Environ Monit Assess (2014) 186:4669–4684
DOI 10.1007/s10661-014-3729-2

Human health risk assessment of groundwater in Hetao Plain (Inner Mongolia Autonomous Region, China)

Yilong Zhang · Rong Ma · Zhenghong Li

Received: 3 June 2013 / Accepted: 13 March 2014 / Published online: 5 April 2014

Abstract Groundwater quality significantly affects public health. In order to better understand groundwater suitability, a total of 887 shallow groundwater samples were collected from the Hetao Plain (HP), Inner Mongolia, China; the maximum and minimum health guideline values of each element were established in this work. Subsequently, the desirability functions (DFs) theory was employed to evaluate the human health risk of groundwater. The results indicate that 780 of the samples were unsuitable for drinking purposes due to the iron, total dissolved solids (TDS), arsenic, strontium, fluoride, and manganese concentrations present, all of which exceeded their maximum guideline value (MaGV). Only 107 samples were suitable for drinking use; however, these samples also have adverse effects on human health to some extent, due to the extremely lower concentrations of nutrient elements and existence of non-nutrient elements. Based on the observed results, groundwater that is unsuitable for drinking use must undergo bacteriological treatment prior to consumption. It was necessary for residents in the western, central, and northeastern parts of the study area are required to be supplied with certain nutrient elements, such as iron, iodine, molybdenum, manganese, and lithium. According to the human health risk assessment of groundwater, the general public can safely and reasonably consume the groundwater for drinking, agriculture irrigation, and industrial purposes.

Keywords Agriculture irrigation · Desirability functions · Hetao Plain · Health risk · Nutrient elements

Introduction

Safe drinking water is the birthright of all humankind, and as much a birthright as clean air (TWAS 2002). Groundwater is the primary water supply source for large cities and counties in the Hetao Plain (HP), the pollution of which is slowly reaching an alarming stage. It is well known that groundwater contamination is harmful not only to crops and industrial products, but also to human health. There have been various attempts to assess groundwater quality for drinking, agriculture irrigation, and industrial purposes (Jalali and Merrikhpour 2007; Goyal et al. 2010; Yidana and Yidana 2010; Singh et al. 2012). The water quality index (WQI) was established to evaluate groundwater quality using the fuzzy set theory (Muhammetoglu and Yardimci 2006), the Bhargava method (Avvannavar and Shrihari 2008), the multivariate analysis (Stigter et al. 2006; Yidana and Yidana 2010), and the probabilistic neural networks (Nikoo et al. 2011).

Undoubtedly, the aforementioned methods are useful to the public for assessing groundwater quality. However, each approach has its inherent limitations. First, the meaning of WQI can differ depending on the paper in which the term is used. For example,

Y. Zhang · R. Ma (✉) · Z. Li
Institute of Hydrogeology and Environmental Geology,
No. 268, Zhonghua North Street, Shijiazhuang City,
Hebei Province 050061, China
e-mail: margroundwater@gmail.com

Muhammetoglu and Yardimci (2006) reported computation WQI values varying in range from 1 to 200, categorizing contamination level as low, moderate, high, and very high pollution. Yidana and Yidana (2010) used a numbered range spanning from 0 to 300, dividing the groundwater quality into excellent, good, and poor. It is difficult for the general public to understand the difference in quality between "good" and "excellent" water. Second, it should be noted that both the higher and lower concentrations of nutrient elements in drinking water have adverse impacts on living organisms (Phan et al. 2010). However, these investigations only considered the health effects resulting from higher concentrations of hydrochemical elements, rather than those from extremely low concentrations of nutrient elements. Good groundwater quality should have two characteristics: first, the lower the concentrations of non-nutrient elements, the better the groundwater quality. The ideal case is when each non-nutrient element concentration is equal to 0 in the groundwater system (Dauvalter and Kashulin 2010). Second, the concentrations of nutrient elements should remain within a certain range that is functionally intrinsic to the human body in reasonable concentrations (World Health Organization (WHO) (2006)). Manganese in water, like other nutrient elements, both deficiencies and excesses can lead to severe metabolic disorders. Epidemiological studies (GB 5749-2006 2006; WHO 2006; Homoncik et al. 2010) have described low manganese level results in manganese deficiency disorders, such as weight loss, hypo sexuality, and gray hair, while high level of manganese causes Wilson disease and parkinsonism syndrome.

Generally speaking, the most frequent and common route of nutrient element intake occurs through the consumption of food and drinking water. In the case of manganese, drinking water, nuts, tea, and vegetable are all major sources of ingestion; their contributions to manganese are 37, 28, 15, and 20 %, respectively (Iwami et al. 1994). Therefore, the nutrient element contents should remain in a reasonable range in the groundwater system to maintain physiological balance and stabilization of the body. The early studies stated that lower concentrations of these elements mean a lower WQI and better groundwater quality. Those researchers did not take into account the adverse effects of drinking water with extremely low concentrations of nutrient elements on human beings.

Accordingly, the objectives of this paper are (1) to identify which groundwater samples are unsuitable for drinking use due to one or more element concentrations exceeding their maximum guideline value (MaGV); (2) to calculate the health risks of the groundwater samples that are suitable for drinking purposes. There are two causes for potential health risks. First, cases wherein the concentrations of nutrient elements are lower than their minimum guideline value (MiGV), which would lead to some nutrient element deficiencies in the human body, resulting in growth as well as mental retardation. Second, although the non-nutrient elements concentrations do not exceed the MaGV for these groundwater samples, they can still cause adverse impacts on human health to some extent; and (3) to characterize the distribution range of the nutrient elements with extremely low concentrations in groundwater samples that are suitable for drinking use.

For the purposes of this article, the human health risk assessments of groundwater were carried out using the desirability functions (DFs). This approach is different from previous studies in several respects. First, health risk assessments in this work consider not only the MaGV of nutrient elements, but also the MiGV; second, the overall desirability (*D*) was computed using the DFs. This value does not classify groundwater quality into different types; it only tells the general public which groundwater sample is unsuitable for drinking; and how great the health risks are in the groundwater sample that are suitable for drinking purposes.

Groundwater is the major drinking water source in HP, which has a typical continental climate (Yu et al. 2010). A vast groundwater quality assessment in HP has been carried out over recent years (Guo et al. 2011; Neidhardt et al. 2012; Yang et al. 2012; Zhang et al. 2013). However, the MiGV of nutrient elements are firstly considered to evaluate the human health risks of groundwater in HP.

Materials and methods

Study area

HP is located in the western part of the Inner Mongolia Autonomous Region of China, to the south of the Yellow River, to the east of the Daqing Mountain, to the north border of Lang and Wulaer Mountains, with a total area of 13, 040 km^2 and a population of 900, 000. Since the Qin Dynasty, the Yellow River has been employed across this area for irrigation purposes; an annual average of approximately five billion cubic meters of water from the Yellow River is delivered into HP for agriculture irrigation. Due to a shallow water table and strong evapotranspiration, about half the surface soils are saline, which leads to seasonal accumulation of salts in this plain. The climate is semi-arid with an annual rainfall between 150 and 400 mm; evaporation runs between 2, 000 to 2, 500 mm with an average value of 2, 180 mm. The average annual air temperatures are between 5.6 and 7.8 °C. The average elevation ranges from 900 to 1, 200 m in the HP area. The following lake and rivers represent the surface water hydrology in the study area: Wuliangsuhai Lake, the Yellow River, and the Dahei River. The shallow groundwater has a close hydraulic connection with the surface water; it is mainly recharged by irrigation water, surface water, and vertically infiltration precipitation and discharged mainly by evaporation, drainage, and human extraction. There are two aquifer systems: one is an unconfined aquifer system; its sediments are derived from the Lang, Wulaer, and Daqing Mountains and partly from fluvial deposits of the Yellow River, which are comprised of alluvial-pluvial sand, sandy silt, lacustrine and fluvial-lacustrine sandy silt, silt clay, and clay rich in organic matter in the central part of the plain. The general direction of groundwater flow is from recharge areas to discharge areas. Figure 1 describes the shallow groundwater level; this figure shows the shallow groundwater flows from the Yellow River recharge areas to discharge into drains and lake in western of HP, these flow paths are comparatively short; in eastern of HP, horizontal groundwater flow is directed toward east-west. The other system is a confined aquifer recharged from the leaking recharge; the lithology is medium sand, coarse sand, and silt sand.

