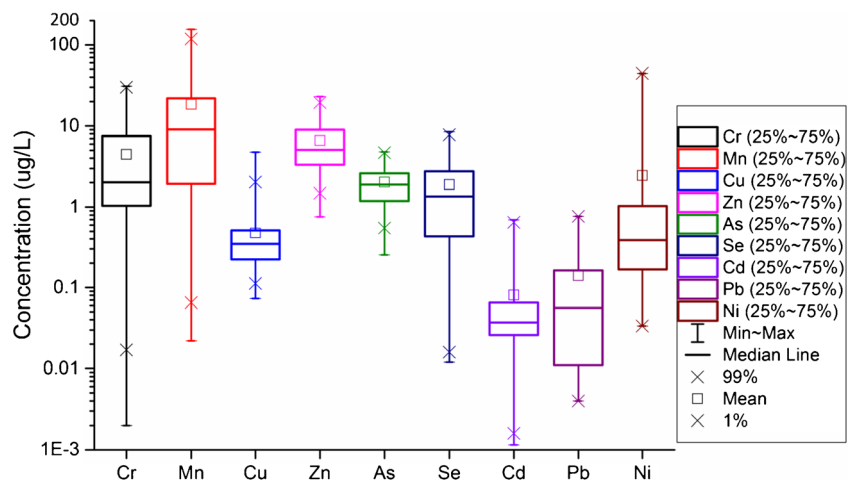
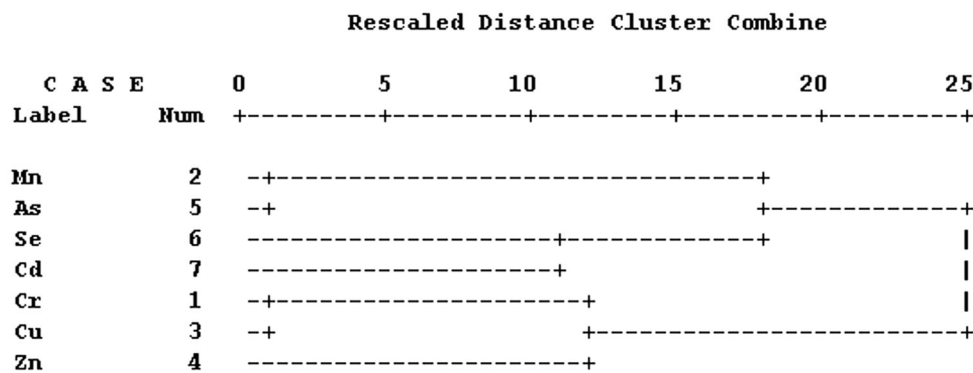


Fig. 5 Dendrogram derived from the hierarchical cluster analysis of metals

Dendrogram using Ward Method



substances. In this study, the non-carcinogenic risk (HI_{total}) and the carcinogenic risk (R_{total}) are calculated using the following equations (Eqs. 3 to 8) (EPA 2004); $HI_{total} > 1$ indicates a potential adverse effect on human health. The reported acceptable levels of carcinogenic risk ($R_{ingestion}$ and R_{dermal}) in the relative studies are variable, some quote thresholds of 1×10^{-6} (EPA 2004), 1×10^{-5} (De Miguel et al. 2007; Ma et al. 2014), or 1×10^{-6} to 1×10^{-4} (Yang et al. 2011). In this study, ranging from 1×10^{-6} to 1×10^{-4} is adopted as the level for carcinogenic risk assessment, as it is the risk level typically applied in China (Yang et al. 2011).

