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Investigation of Groundwater Contamination and Health Implications in a Typical Semiarid Basin of North China

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Abstract: Groundwater chemistry and its potential health risks are as important as water availability in arid and semiarid regions. This study was conducted to determine the contamination and associated health threats to various populations in a semiarid basin of north China. A total of 78 groundwater samples were collected from the shallow unconfined aquifers. The results showed that the phreatic water was slightly alkaline, hard fresh water with ions in the order of $Ca^{2+} > Na^++K^+ > Mg^{2+}$ and $HCO_3^- > SO_4^{2-} > Cl^-$. Four hydrochemical elements, NO_3^- , F^- , Mn and Zn, exceeded the permissible limits. NO_3^- and F^- contaminants may pose health risks to local residents, while the risks of Mn and Zn are negligible. Dermal exposure is safe for all populations, while the oral pathway is not. Minors (i.e., infants and children) are susceptible to both NO_3^- and F^- contaminants, and adults only to NO_3^- . The susceptibility of various populations is in the order of infants > children > adult males > adult females. Anthropogenic activities are responsible for the elevated levels of NO_3^- , Zn, Total dissolved solids (TDS), while F^- and Mn are from geogenic sources. Thus, differential water supplies, strict control of waste, and rational irrigation practices are encouraged in the basin.

Keywords: groundwater contamination; hydrochemistry; health risk assessment; nitrate; arid basin

1. Introduction

Freshwater accounts for only approximately 2.5% of the total water on earth [1]. Furthermore, most freshwaters exist in the forms of ice or snow making them difficult to utilize by human society. Surface water and groundwater are the main water bodies accessed by ecological and social consumers. In contrast with surface water, groundwater has unparalleled advantages of spatio-temporal availability, good stability, easy accessibility, good quality, resistance to pollution, etc. [2,3]. Thus, groundwater has been the primary water resource supporting socio-economic development [4]. It is estimated that over 50% of the global population relies on groundwater resource to satisfy daily water demands, and groundwater is the sole available water resource for people living in many arid and semiarid regions [5,6]. Hydrochemical quality is the prerequisite of groundwater usage, and is crucial to human



health and social development [7]. Understanding groundwater chemistry and its associated potential threats to humans is vital for society and human sustainable development, especially in the regions facing surface water scarcity.

Groundwater is characterized by extremely low flow rate, with a mean residence time of ~1500 years in the aquifers [8]. During the long residence time, it has sufficient time to interact with the surrounding media of the aquifers [9,10], and harmful elements such as fluoride, arsenic, and other toxic elements can become dissolved [11–14]. In addition, many external elements in groundwater have been shown to be elevated in recent decades in many regions around the world [15–20]. For instance, nitrogen including nitrates, nitrites, and ammonia in aquifers have been found to be elevated in both urban and agricultural areas. The origins of these compounds could vary from domestic sources, like effluents and septic tanks, to agricultural practices [21–23]. The levels of toxic metals in groundwater have also demonstrated rapid increases in many sites such as landfill sites, wastewater/reclaimed water irrigation lands, mining areas, and industrial sites [16,19,24–26]. The deterioration of water quality has been reported in many aquifers around the world [26–28]. Deteriorated groundwater quality will further intensify the scarcity of water resources and poverty, especially in arid and semiarid areas of developing countries, and finally, threaten the stability and sustainable development of society.

The deterioration of groundwater quality has attracted the attention pf researchers, as high concentrations of certain elements could potentially cause adverse health effects, including a variety of cancers and noncarcinogenic illnesses like bone and kidney diseases [1]. Due to physical and behavioral differences, various populations would have different sensitivities to the toxic chemical elements contents of groundwater [29]. Considering the preciousness of available water resources, groundwater should not be abandoned once showing high concentrations of certain elements. The smart decision is to supply the water differently to various consumers according to its quality and requirements. Therefore, investigation and assessment of the potential health risks for various populations posed by harmful elements in groundwater, along with the identification of their sources, are the prerequisites to realize safety and sustainability of water supplies [24]. Human health risk assessments proposed by the United States Environmental Protection Agency (USEPA) [30] are among the most useful approaches for quantifying the degrees of potential risks for water contaminants. This approach has been widely used to evaluate the potential health risks from water contaminants and provide scientific guidance for differential water supplies and cost-effective water treatments [13,31–34].

In arid and semiarid regions, attention should be adequately paid to groundwater supply in terms to water shortages and potential threats to human health. The present study focuses on the groundwater in a typical semiarid basin of north China. The specific objectives are to: (1) delineate the hydrochemical characteristics and contamination of groundwater in the basin, (2) assess the potential health risk for various segments of the population posed by contaminant(s) via different exposure pathways, and (3) identify sources of contaminant(s) for scientific and sustainable groundwater resource management.

2. Study Area

The study area, i.e., the Yanqing basin, is a typical semiarid basin in north China (Figure 1). The area extends between latitudes of 40°17′37″–40°35′28″ N and longitudes of 115°44′43″–116°15′9″ E and covers an area of about 540 km². This basin is surrounded by mountains in three directions and is adjacent to a big reservoir in the southwest. Weishui River is the main river in the basin, running from northeast to southwest. The Yanqing basin is characterized by a temperate continental monsoon climate with an average temperature of 8.8 °C. The mean annual precipitation is about 430 mm, with more than 70% occurring from June to September. The average annual potential evaporation reaches 1652 mm, which is about four times the annual precipitation.