Sample collection

The first aquifer is the current major source for human consumption; out of the 887 collected groundwater samples, 612 were from tube wells and 275 were from open wells in this aquifer for hydrochemical variable analysis. These wells are directly used for drinking, irrigation, and industrial purposes without future treatment prior to consumption. In the case of the wells, the water samples were collected after pumping for 10–20 min. This was done to remove groundwater stored in the well. For all collected samples, the electrical conductivity (EC), temperature (T), total dissolved solids (TDS), and pH values were measured in situ using a multi parameter water quality meter. The remaining variables, such as major elements and trace elements, were analyzed at the laboratory of the Institute of Hydrogeological and Environmental Geology immediately after transportation to the laboratory. In these samples, sodium and magnesium are the predominant cations, while chloride and bicarbonate are the predominant anions; 887 samples can be divided into 28 distinct water types. Of samples, 8.34 % are rich in sodium, magnesium, chloride, and bicarbonate reflecting Na-Mg-Cl-HCO_3 type, which is the dominant water type in HP; the Ca-Mg-HCO_3 is the second dominant water type. The percent of these samples that fall in this type can reach 7.66 %; the third groundwater type belongs to the Na-Mg-Cl-SO_4-HCO_3 type, which is present in 6.31 % of the samples.

Desirability functions

The DFs theory, developed by Harrington (1965), has often proved to be a useful tool in dealing with multi-response problems. The basic idea of the DFs is to convert a multiple response problem into a single response problem by means of mathematical transformations. In this article, x_i element was converted into an individual desirability function (d_i) with a value between 0 and 1 according to the equations below.

1) Larger the best (LTB) type

$$d_i = \begin{cases} [0,1) & x_i < MaGV_i \\ 1 & x_i \geq MaGV_i \end{cases} \quad (1)$$

2) Smaller the best (STB) type

$$d_i = \begin{cases} 0 & x_i \geq MaGV_i \\ (0,1) & MiGV_i < x_i < MaGV_i \\ 1 & x_i \leq MiGV_i \end{cases} \quad (2)$$

3) Nominal the best (NTB) type

$$d_i = \begin{cases} [0,1) & x_i < MiGV_i \\ 1 & MiGV_i \leq x_i < MaGV_i \\ 0 & x_i \geq MaGV_i \end{cases} \quad (3)$$

where x_i represents the concentration of ith element; $MaGV_i$ is the MaGV of ith element; $MiGV_i$ is the MiGV of ith element; d_i denotes the desirability function of x_i element; i=1, 2, …, m, m is the number of elements.

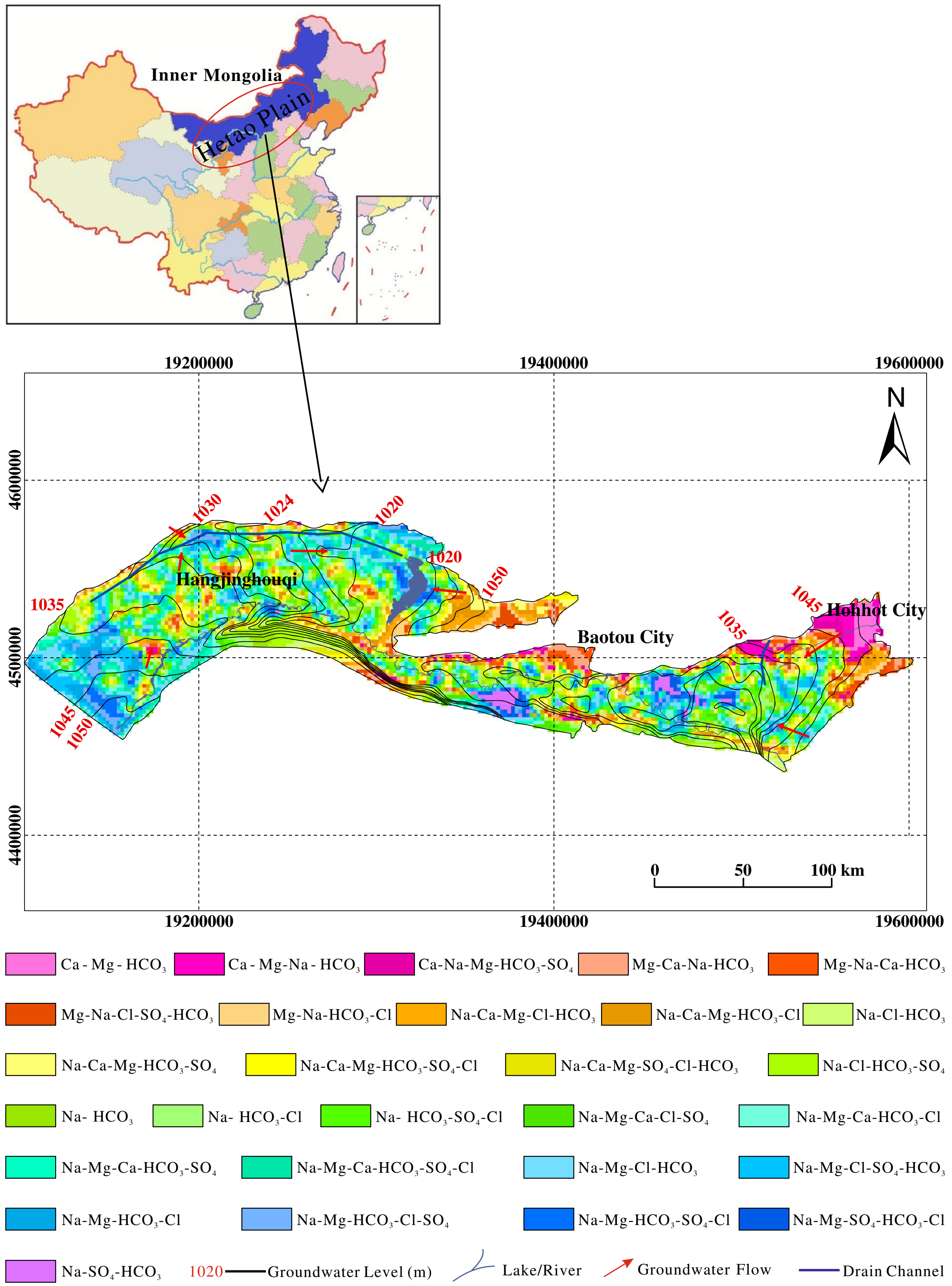


Fig. 1 Study area and shallow groundwater type

There are three forms of the desirability function depending on hydrochemical variable's characteristic: (1) the LTB type, it means the higher concentration of ith element, the greater is the d_i value; however, this characteristic is not consistent with the actual situation of drinking water quality assessment; (2) the STB type denotes the non-nutrient element, the d_i value decreases as the ith non-nutrient element concentration increases in groundwater; when the ith non-nutrient element content falls above its MaGV_i value, the d_i value decreases to 0, it means groundwater is unsuitable for drinking use; (3) the NTB type reflects the ith nutrient element, when the ith nutrient element content between MiGV_i and MaGV_i value, the d_i value is equal to 1, it demonstrates groundwater has no adverse effects on human health; if ith nutrient element concentration is greater than MaGV_i, groundwater is unsuitable for drinking use, and therefore, d_i value is equal to 0; if this element content falls within MiGV_i, groundwater is suitable for use in drinking; however, it can still cause health risk on human body for long periods of time, d_i value is less than 1.

Subsequently, the overall desirability function (D) can then be calculated using the geometric mean of d values according to Eq (4).

$$D = \left(\prod_{i=1}^{m} d_i(x_i)^{w_i} \right)^{\frac{1}{\sum w_i}} \tag{4}$$

where w_i represents the weight coefficient of x_i element. In Eq. (4), w value between 0 and 1, and $w_1+w_2+w_i\ldots w_m=1$ (Li et al. 2007).

D value exists in the range from 0 to 1. For a value of D close to 1, the combination of different criteria is globally optimum, i.e., the variable values are near the target values; if its value is equal to 0, the element exceeds the desirable value. In recently years, DFs are widely applied in industrial management (Li et al. 2003), drug production (Li et al. 2007), volatile organic compounds (VOCs) pollution assessment (Cojocaru et al. 2009), and water quality analysis (Zobkov 2012). However, it has not been used for human health risk assessments of groundwater.