$$HI_{ingestion} = \frac{Intake_{ingestion}}{RfD_{ingestion}} \tag{3}$$

$$HI_{dermal} = \frac{Intake_{dermal}}{RfD_{dermal}} \tag{4}$$

$$HI_{total} = \sum_{i=1}^n (HI_{ingestion} + HI_{dermal}) \tag{5}$$

$$R_{ingestion} = Intake_{ingestion} \times SF_{ingestion} \tag{6}$$

$$R_{dermal} = Intake_{dermal} \times SF_{dermal} \tag{7}$$

$$R_{total} = \sum_{i=1}^n (R_{ingestion} + R_{dermal}) \tag{8}$$

In the above equations, $intake_{ingestion}$ is the intake dose through ingestion ($ug \cdot kg^{-1} \cdot day^{-1}$); $intake_{dermal}$ is the intake dose through dermal absorption ($ug \cdot kg^{-1} \cdot day^{-1}$); C_{water} is the concentration of pollutants in water (concentration of heavy metals in groundwater samples in this study, ug/L); $IR_{ingestion}$ is the ingestion rate (L/day), which is 1.8 in this study (Schmitt et al. 2005); EF is exposure frequency (days/a); ED is the

exposure duration (a); BW is the body weight (kg), which is 57.1 kg (the average of the average male weight and the average female weight in China (61.0 and 53.2 kg, respectively; Yang et al. 2005); AT is the average exposure duration time in days; EV is the frequency of bathing/cleaning (event/day); SA is the exposed skin area (cm^2); Kp is the dermal permeability coefficient (cm/h); t is the event duration ($h/event$); CF is the unit conversion factor ($10^{-3}, cm^3/L$); $RfD_{ingestion}$ is the reference dose of pollutants through ingestion ($ug \cdot kg^{-1} \cdot day^{-1}$); RfD_{dermal} is the reference dose of pollutants through dermal absorption ($ug \cdot kg^{-1} \cdot day^{-1}$); $SF_{ingestion}$ is the cancer slope factor through ingestion ($(mg \cdot kg^{-1} \cdot day^{-1})^{-1}$); SF_{dermal} is the cancer slope factor through dermal absorption ($(mg \cdot kg^{-1} \cdot day^{-1})^{-1}$). The values of these parameters are summarized in Tables 3 and 4 (EPA 2004; IRIS 2014). It should be noted that the water conservancy departments in the study area are promoting centralized water supply from the cities to the villages, and the rural pumping wells will gradually be phased out or replaced by deep wells (over 300 m) in the future; so, the ED value used to calculate the carcinogenic risk in this study varies on a decadal scale, from 10 to 70a.

Risk assessment is conducted for all of the groundwater samples ($n=139$). The results of the non-carcinogenic (chronic) risk assessment are summarized in Table 5. The average values of $HI_{ingestion}$ are 2 to 4 orders of magnitude higher than the values of HI_{dermal} , which indicates that ingestion of water is the dominant pathway through which the local residents are exposed to heavy metals. All of the HI_{total} values are smaller than 1 (from 1.28×10^{-2} to 5.54×10^{-1}), indicating no or a slight chronic risk to residents from heavy metals in groundwater. Moreover, $HI_{ingestion}$ order of heavy metals ($As > Cr > Se > Cd > Mn > Ni > Pb > Zn > Cu$) and HI_{dermal} order ($As > Cr > Se > Cd > Mn > Ni > Zn > Cu > Pb$) are mainly the

Table 3 Parameters for human health risk assessment calculation

parameters	$IR_{ingestion}$ (L/day)	EF (days/a)	ED (a)	BW (kg)	AT (days)	EV (event/day)	SA (cm^2)	t (h/event)
Value	1.8	365	10~70	57.1	25550	1	18000	0.33

Table 4 Toxicological parameters of heavy metals for human health risk assessment calculation