Human health risk assessment

Fifty-six hydrochemical elements were measured in this work; however, the concentrations of copper, lead, aluminum, nickel, and mercury in groundwater were between MiGV and MaGV. More importantly, their content was distributed homogeneously in study area. Therefore, these elements were not incorporated into human health risk assessments of groundwater; only 16 elements (TDS, bromide, fluoride, iron, iodine, ammonium, nitrate, nitrite, pH, arsenic, barium, lithium, manganese, molybdenum, strontium, and zinc) were selected to evaluate the health risks associated with groundwater using the DFs theory.

More details regarding the computation process of the drinking water health risks assessments are shown in the following steps. The first step was to establish the MiGV and MaGV for hydrochemical elements in drinking water. A number of studies reported that the lower the concentration of each element, the better the groundwater quality. Therefore, the researchers only ensured that no element concentration exceeded the MaGV for evaluation of groundwater quality (Avvannavar and Shrihari 2008; Haritash et al. 2008; Yidana and Yidana 2010; Ketata et al. 2011). However, in a real situation, this assumption is only suitable for non-nutrient elements; there is no indication or medical evidence supporting that arsenic, bromide, barium, nitrate, and nitrite are essential elements for human health. In contrast, fluoride, iron, iodine, pH, lithium, manganese, molybdenum, strontium, and zinc are nutrient elements (Iwami et al. 1994; Haddadin et al. 2002), and therefore, their concentrations in groundwater should be remained within a certain range (Dauvalter and Kashulin 2010; Phan et al. 2010).

With regard to the nutrient elements, the MaGV were easily established according to the various water quality standards (GB/T 14848-93 1993; GB 15193.18-2003 2003; GB 5749-2006 2006; WHO 2006) and early studies (Muhammetoglu and Yardimci 2006; Jalali and Merrikhpour 2007; Goyal et al. 2010; Singh et al. 2012); the MiGV in drinking water was calculated using Eqs. (5)–(6), which are defined as follows:

$$\mathrm{MiGV} = (\mathrm{RNI} * P)/C \tag{5}$$

$$\mathrm{MiGV} = (\mathrm{AI} * P)/C \tag{6}$$

where reference nutrient intake (RNI) is the recommended nutrient intake (mg/day); if RNI values for some nutrient elements are not proposed, application of the adequate intake (AI) (mg/day) instead of RNI to calculate MiGV; P represents the fraction of the RNI/AI

Table 1 MiGV, MaGV, and weight coefficient of each hydrochemical element in study area mg/l

Parameters	Characteristic	MiGV	MaGV	Weight (w)	Relative weight (W) $W_i = \frac{w_i}{\sum_{i=1}^{m} w_i}$
TDS	Non-nutrient element	0	1, 000	1	0.0204
Br	Non-nutrient element	0	6	2	0.0408
F	Nutrient element	0.1500	1	5	0.1020
Fe	Nutrient element	0.0400	0.3	3	0.0612
I	Nutrient element	0.0150	0.2	4	0.0816
NH_4	Non-nutrient element	0	0.2	3	0.0612
NO_2	Non-nutrient element	0	0.2	4	0.0816
NO_3	Non-nutrient element	0	50	3	0.0612
pH	Nutrient element	6.5	8.5	1	0.0204
As	Non-nutrient element	0.0012	0.01	5	0.1020
Ba	Non-nutrient element	0	0.7	4	0.0816
Li	Nutrient element	0.02	0.06	2	0.0408
Mn	Nutrient element	0.1150	0.4	2	0.0408
Mo	Nutrient element	0.0045	0.07	3	0.0612
Sr	Nutrient element	0.19	1.9	3	0.0612
Zn	Nutrient element	0.275	1	4	0.0816
				$\sum_{i=1}^{m} w_i = 49$	$\sum_{i=1}^{m} W_i = 1.0000$

allocated to drinking water; C is a daily drinking water consumption (L/day). There is variation in both the volume of water consumed by and the body weight of consumers; therefore, some assumption is employed to calculate the MiGV. The default assumption for water consumption by an adult is 2 L/day, while the default assumption for body weight is 60 kg (WHO 2006).

The MaGV of the non-nutrient elements, such as arsenic, ammonium, nitrate, and nitrite, were established according to the aforementioned studies and drinking water standards. Even though these non-nutrient elements are present at extremely low concentrations in drinking water, many of them can raise considerable toxicological concerns. The ideal case is when these element concentrations are equal to 0; at that point, the groundwater is the most suitable for human consumption and has no danger to human health. Therefore, this paper let the MiGV of these non-nutrient elements be equal to 0. In spite of the fact that TDS is a nutrient element, drinking water with extremely low concentration of TDS may be also unacceptable to consumers because of its flat and insipid taste; most people can gain adequate levels of TDS from other sources. Therefore, the TDS was defined as a non-nutrient element in this paper; the MaGV was assigned 1,000 mg/l according to the WHO (2006), and the MiGV was also given 0.

Currently, the MiGV and MaGV of every variable are listed in Table 1. The second step was to assign a weight coefficient to each element. In general, higher levels of

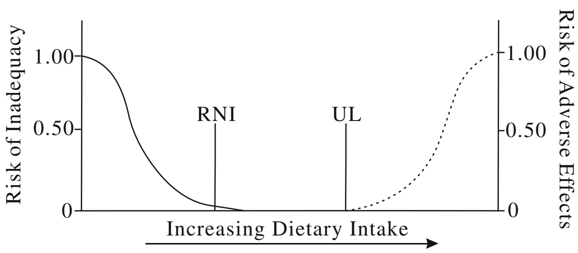


Fig. 2 Relationship of RNI values to risk of nutrient element inadequacy and risk of adverse health effects

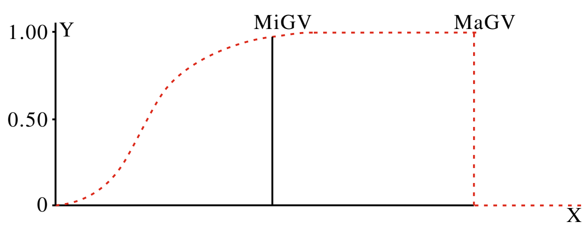


Fig. 3 Relationship of nutrient element concentration to desirability function value (d)

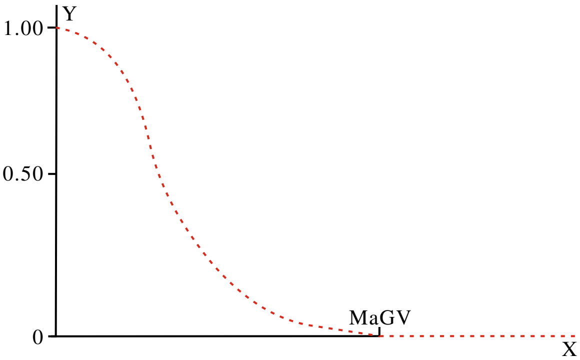


Fig. 4 Relationship of non-nutrient element concentration to desirability function value (*d*)

sodium, calcium, magnesium, and chloride can cause high blood pressure, heart disease, and renal calculi; however, the contribution of drinking water to the daily intake of these elements is small, and their concentrations in groundwater have an insignificant impact on human beings. In contrast, if people who have been exposed to higher concentrations of trace elements in drinking water over long periods of time began to demonstrate an increase in bone disorders, skin cancer, ventricular tachycardia, muscle weakness, and paralysis, it would be likely that those trace elements played a key role in the human body. Based on the above analysis, each element was given a weight coefficient according to its significance on human health. Subsequently, Eq. (7) was used to calculate the relative weight (W) of each hydrochemical element (Table 1).

$$W_i = \frac{w_i}{\sum_{i=1}^{m} w_i} \quad (7)$$

where w_i is the weight value of ith hydrochemical element; W_i is the relative weight of ith hydrochemical element.

Third, each element was transformed to d value that varied over a range of $0 \le d \le 1$ according to the DFs theory. The nutrient element content should range between MiGV and MaGV for good groundwater; therefore, it is the NTB type for an objective function required to achieve a particular target value in the DFs. Figures 2 and 3 are used to transform the nutrient elements to d values, more details of the transformation process are described in the following section.

1. Refereeing Fig. 2 to establish the conversion curve (Fig. 3) for ith nutrient element;
2. Inputting the MiGV and MaGV of ith nutrient element into Fig. 3;
3. The MATLAB program is used to interpolate the curve, after which the d_i value of ith nutrient element can be calculated;
4. Repeating the steps (2)-(3), the d value of each nutrient element was established.