	RfD _{ingestion} (ug·kg ⁻¹ ·day ⁻¹)	RfD _{dermal} (ug·kg ⁻¹ ·day ⁻¹)	SF _{ingestion} (mg·kg ⁻¹ ·day ⁻¹) ⁻¹	SF _{dermal} (mg·kg ⁻¹ ·day ⁻¹) ⁻¹	Kp (cm/h)
As	0.30	0.30	1.50	1.50	0.0010
Pb	3.60	3.60	–	–	0.0001
Cr	3.00	3.00	0.50	0.50	0.0015
Cd	0.50	0.50	0.38	0.38	0.0010
Ni	20.00	20.00	–	–	0.0002
Mn	140.00	140.00			0.0010
Se	5.00	5.00			0.0010
Zn	300.00	300.00			0.0006
Cu	40.00	40.00			0.0010

same, indicating similar risk tendency from ingestion and dermal absorption. Besides, HI values of As, Cr, and Cd are orders of magnitude higher than the other heavy metals, which account for about 89 % (average values) of the HI_{total} as a whole (ED=70a).

A carcinogenic risk assessment is carried out for As, Cd, and Cr. The average values of $R_{\text{ingestion}}$ range from 7.02×10^{-5} to 1.00×10^{-5} for Cr, 9.59×10^{-5} to 1.37×10^{-5} for As, 9.17×10^{-7} to 1.39×10^{-7} for Cd; the values of R_{dermal} range from 8.19×10^{-7} to 1.17×10^{-7} for Cr, 7.46×10^{-7} to 1.07×10^{-7} for As, and 7.55×10^{-9} to 1.08×10^{-9} for Cd. The values of $R_{\text{ingestion}}$ are 2 to 3 orders of magnitude higher than those for R_{dermal} , which suggests a much higher risk through ingestion than through dermal absorption. All of the calculated R values are between 1×10^{-6} and 1×10^{-4} , indicating a slight risk of cancer from heavy metal ingestion for the residents, but the risk would increase if the period of ingestion and heavy metal concentrations in water increased, which agrees with the findings of previous studies (Mo et al. 2006; Cui et al. 2013). Compared to the health risks assessment of heavy metals in groundwater that conducted in other regions of China, the results for the carcinogenic risk assessments of heavy metals in local groundwater are relatively low. For example, Ma et al. (2014) stated that the highest $R_{\text{ingestion}}$ of heavy metals in groundwater in Heilongjiang Province of China reached 1.5×10^{-3} . Studies of As levels and health risks conducted by Cui et al. (2013) in Shanxi showed that the mean cancer risk was about 4 in 1000 exposure ($n=131$) and ranged from 4

in 10000 to 2 in 100, indicating a severe health risk in the study area. As and Cr should be considered as primary pollutants in local groundwater, as the risks to human health from these metals are much greater than Cd (average $R_{\text{ingestion}}$ values of Cr, As and Cd are 1.00×10^{-5} , 1.37×10^{-5} and 1.39×10^{-7} , respectively).

Considered as a potential human health threat, heavy metals in groundwater should be well monitored, especially for As and Cr in the study area. The total values of HI show a slightly decreasing tendency which change from 4.21×10^{-2} in 2010 to 1.72×10^{-2} in 2012 while the total values of R increase from 2.11×10^{-5} in 2010 to 2.16×10^{-5} in 2012, indicating relative steady tendency of concentration and health risks of heavy metals in local groundwater. However, it should be noticed that the health risk assessment of Cr shows an increasing tendency yearly of which the $R_{\text{ingestion}}$ values are 4.46×10^{-6} in 2010, 7.91×10^{-6} in 2011 and 2.13×10^{-5} in 2012, while $R_{\text{ingestion}}$ values of other heavy metals decrease from 2010 to 2012, indicating a possible aggravated Cr pollution in local groundwater since 2010. Because of the complex structure of vadose zone and lack of pollution monitoring data, the origin of heavy metals in local groundwater cannot be well explained and the contribution of natural and anthropogenic sources of heavy metals need to be determined by further work.