Figure 2 is developed by the Food and Agriculture Organization of the United Nations (FAO) (Suitor and Meyers 2007), which can provide risk information of nutrient element inadequacy and excess intake on human body. The risk decreases as long as the dietary intake (DI) increases from 0 to RNI; when the DI value is between RNI and upper intake level (UL), the nutrient element can meet the physiological balance of human body; it has no adverse effects on human body, health risk is close to 0; when the DI value is greater than UL, the risk increases with an increase in the DI value, it means that individuals whose DI value exceeds the UL may be at risk of adverse health impacts due to the excess intake.

Based on refereed Fig. 2, Figs. 3 and 4 were established using Eqs. 2 and 3, the MiGV, MaGV, and d (d=1−health risk value) values corresponding to the RNI, UL, and health risk values in Fig. 2. Figure 3 reveals that when the concentration of the ith nutrient

Table 2 Statistical summary of the hydrochemical element from wells in the study area mg/l

Parameters	Min	Max	Mean	Stand. dev
TDS	136.92	9,702	1,467.6654	1,295.7147
Br	0.05	10.6	0.3213	0.6928
F	0.05	20	0.9139	1.375
Fe	0.02	55	1.7068	3.6834
I	0.01	3	0.1127	0.2114
NH_4	0.02	28	0.3352	1.6985
NO_2	0.001	88	0.6445	3.9895
NO_3	0.02	495	24.0697	56.3519
pH	7.15	9.26	7.8657	0.3455
As	0.0001	0.9172	0.0431	0.0919
Ba	0.012	2.7998	0.143	0.2026
Li	0.003	0.2862	0.0287	0.0276
Mn	0.0005	5.9757	0.3157	0.5642
Mo	0.003	0.0867	0.0054	0.0074
Sr	0.083	19.1243	1.5613	1.3583
Zn	0.001	1.7903	0.0258	0.0679

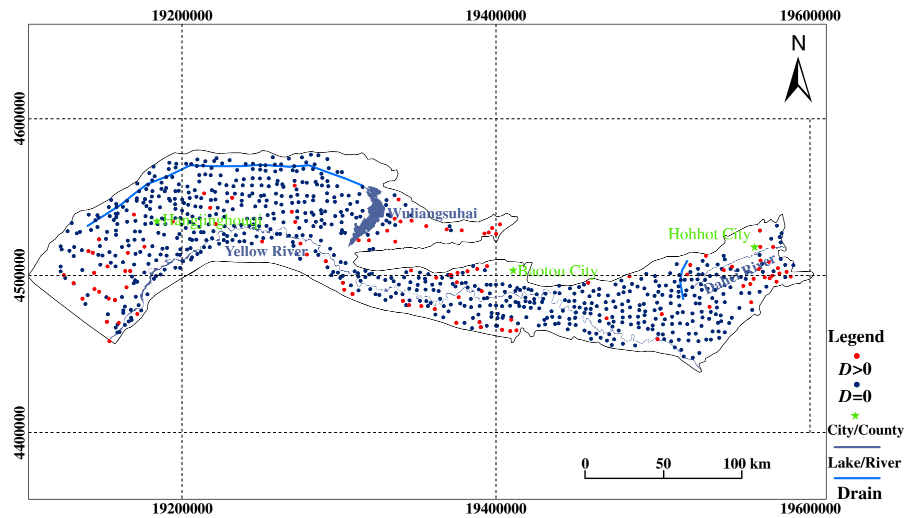


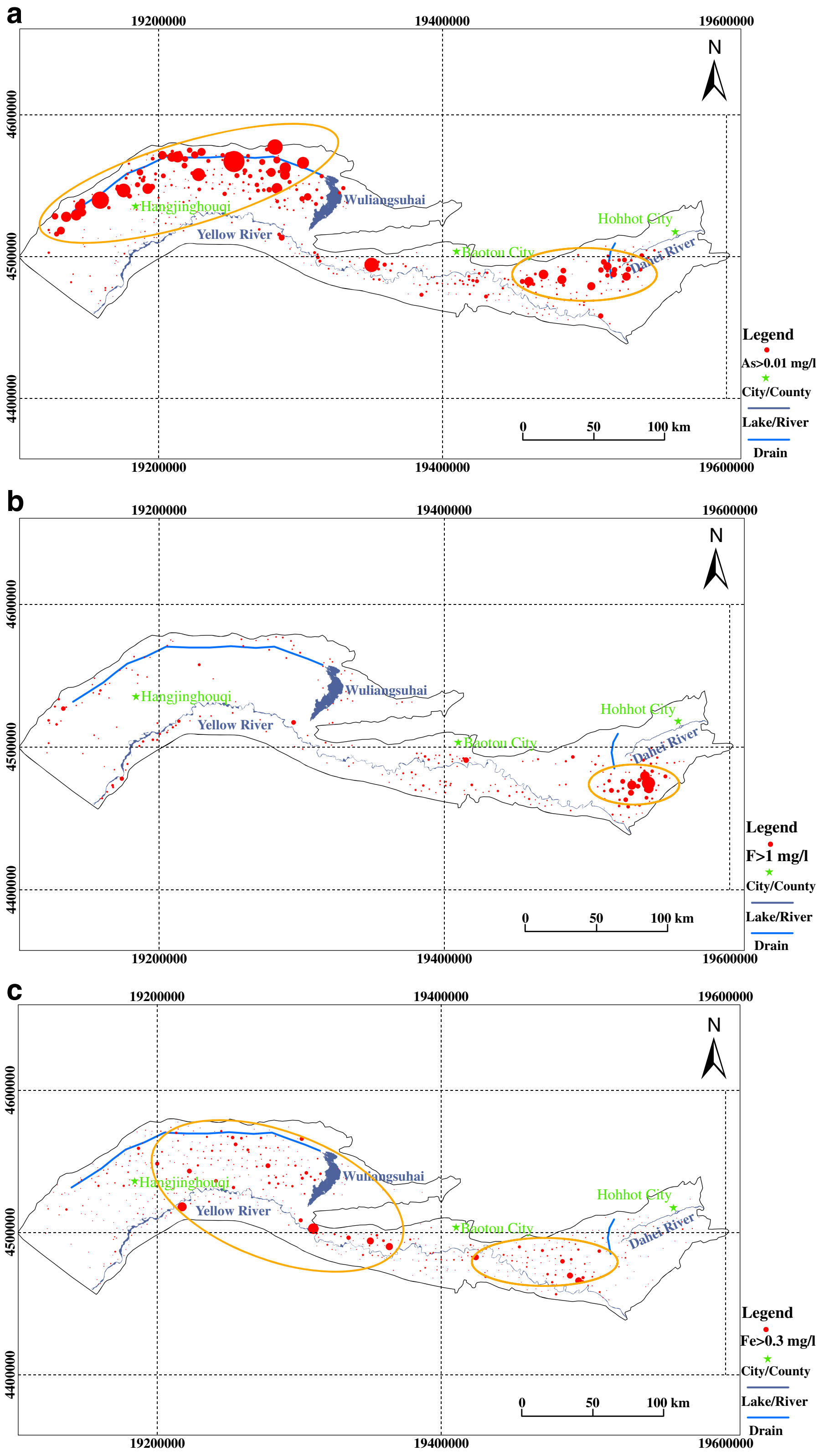
Fig. 5 Health risk assessment results of groundwater samples

element falls within the $MiGV_i$ and the d_i value falls between 0 and 1, it means the consumer is not totally satisfied with this groundwater quality. Extremely low concentration of this element can result in health risks from inadequate *i*th nutrient element intake over long periods of time. If the concentration of *i*th nutrient element ranges from $MiGV_i$ to $MaGV_i$ and the d_i value is close to 1, it represents that the *i*th nutrient element content in groundwater has no adverse effects on human health and can maintain the physiological equilibrium of human body. A large body of studies have proven that human and animal exposure to high-dose of nutrient elements can cause a series of disorders, including muscle weakness and paralysis, heart trouble, and premature aging. When the *i*th nutrient element concentration is above the $MaGV_i$ and d_i is set equal to 0, it denotes that groundwater is unsuitable for drinking use.

The lower the concentrations of non-nutrient elements and TDS, the better the groundwater quality. These elements belong to the SBT for an objective to be minimized value in the DFs. Figure 4 was used to convert the non-nutrient elements and TDS to *d* values using a similar method for the nutrient elements. Figure 4 shows the d_i value decreased as the concentration of the *i*th non-nutrient element increased from 0 to $MaGV_i$ and when the *i*th non-nutrient element concentration exceeded their $MaGV_i$, the d_i decreases to 0, which reflects the groundwater is unsuitable for use in drinking.

The *d* value of each element was obtained, at which point the final step was to calculate the overall desirability (*D*) according to Eq. (4). The *D* value denotes the degree of synthesis satisfaction with the groundwater sample. The higher the *D* value, the better the groundwater quality, and the lower the groundwater's health risks on human. Its value falls within a ranges of $0 \le D \le 1$, which is defined by aggregating the geometric mean of different *d* values. The primary goals of DFs applications in this paper are obtained as follows. If one or more elements exceed the MaGV, their *d* values are equal to 0. According to Eq. (4), *D* value is also equal to 0, which means this groundwater sample is unsuitable for drinking use. A value of *D* close to 1 implies that all the nutrient element contents are within a desirable range [MiGV, MaGV] and the non-nutrient elements concentrations are simultaneously close to 0, reflecting this groundwater sample as totally suitable for human consumption. For *D* values ranging from 0 to 1, the groundwater is suitable for drinking use; however, if people were exposed to this groundwater for long periods of time, it could lead to health risks. There are two reasons for this risk; the first is nutrient element concentrations lower than MiGV, resulting in inadequate nutrient element intake from

Fig. 6 **a** Arsenic concentration spatial distribution map of groundwater samples in cluster 1. **b** Fluoride concentration spatial distribution map of groundwater samples in cluster 1. **c** Iron concentration spatial distribution map of groundwater samples in cluster 1. **d** Manganese concentration spatial distribution map of groundwater samples in cluster 1. **e** Strontium concentration spatial distribution map of groundwater samples in cluster 1. **f** TDS concentration spatial distribution map of groundwater samples in cluster 1. In Fig.6, the higher the concentration of element, the larger the circle diameter and the deeper the color ▶


a
19200000
19400000
19600000
4600000
4500000
4400000
N
Wuliangsuhai
Hangjinghouqi
Yellow River
Hohhot City
Baotou City
Dahei River
0 50 100 km
Legend
As>0.01 mg/l
City/County
Lake/River
Drain
b
F>1 mg/l
c
Fe>0.3 mg/l

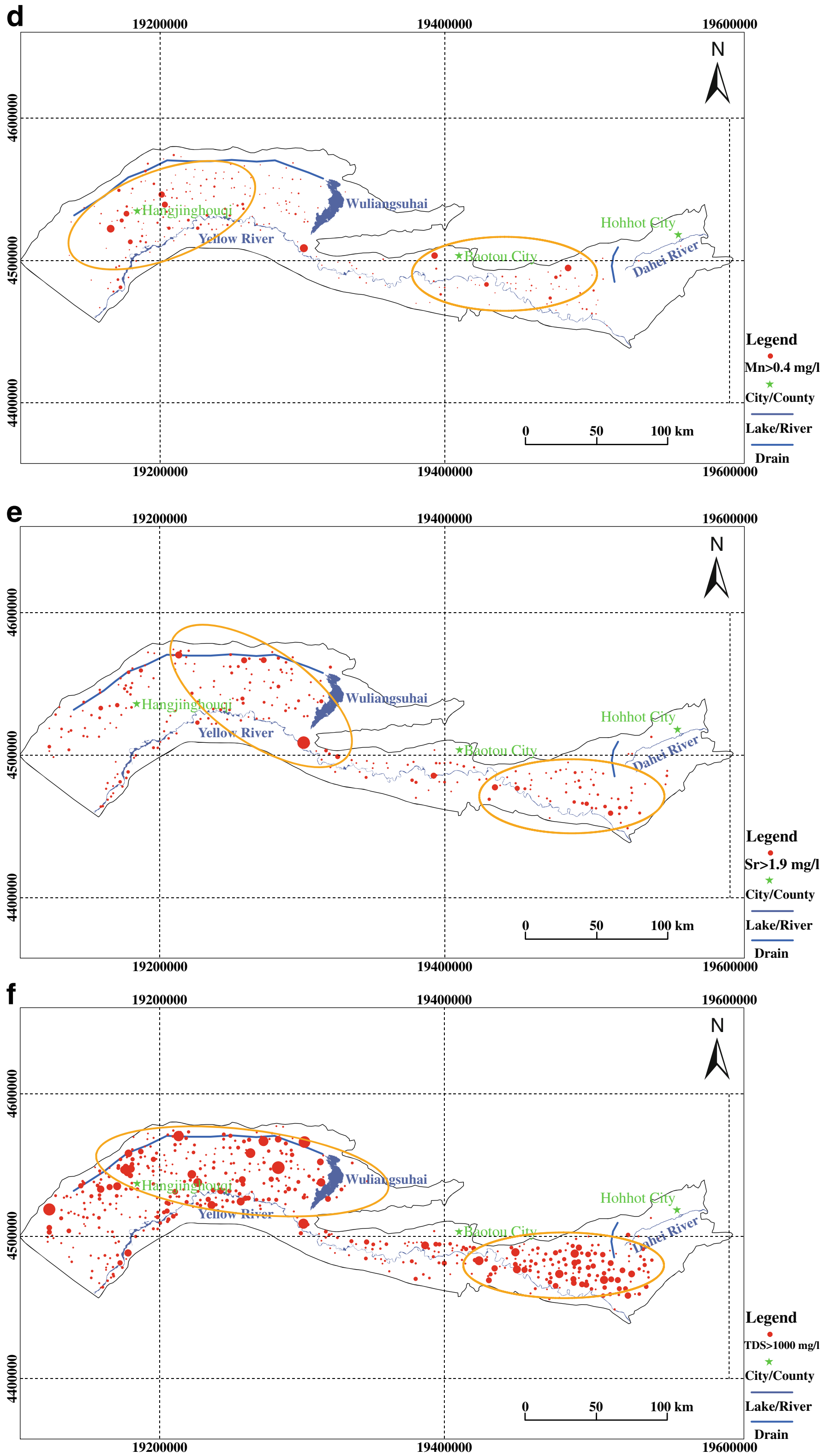


Fig. 6 (continued)

drinking water. Second, with respect to the non-nutrient element, although their concentrations fall within the MaGV in groundwater, it can still cause adverse impacts on the human body to some extent.

Results and discussion

A statistical summary of the hydrochemical variables analyzed for this study is presented in Table 2. According to this table, the pH values in these groundwater samples varied from 7.10 to 9.26 with an average value of 7.86. Of samples, 8.31 % exceeded the MaGV of 8.5 (WHO 2006); the concentration of arsenic varied from 0.0001 to 0.917 mg/l with a mean value of 0.043 mg/l; 45.29 % samples exceeded the MaGV of 0.01 mg/l. The fluoride concentration was very high ranging from 0.05 to 20 mg/l with an average value of 0.91 mg/l. Of samples, 15.13 % fell above the MaGV (1.50 mg/l) specified for fluoride. The concentration of nitrate varied from 0.02 to 495 mg/l with a mean value of 24.07 mg/l; 12.41 % of samples were above the MaGV of 50 mg/l, while 14.03 % of samples exceeded the MaGV (0.20 mg/l) of nitrite with the concentration ranging between 0.001 and 88.00 mg/l, with a mean value of 0.64 mg/l. It is obvious from Table 2 that groundwater pollution has reached concerning levels in HP, and it is therefore necessary to evaluate human health risks of groundwater.

The groundwater samples were divided into two clusters according to their D values; the first cluster included 780 (88.04 %) samples, with D values equal to 0, which means these samples are at the highest risk of being unsuitable for drinking use (Fig. 5); the second group consisted of 107 (11.96 %) samples with D values ranging from 0 to 1; this denotes that the groundwater is suitable for drinking purposes; however, if people were exposed to this drinking water over the long term, they would still confront some health risks. The groundwater sample with the maximum D value (0.98) is located in the Hangjinhouqi, which indicates that it has the best groundwater quality in HP. It is apparent that this sample has no health risks from nutrient or non-nutrient elements. The concentrations of nutrient element exist in the range between MiGV and MaGV, and the non-nutrient element content are simultaneously close to 0 for this sample. The concentration of each element in this groundwater sample can meet the physiological demand of human body. The calculation results presented here demonstrate that the evaluation of health risks can characterize the suitability of groundwater in HP.