To protect the health of rural residents, and to ensure the safety of drinking water, several policies have been implemented in the study area. For instance, the first phase of the

Table 5 Non-carcinogenic risk assessment results from heavy metals (ED=70a)

Values	Cr	Mn	Cu	Zn	As	Se	Cd	Pb	Ni
HI _{ingestion} min	2.10E-5	4.95E-6	5.75E-5	7.99E-5	2.66E-2	7.57E-5	7.27E-5	3.50E-5	5.30E-5
HI _{ingestion} max	3.24E-1	3.51E-2	3.75E-3	2.43E-3	5.04E-1	5.36E-2	4.38E-2	6.74E-3	7.00E-2
HI _{ingestion} average	4.68E-2	4.17E-3	3.75E-4	6.95E-4	2.13E-1	1.20E-2	5.11E-3	1.22E-3	3.85E-3
HI _{dermal} min	2.45E-7	3.85E-8	4.47E-7	3.73E-7	2.07E-4	5.88E-7	5.65E-7	2.72E-8	8.25E-8
HI _{dermal} max	3.78E-3	2.73E-4	2.92E-5	1.13E-5	3.92E-3	4.17E-4	3.40E-4	5.24E-6	1.09E-5
HI _{dermal} average	5.46E-4	3.24E-5	2.91E-6	3.24E-6	1.66E-3	9.30E-5	3.97E-5	9.53E-7	5.99E-6

middle route of the South-to-North Water Diversion Project, which conveys water from the Danjiangkou Reservoir to Beijing via a branch of the Yangtze River, will be completed after the fall of 2014 and will convey about 3.5 billion m³ of water to Hebei Province (which accounts for the largest part of the study area) each year, and will alleviate the shortage of water resources in the study area. Moreover, centralized water supply projects have been set up among villages, in accordance with the National Rural Drinking Water Safety Project, outlined in the 12th Five-Year Plan (NDRC 2012). According to field investigation, the percentage of use of domestic water that pumped from rural wells is decreasing and lots of old rural wells have been abandoned owing to the centralized water supply projects, which means that the human health risk calculated above are based on natural situations and the real human health risk may be lower than expected. The proportion of centralized water supplied to the rural population will increase to about 80 % in 2015, ensuring rural residents will have a safe drinking water supply.

Conclusion

Heavy metal pollution in local groundwater is more serious in the suburban parts of cities, and the pollution tends to spread from cities to villages. The groundwater concentrations of Mn, Zn, Cr, and Ni are much higher than the concentrations of other heavy metals in the study area. Mn–As and Cr–Cu are divided into groups by cluster analysis, indicating the same source or similar transport behaviors. Though most of the heavy metals concentrations in the groundwater samples are below the EPA and MOH drinking water standards, there should be concern about the carcinogenic risk from ingesting As, Cr, and Cd, and the safety of rural domestic water should be emphasized in future.

Acknowledgments This work was supported by the Major State Basic Research Development Program of China (973 Program NO. 2010CB428801, 2010CB428804-2) and the National Environmental Protection Public Welfare Industry Targeted Research Fund, People's Republic of China (201309003). The authors gratefully acknowledge Xiao-hui Qiao for the groundwater samples test and Jian-hui Zhao, Zhi-yu Li, Min Zhang, Bo Liu, Ya-wei Chen, and Chang-yuan Wan for their significant contributions to groundwater sampling. The authors are grateful to the anonymous reviewers for their constructive comments and suggested revisions.