According to Table 1, it was found that the concentrations of some elements, such as iron, TDS, arsenic, fluoride, manganese, and strontium, exceeded the MaGV, resulting in 780 samples that are unsuitable for drinking use. Their concentration spatial distribution maps in cluster 1 are described in Fig. 6. Out of 780 samples, 64.94 % of samples are found to be above the MaGV for iron; these samples are located primarily in the northwestern and northeastern parts of the study area; 58.74 % of sample contents fell above the MaGV for TDS. It is obvious that most of the outline values of TDS concentrations appeared at Lang Mountain front; 49.66 % of samples show arsenic concentrations higher than MaGV (0.01 mg/l) in the groundwater. These samples were also located in the northeastern and northwestern sections of the study area. Of strontium concentrations, 28.90 % were found to be exceeding the MaGV. It is observed that the strontium concentrations were appreciably greater than MaGV, reflecting its pollution was not serious. Of samples concentrations, 33.36 % fell above the MaGV for fluoride; 31.41 % of samples indicated manganese concentrations higher than the MaGV (0.40 mg/l) for groundwater.

High trace elements in groundwater have posed significant health impacts on thousands of millions of people. In general, the groundwater contamination problems occur only under special natural circumstances relating to geochemical environment and hydrological condition, and therefore, two necessary conditions are met: (1) abundant source of pollutants and (2) its transportation from the source to water and accumulation. It is well known that arsenic existence in drinking water is mainly due to human activities in south of China (He and Charlet 2013); on the contrary, it mainly derives from nature process in arid and semi-arid north of China. The authors' previous investigation has indicated that water rock interaction responsible for higher concentration of arsenic in HP, which is not influenced by anthropogenic activities (Zhang et al. 2013). Although the arsenic content in mineral in HP is lower than background value of total arsenic in rocks/soil of China (5 mg/kg), it can release from aquifer sediment under reducing conditions and accumulate in some special regions due to the special hydrogeology condition and land uses, causing adverse effects on human body. Previous studies have demonstrated that water table,

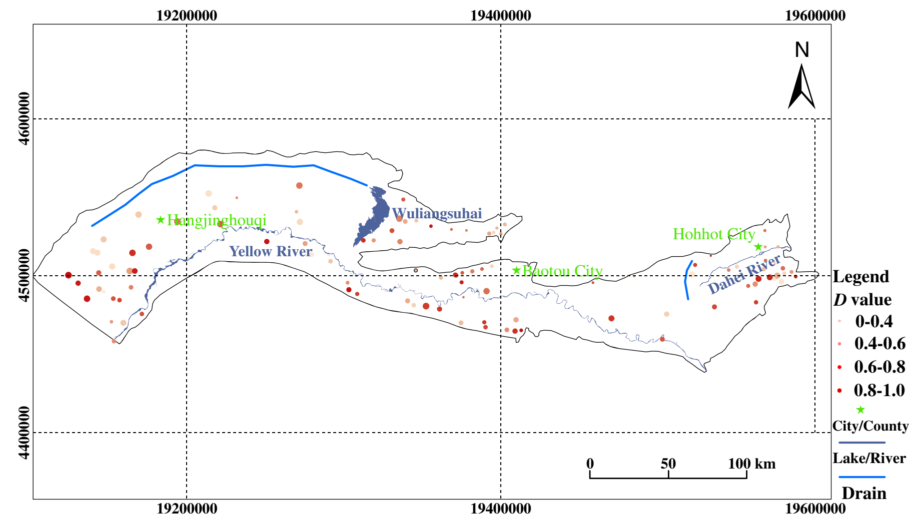


Fig. 7 *D* value spatial distribution map of groundwater samples in cluster 2. In Fig.7, the higher the D value, the larger the circle diameter and the deeper the color

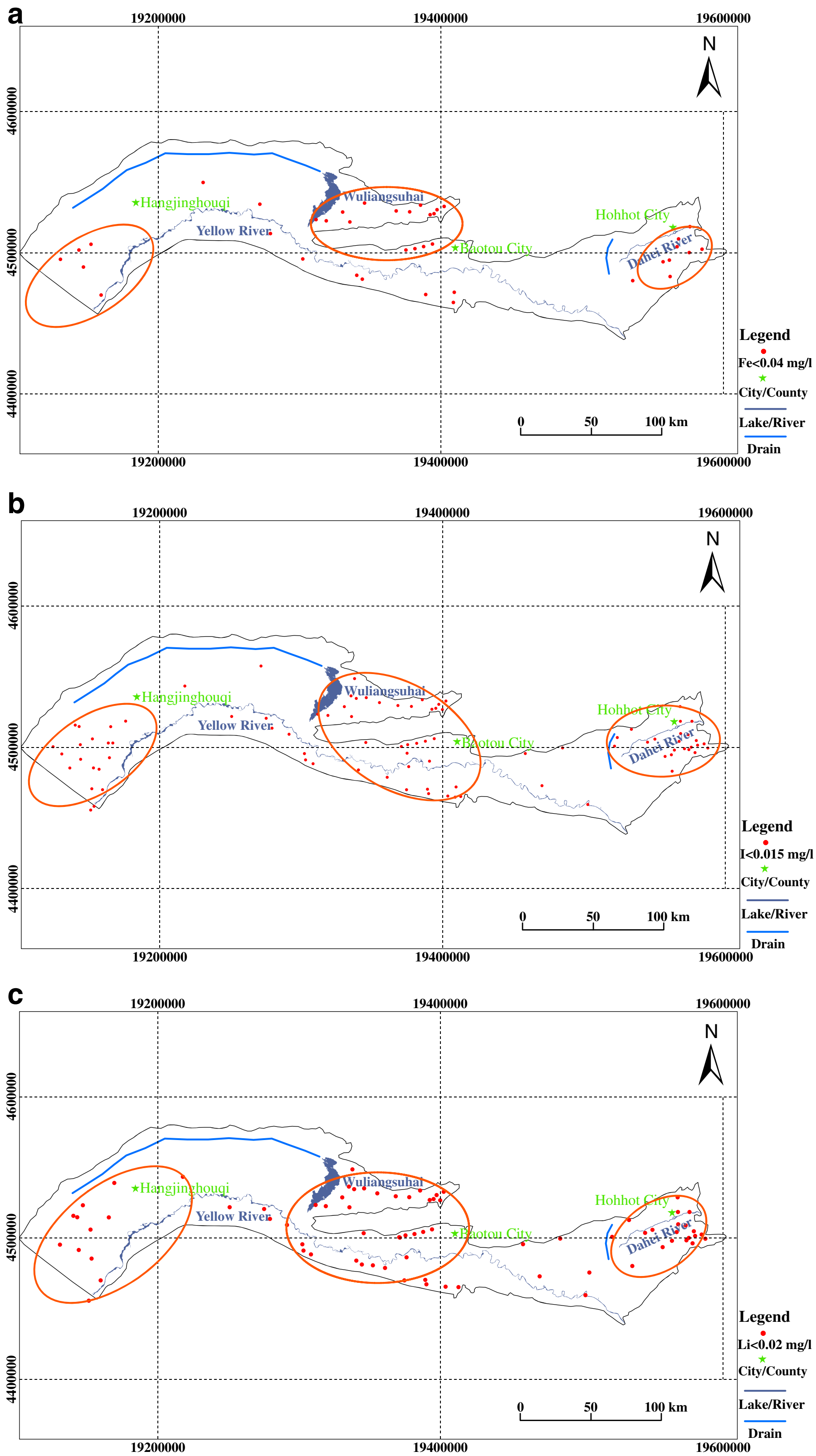
land use, clay layer, and hydraulic gradient of groundwater have significant impacts on groundwater arsenic concentration (Guo et al. 2012; Zhang et al. 2013). There are many irrigation channels from south to north in northwestern of HP; the density of irrigation channels is high, at 0.52 km/km^2 in this region, where the Yellow River was used for irrigation. The infiltration of irrigation water recharged the shallow groundwater, causing the rising of groundwater table. In addition, owing to the gentle land surface in northeastern of HP, groundwater flow conditions are generally sluggish; their hydraulic gradient is less than 0.67%, and therefore, groundwater moves extremely slowly in this region. Both the land surface irrigation and slow groundwater flow can restrict dispersion of atmospheric oxygen into the aquifers, causing reducing condition in this aquifer system, which promoted the release of arsenic from the aquifer sediments. Therefore, the arsenic content is higher in northwestern and northeastern sections of the study area.

Figure 6b indicates that higher concentration of fluoride mainly distributes in northeastern of study area; this region is the main discharge zone of HP. In addition, due to the stronger evaporation process, TDS and pH content are higher in this region. The hydroxide ion can replace the exchangeable fluoride from F-bearing minerals and enhance the groundwater fluoride content under the alkaline conditions. Agricultural activities have directly or indirectly influenced the concentrations of a large body of hydrochemical variables (Baba and Tayfur 2011), groundwater fluoride contamination results from fertilizers and pesticides used in agricultural activities in HP.

Based on the above analysis, the following conclusions can be drawn: with respect to iron and manganese, some ions release from aquifer sediment together with the arsenic under the reduction conditions; the others derive from the anthropogenic activities, such as industrial sewage/sludge discharge, agricultural pesticides and fertilizers, waste disposal sites, imperfect well construction, air pollution, and mining tailing. Therefore, the higher concentrations of TDS, iron, arsenic, fluoride, and manganese in shallow groundwater are a result of water rock interaction, evaporation, and anthropogenic activities.

One hundred seven groundwater samples in group 2 were suitable for drinking use over the short term. These groundwater samples were located in the northern bank of the Yellow River (Fig. 7). Owing to the extremely low concentrations of nutrient element and non-nutrient element emergency, people exposed to this groundwater would experience certain disorders for long periods of time. Comparisons are made to the nutrient element MiGV in Table 1, to identify which

Fig. 8 **a** Iron concentration spatial distribution map of groundwater samples in cluster 2. **b** Iodine concentration spatial distribution map of groundwater samples in cluster 2. **c** Lithium concentration spatial distribution map of groundwater samples in cluster 2. **d** Manganese concentration spatial distribution map of groundwater samples in cluster 2. **e** Molybdenum concentration spatial distribution map of groundwater samples in cluster 2 ▶


a
19200000
19400000
19600000
4600000
4500000
4400000
N
Hangjinghouqi
Yellow River
Wuliangsuhai
Hohhot City
Baotou City
Dahei River
0 50 100 km
Legend
Fe<0.04 mg/l
City/County
Lake/River
Drain
b
19200000
19400000
19600000
4600000
4500000
4400000
N
Hangjinghouqi
Yellow River
Wuliangsuhai
Hohhot City
Baotou City
Dahei River
0 50 100 km
Legend
I<0.015 mg/l
City/County
Lake/River
Drain
c
19200000
19400000
19600000
4600000
4500000
4400000
N
Hangjinghouqi
Yellow River
Wuliangsuhai
Hohhot City
Baotou City
Dahei River
0 50 100 km
Legend
Li<0.02 mg/l
City/County
Lake/River
Drain

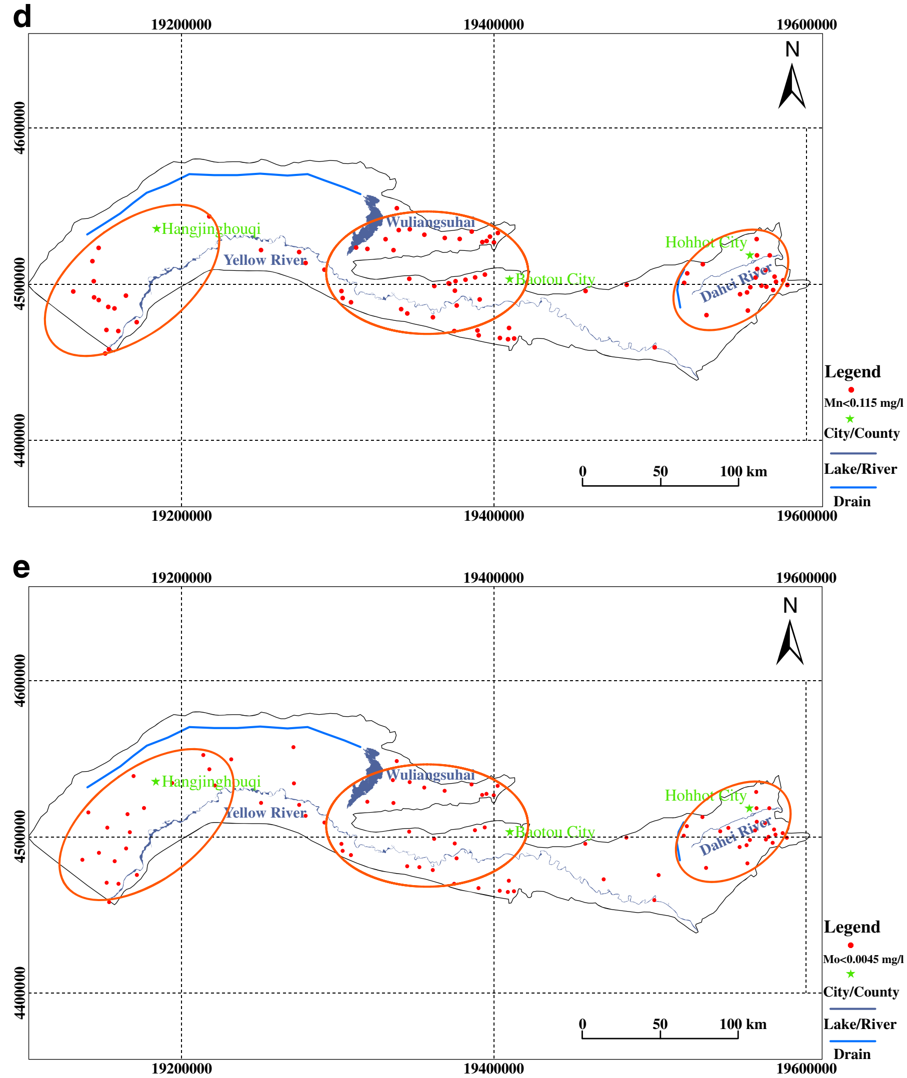


Fig. 8 (continued)

nutrient element content does not satisfy people physiological demands. It is found that the percentages of iodine, molybdenum, manganese, lithium, and iron that have extremely lower concentrations than their MiGV in cluster 2 are 84.91, 79.25, 78.30, 71.70, and 38.70 %, respectively. Figure 8 shows that the samples with such low concentrations of these nutrient element are distributed in the western, central, and northeastern parts of the study area. There are several reasons for this: first, the aforementioned nutrient element concentrations in the Yellow River, the Dahei River, and Wuliangsuhai Lake are lower (Bulletin of Yellow River Resources 2011; Qin et al. 2011); there are close hydraulic connections and frequent conversion relationships between the surface water and shallow groundwater in these three regions. The lake and rivers are major controlling factors of groundwater quality. Second, it is important to note that groundwater is so severely exploited in these three areas that it has a larger renewal rate. Therefore, the quality of the shallow groundwater is similar to the surface water resources with extremely low concentrations of iodine, iron, fluoride, and manganese.

The results from the present study can be utilized to appreciate the suitability of shallow groundwater for drinking, agricultural irrigation, and industrial uses in HP. For example, 107 groundwater samples in cluster 2 can be used for drinking; out of 780 groundwater samples in group 1, the samples with higher concentrations of arsenic, fluoride, iron, manganese, and strontium are only suitable for industrial use; if it used for irrigation purposes, these elements can accumulate in the edible parts of crops, posing considerable health risk to humans and animals; the samples with higher TDS are unsuitable for use in irrigation and industrial. The high TDS groundwater can not only result in the formation scale effect, the barbotage effect, and the corrosive effect for industrial purpose, but also lead to the salinity hazard and permeability problem for agriculture irrigation use, the problems of which in the latter case will reduce the osmotic activity of plants and thus interfere with the absorption of water and nutrients from the soil (Shi et al. 2013). Accordingly, the irrigation water mainly depends on the Yellow River, evidenced by high density agriculture channels in HP.

Conclusions

From the human health risk assessments, 780 groundwater samples were found to be unsuitable for drinking use; if no effective measures are taken, it will result in harmful effects on human life, such as diabetes, high blood pressure, skin cancer, and kidney cancer. Only 107 groundwater samples were suitable for drinking purposes; the residents in the western, central, and northeastern parts of the study area must be careful of the nutrient element equilibrium, supplementing the iron, iodine, lithium, manganese, and molybdenum through diet or medication. The safest groundwater is found in Hangjinhouqi; it has no adverse impacts on the human body and is totally suitable for drinking use. Therefore, this article can provide significant information for the non-technical decision maker to achieve sustainable groundwater resource management in HP over the coming years.