References

- Alley WM, Healy RW, LaBaugh JW, Reilly TE (2002) Flow and storage in groundwater systems. *Science* 296:1985–1990
- Bhuiyan MAH, Parvez L, Islam MA, Dampare SB, Suzuki S (2010) Heavy metal pollution of coal mine-affected agricultural soils in the northern part of Bangladesh. *J Hazard Mater* 173(1):384–392
- Cao GL, Zheng CM, Scanlon BR, Liu J, Li W (2013) Use of flow modeling to assess sustainability of groundwater resources in the North China Plain. *Water Resour Res* 49:159–175
- Chen ZY, Qi JX, Xu JM, Xu JM, Ye H, Nan YJ (2003) Paleoclimatic interpretation of the past 30 ka from isotopic studies of the deep confined aquifer of the North China Plain. *Appl Geochem* 18: 997–1009
- Cui J, Shi J, Jian G, Jin C (2013) Arsenic levels and speciation from ingestion exposures to biomarkers in Shanxi, China: implications for human health. *Environ Sci Technol* 47:5419–5424
- De Miguel E, Iribarren I, Chacón E, Ordoñez A, Charlesworth S (2007) Risk-based evaluation of the exposure of children to trace elements in playgrounds in Madrid (Spain). *Chemosphere* 66:505–513
- Dwivedi AD, Vankar PS (2014) Source identification study of heavy metal contamination in the industrial hub of Unnao, India. *Environ Monit Assess* 186:3531–3539
- Giri S, Singh AK (2015) Human health risk assessment via drinking water pathway due to metal contamination in the groundwater of Subamarekha River Basin, India. *Environ Monit Assess* 187:63–76
- Gu X, Evans LJ, Barabash SJ (2010) Modeling the adsorption of Cd (II), Cu (II), Ni (II), Pb (II) and Zn (II) onto montmorillonite. *Geochim Cosmochim Acta* 4:5718–5728
- Han DM, Tong XX, Currell MJ, Cao GL, Jin MG, Tong CS (2014) Evaluation of the impact of an uncontrolled landfill on surrounding groundwater quality, Zhoukou, China. *J Geochem Explor* 136:24–39
- Hu YH, Wang XM, Dong ZB, Liu GJ (2015) Determination of heavy metals in the groundwater of the Hubei plain, China, to characterize potential effects on human health. *Anal Lett* 48:349–359
- IARC, International agency for research on cancer (2014) Agents classified by the IARC monographs 1-109. <http://monographs.iarc.fr/ENG/Classification/>. Accessed 15 March 2013
- IRIS, Integrated Risk Information System, United States Environmental Protection Agency (2014) <http://cfpub.epa.gov/ncea/iris/index.cfm?fuseaction=iris.showSubstanceList>. Accessed 20 August 2013
- Khalil HE, Hamiani OE, Bitton G, Ouazzani N, Boularbah A (2008) Heavy metal contamination from mining sites in South Morocco: monitoring metal content and toxicity of soil runoff and groundwater. *Environ Monit Assess* 136:147–160
- Khatri N, Tyagi S (2015) Influences of natural and anthropogenic factors on surface and groundwater quality in rural and urban areas. *Front Life Sci* 8(1):23–39
- Kim JY, Kim KW, Ahn JS, Ko I, Lee CH (2005) Investigation and risk assessment modeling of As and other heavy metals contamination around five abandoned metal mines in Korea. *Environ Geochem Health* 27:193–203
- Knight C, Kaiser GC, Robothum LH, Witter JV (1997) Heavy metals in surface water and stream sediments in Jamaica. *Environ Geochem Health* 19:63–66
- Krishna AK, Mohan KR (2014) Risk assessment of heavy metals and their source distribution in waters of a contaminated industrial site. *Environ Sci Pollut Res* 21:3653–3669
- Lee SW, Lee BT, Kim JY, Kim KW, Lee JS (2006) Human risk assessment for heavy metals and As contamination in the abandoned metal mine areas, Korea. *Environ Monit Assess* 119:233–244
- Liu CP, Luo CL, Gao Y, Li FB, Lin LW, Wu CA, Li XD (2010) Arsenic contamination and potential health risk implications at an abandoned tungsten mine, southern China. *Environ Pollut* 158:820–826
- Ma LX, Qin XB, Sun N, Yang GT (2014) Human health risk of metals in drinking-water source areas from a forest zone after long-term excessive deforestation. *Hum Ecol Risk Assess* 20:1200–1212
- MEP, Ministry of Environmental Protection of the People's Republic of China (1993) Quality standard for groundwater. GB14848-93
- MEP, Ministry of Environmental Protection of the People's Republic of China (2011) National groundwater pollution prevention plan (2011-2020)

- Mo MH, Chen WM, Su HY, Zhang KQ, Duan CQ, He DM (2006) Heavy metal tolerance of nematode-trapping fungi in lead-polluted soils. *Appl Soil Ecol* 31:11–19
- MOH, Ministry of Health of the People's Republic of China (2006) Standard examination methods for drinking water. GB5750.1-2006
- MOH, Ministry of Health of the People's Republic of China (2006) Standards for drinking water quality. GB5749-2006
- Mtoni Y, Mjemah IC, Bakundukize C, Camp MV, Martens K, Walraevens K (2013) Saltwater intrusion and nitrate pollution in the coastal aquifer of Dares Salaam, Tanzania. *Environ Earth Sci* 70:1091–1111
- Mudiam MKR, Pathak SP, Gopal K, Murthy RC (2012) Studies on urban drinking water quality in a tropical zone. *Environ Monit Assess* 184:461–469
- Muhammad S, Shah MT, Khan S (2011) Health risk assessment of heavy metals and their source apportionment in drinking water of Kohistan region, northern Pakistan. *Microchem J* 98:334–343
- NDRC, National Development and Innovation Committee of the People's Republic of China, MOH, Ministry of Health of the People's Republic of China, MEP, Ministry of Environmental Protection of the People's Republic of China, MWR, Ministry of water resources of the People's Republic of China (2012) National rural drinking water safety project, the 12th five-year plan
- Nouri J, Mahvi AH, Jahed GR, Babaei AA (2008) Regional distribution pattern of groundwater heavy metals resulting from agricultural activities. *Environ Geol* 55:1337–1343
- Parameswari K, Mudgal BV (2014) Geochemical investigation of groundwater contamination in Perungudi dumpsite, South India. *Arab J Geosci* 7:1363–1371
- Perrodin Y, Donguy G, Emmanuel E, Winiarski T (2014) Health risk assessment linked to filling coastal quarries with treated dredged seaport sediments. *Sci Total Environ* 485:387–395
- Pradhan JK, Kumar S (2014) Informal e-waste recycling: environmental risk assessment of heavy metal contamination in Mandoli industrial area, Delhi, India. *Environ Sci Pollut Res* 21:7913–7928
- Prasanna MV, Praveena SM, Chidambaram S, Nagarajan R, Elayaraja A (2012) Evaluation of water quality pollution indices for heavy metal contamination monitoring: a case study from Curtin Lake, Miri City, East Malaysia. *Environ Earth Sci* 67(7):1987–2001
- Rahman MM, Asaduzzaman M, Naidu R (2013) Consumption of arsenic and other elements from vegetables and drinking water from an arsenic-contaminated area of Bangladesh. *J Hazard Mater* 262:1056–1063
- Ravenscroft P, McArthur JM, Hoque MA (2013) Stable groundwater quality in deep aquifers of Southern Bangladesh: the case against sustainable abstraction. *Sci Total Environ* 454:627–638
- Rina K, Singh CK, Datta PS, Singh N, Mukherjee S (2013) Geochemical modelling, ionic ratio and GIS based mapping of groundwater salinity and assessment of governing processes in Northern Gujarat, India. *Environ Earth Sci* 69(7):2377–2391
- Saha N, Zaman MR (2011) Concentration of selected toxic metals in groundwater and some cereals grown in Shibganj area of Chapai Nawabganj, Rajshahi, Bangladesh. *Curr Sci* 101(3):427–431
- Schmitt MT, Schreinemachers D, Wu K, Ning Z, Zhao B, Le XC, Mumford JL (2005) Human nails as a biomarker of arsenic exposure from well water in inner Mongolia: comparing atomic fluorescence spectrometry and neutron activation analysis. *Biomarkers* 10(2-3):95–104
- Sparks DL (2003) *Environmental soil chemistry*. Academic Press, pp 172–182