Acknowledgment This study was supported by the Geological Survey Projects Foundation of China (SK201308 and NO. 1212011121141)

References

Avvannavar, S. M., & Shrihari, S. (2008). Evaluation of water quality index for drinking purposes for river Netravathi, Mangalore, South India. *Environmental Monitoring & Assessment, 143*(1–3), 279–290.

Baba, A., & Tayfur, G. (2011). Groundwater contamination and its effect on health in Turkey. *Environmental Monitoring and Assessment, 183*(1–4), 77–94.

Bulletin of Yellow River Resources. (2011). *Yellow River Basin Water Resources Protection Bureau, 2*(26), 1–22.

Cojocaru, C., Khayet, M., Zakrzewska-Trznadel, G., & Jaworska, A. (2009). Modeling and multi-response optimization of pervaporation of organic aqueous solutions using desirability function approach. *Journal of Hazardous Materials, 167*(1–3), 52–63.

Dauvalter, V. A., & Kashulin, N. A. (2010). Chalcophile elements (Hg, Cd, Pb, As) in Lake Umbozero, Murmansk province. *Water Resources, 37*(4), 497–512.

GB 15193.18-2003. (2003). Acceptable daily intake estimation. *Ministry of Health of the People's Republic of China, 3*, 115–120.

GB 5749-2006. (2006). Standards for drinking water quality, Ministry of Health of the People's Republic of China, 2-4.

GB/T 14848-93. (1993). Quality standard for ground water, China Geology Survey, 3-9.

Goyal, S. K., Chaudhary, B. S., Singh, O., Sethi, G. K., & Thakur, P. K. (2010). GIS based spatial distribution mapping and suitability evaluation of groundwater quality for domestic and agricultural purpose in Kaithal district, Haryana state, India. *Environmental Earth Sciences, 61*(8), 1587–1597.

Guo, H., Zhang, B., & Zhang, Y. (2011). Control of organic and iron colloids on arsenic partition and transport in high arsenic groundwaters in the Hetao basin, Inner Mongolia. *Applied Geochemistry, 26*(3), 360–370.

Guo, H., Zhang, Y., Xing, L., & Jia, Y. (2012). Spatial variation in arsenic and fluoride concentrations of shallow groundwater from the town of Shahai in the Hetao basin, Inner Mongolia. *Applied Geochemistry, 27*(11), 2187–2196.

Haddadin, M., Caretto, S. K. D., & Robinson, R. (2002). Potential intake of lithium by the inhabitants of different regions in Jordan. *Pakistan Journal of Nutrition, 1*(1), 39–40.

Haritash, A. K., Kaushik, C. P., Kaushik, A., Kansal, A., & Yadav, A. K. (2008). Suitability assessment of groundwater for drinking, irrigation and industrial use in some North Indian villages. *Environmental Monitoring and Assessment, 145*(1–3), 397–406.

Harrington, J. (1965). The desirability function. *Industrial Quality Control, 21*(10), 494–498.

He, J., & Charlet, L. (2013). A review of arsenic presence in china drinking water. *Journal of Hydrology, 492*(7), 79–88.

Homoncik, S. C., Macdonald, A. M., Heal, K. V., Dochartaigh, B. E., & Ngwenya, B. T. (2010). Manganese concentrations in Scottish groundwater. *Science of the Total Environment, 408*(12), 2467–2473.

Iwami, O., Watanabe, T., Moon, C.-S., Nakatsuka, H., & Ikeda, M. (1994). Motor neuron disease on the Kii Peninsula of Japan: excess manganese intake from food coupled with low magnesium in drinking water as a risk factor. *Science of The Total Environment, 149*(1–2), 121–135.

Jalali, M., & Merrikhpour, H. (2007). Effects of poor quality irrigation waters on the nutrient leaching and groundwater quality from sandy soil. *Environmental Geology, 53*(6), 1289–1298.

Ketata, M., Gueddari, M., & Bouhlila, R. (2011). Suitability assessment of shallow and deep groundwaters for drinking and irrigation use in the El Khairat aquifer (Enfidha, Tunisian Sahel). *Environmental Earth Sciences, 65*(1), 313–330.

Li, T. S., Su, C. T., & Chiang, T. L. (2003). Applying robust multi-response quality engineering for parameter selection using a novel neural–genetic algorithm. *Computers in Industry, 50*(1), 113–122.

Li, J., Ma, C., Ma, Y., Li, Y., Zhou, W., & Xu, P. (2007). Medium optimization by combination of response surface methodology and desirability function: an application in glutamine production. *Applied Microbiology and Biotechnology, 74*(3), 563–571.

Muhammetoglu, A., & Yardimci, A. (2006). A fuzzy logic approach to assess groundwater pollution levels below agricultural fields. *Environmental Monitoring and Assessment, 118*(1–3), 337–354.

Neidhardt, H., Norra, S., Tang, X., Guo, H., & Stuben, D. (2012). Impact of irrigation with high arsenic burdened groundwater on the soil-plant system: results from a case study in the Inner Mongolia, China. *Environmental Pollution, 163*, 8–13.

Nikoo, M. R., Kerachian, R., Malakpour-Estalaki, S., Bashi-Azghadi, S. N., & Azimi-Ghadikolaee, M. M. (2011). A probabilistic water quality index for river water quality assessment: a case study. *Environmental Monitoring and Assessment, 181*(1–4), 465–478.

Phan, K., Sthiannopkao, S., Kim, K.-W., Wong, M. H., Sao, V., Hashim, J. H., et al. (2010). Health risk assessment of inorganic arsenic intake of Cambodia residents through groundwater drinking pathway. *Water Research, 44*(19), 5777–5788.

Qin, Y., Zhang, X., Wang, F., Yan, H., & Han, H. (2011). Scour and silting evolution and its influencing factors in Inner Mongolian Reach of the Yellow River. *Journal of Geographical Sciences, 21*(6), 1037–1046.

Shi, J., Ma, R., Liu, J., & Zhang, Y. (2013). Suitability assessment of deep groundwater for drinking, irrigation and industrial purposes in Jiaozuo City, Henan Province, north China. *Chinese Science Bulletin, 58*(25), 3098–3110.

Singh, V. K., Bikundia, D. S., Sarswat, A., & Mohan, D. (2012). Groundwater quality assessment in the village of Lutfullapur Nawada, Loni, District Ghaziabad, Uttar Pradesh, India. *Environmental Monitoring and Assessment, 184*(7), 4473–4488.

Stigter, T. Y., Ribeiro, L., & Carvalho Dill, A. M. M. (2006). Application of a groundwater quality index as an assessment and communication tool in agro-environmental policies—two Portuguese case studies. *Journal of Hydrology, 327*(3–4), 578–591.

Suitor, C. W., & Meyers, L. D. (2007). *Dietary reference intakes research synthesis: workshop summary*. Washington: National Academies Press. 12 pp.

Third World Academy of Sciences (TWAS). (2002). *Safe drinking water the need, the problem, solutions and an action plan, Report of the Third World Academy of Sciences*. Trieste Italy: Third World Academy of Science.

World Health Organization (WHO). (2006). Guidelines for drinking water quality, *vol. 1 recommendations* (3rd).

Yang, Y., Shang, S., & Jiang, L. (2012). Remote sensing temporal and spatial patterns of evapotranspiration and the responses to water management in a large irrigation district of North China. *Agricultural and Forest Meteorology, 164*, 112–122.

Yidana, S. M., & Yidana, A. (2010). Assessing water quality using water quality index and multivariate analysis. *Environmental Earth Sciences, 59*(7), 1461–1473.

Yu, R., Liu, T., Xu, Y., Zhu, C., Zhang, Q., Qu, Z., et al. (2010). Analysis of salinization dynamics by remote sensing in Hetao Irrigation District of North China. *Agricultural Water Management, 97*(12), 1952–1960.

Zhang, Y., Cao, W., Wang, W., & Dong, Q. (2013). Distribution of groundwater arsenic and hydraulic gradient along the shallow groundwater flow-path in Hetao plain. Northern China. *Journal of Geochemical Exploration*. doi:10.1016/j.gexplo.2012.12.004.

Zobkov, M. B. (2012). Application of desirability functions for water quality analysis. *Water Resources, 39*(1), 90–97.