- Tang WZ, Ao L, Zhang H, Shan BQ (2014) Accumulation and risk of heavy metals in relation to agricultural intensification in the river sediments of agricultural regions. *Environ Earth Sci* 71:3945–3951
- Ni T-h, Diao W-p, Xu J-g, Liu N (2011) Non-carcinogenic risk assessment of eight metals in the source groundwater of Shaying River Basin. *Ecotoxicology* 20:1117–1123
- U.S.EPA, United States Environmental Protection Agency (2001) Risk Assessment guidance for superfund: volume III-Part A, Process for conducting probabilistic risk assessment. EPA 540-R-02-002
- U.S.EPA, United States Environmental Protection Agency (2004) Risk assessment guidance for superfund volume I: human health evaluation manual (Part E, supplemental guidance for dermal risk assessment). EPA 540-R-99-005
- U.S.EPA, United States Environmental Protection Agency (2012) 2012 Edition of the drinking water standards and health advisories. EPA 822-S-12-001
- Upadhyaya D, Survaiya MD, Basha S, Mandal SK, Thorat RB, Haldar S, Goel S, Dave H, Baxi KH, Trivedi RH, Mody KH (2014) Occurrence and distribution of selected heavy metals and boron in groundwater of the Gulf of Khambhat region, Gujarat, India. *Environ Sci Pollut Res* 21:3880–3890
- Varghese J, Jaya DS (2014) Metal pollution of groundwater in the vicinity of valiathura sewage farm in Kerala, South India. *Bull Environ Contam Toxicol* 93:694–698
- Wasserman G, Liu X, Parvez F, Ahsan H, Levy D, Litvak PF, Kline J, Geen AV, Slavkovich V, Lolacono N, Cheng Z, Zheng Y, Graziano J (2006) Water manganese exposure and children's intellectual functions in Araihaazar, Bangladesh. *Environ Health Perspect* 114:124–129
- WHO, World Health Organization (2006) Protecting groundwater for health: managing the quality of drinking-water sources. IWA Publishing, pp 4–5
- Wu B, Zhang Y, Zhang X, Chen S (2010) Health risk from exposure of organic pollutants through drinking water consumption in Nanjing, China. *Bull Environ Contam Toxicol* 84:46–50
- Wunderlin DA, Diaz MP, Ame MV, Pesce SF, Hued AC, Bistoni MA (2001) Pattern recognition techniques for the evaluation of spatial and temporal variations in water quality. A case study: Suquia river basin (Cordoba, Argentina). *Water Res* 35:2881–2894
- Xing L, Guo H, Zhan Y (2013) Groundwater hydrochemical characteristics and processes along flow paths in the North China Plain. *J Asian Earth Sci* 70:250–264
- Yuan X-y, Zhang L-j, Li J-z, Wang C, Ji J-f (2014) Sediment properties and heavy metal pollution assessment in the river, estuary and lake environments of a fluvial plain, China. *Catena* 119:52–60
- Yang M, Y-h F, Y-w J, H-q L (2011) Human health risk assessment model of organic pollution in groundwater: Shijiazhuang industrial zone. *ACTA Geol Sinica* 85(6):1508–1517
- Yang X-g, Li Y-p, Ma G-s, Hu X-q, Wang J-z, Cui Z-h, Wang Z-h, Yu W-t, Yang Z-x, Zhai F-y (2005) Study on weight and height of the Chinese people and the differences between 1992 and 2002. *Chin J Epidemiol* 26:489–493
- Zhang ZJ, Fei YH (2009) Atlas of sustainable utilization of groundwater in North China Plain. China Map Press, pp 50–51
- Zhang ZJ, Fei YH, Chen ZY, Zhao ZZ, Xie ZH (2009) Investigation and assessment of the sustainable utilization of groundwater resources in North China Plain. Geology Press, pp 59–81
- Zheng C, Liu J, Cao G, Kendy E, Wang H, Jia Y (2010) Can China cope with its water crisis? Perspectives from the North China Plain. *Ground Water* 48:350–354