The terrain of Yanqing basin is flat overall, and gradually inclines from the northeast to the southwest. The elevation of the basin ranges from 474 m in the southwest to approximate 600 m in the northeast. Quaternary deposits dominantly cover the basin, with thicknesses ranging from ~100 m at the mountain front to more than 1000 m at the Guanting reservoir area. The lithology gradually

changes from sandy gravels in the piedmont area to fine sands and silty clay in the southwestern basin, resulting in aquifers varying from single unconfined layers to multilayered structures (Figure 2). Groundwater generally flow from northeast to southwest within the basin.



Figure 1. Location of groundwater samples in the Yanqing basin of North China.



Figure 2. Hydrogeological cross section along the A-A' in Yanqing basin.

3. Materials and Methods

3.1. Sample Collection and Analysis

Groundwater samples were collected from 78 shallow wells with a depth range of 30–50 m across the basin during the October of 2017 (Figure 1). All samples were phreatic water from the shallow unconfined aquifers in the basin. Wells were pumped for at least 15 minutes to remove the stagnant water before in situ measuring and sampling. The pH was measured in situ using a multiparameter device (Multi 350i/SET, Munich, Germany). Groundwaters were sampled in 2.5 L clean high-density polyethylene bottles that had been thoroughly prewashed with the target water. Samples were sent to the Laboratory of Groundwater Sciences and Engineering of the Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences (LGSE-IHEG-CAGS, Shijiazhuang, China) for analysis within 24 hours. Total dissolved solids (TDS) and HCO₃⁻ were determined with the aid of gravimetric analysis and acid–base titration, respectively. NH_4^+ , SO_4^{2-} , Cl^- , NO_3^- , $NO_2^$ and F⁻ were analyzed using ion chromatography (Shimadzu LC-10ADvp, Kyoto, Japan). Major cations (K⁺, Na⁺, Ca²⁺, Mg²⁺) and trace elements (Fe, Mn, Zn) were measured by inductively coupled plasma-maa spectrometry (Agilent 7500ce ICP-MS, Tokyo, Japan) [15,35]. All samples had relative errors within ±6%.

3.2. Health Risk Assessment

The potential health hazards posed by contaminants in groundwater can be quantitatively assessed with the aid of the health risk assessment model proposed by the United States Environmental Protection Agency (USEPA). Dermal contact (i.e. dermal absorption when washing) and drinking water intake (oral pathway) are the dominant potential exposure pathways to groundwater contaminants in daily life. Thus, dermal and oral exposure pathways are considered in the present study. According to physiological and behavioral differences, people relying on groundwater for daily water consumption are divided into four groups: infants (0–6 months), Children (7 months–17 years old), adult females (>18 years old). Noncarcinogenic risk is considered based on the potential contaminants (nitrogen, F^- , Fe, Mn, Zn) of groundwater in this study [36].

The noncarcinogenic risks via dermal contact pathway can be determined as follows:

$$CDI_{dermal} = (C_i \times K \times S_a \times T \times EF \times ED \times EV \times CF) / (BW \times AT)$$
(1)

$$S_a = 239 \times BH^{0.417} \times BW^{0.517}$$
 (2)

$$HQ_{dermal} = CDI_{dermal} / RfD_{dermal}$$
(3)

$$RfD_{dermal} = RfD_{oral} / ABS_{gi}$$
(4)

where CDI_{oral} is the daily exposure dose through drinking water intake pathway [mg/(kg×day)], C_i represents the concentration of the target contaminants in groundwater (mg/L), K represents the skin permeability parameter (cm/h), S_a represents the skin surface area, T represents the contact duration (h/d), EF denotes exposure frequency (days/year), ED indicates exposure duration (years), EV represents the exposure frequency of daily dermal contact (time/day), CF represents the unit conversion factor (L/cm³).,BW is the average body wight (kg), AT expresses the average time (days, AT = ED × 365), BH denotes the average body height (cm), RfD_{oral} signifies the reference dose of a specific pollutant [mg/(kg × day)] through dermal contact pathway, and ABS_{gi} indicates the gastrointestinal absorption factor.

The noncarcinogenic risks through the oral pathway can be assessed as follows:

$$CDI_{oral} = (C_i \times IR \times EF \times ED) / (BW \times AT)$$
(5)

$$HQ_{oral} = CDI / RfD_{oral}$$
(6)

$$HI_{oral} = HQ_{oral,1} + HQ_{oral,2} + \dots + HQ_{oral,i}$$
(7)

where CDI_{oral} is the chronic daily intake dose via drinking water intake pathway $[\text{mg}/(\text{kg} \times \text{day})]$, HQ_{oral} is the hazard quotient of noncarcinogenic risk due to drinking water intake pathway, HI_{oral} represents the overall noncarcinogenic health risks of multiple contaminants (1, 2, ..., i) by drinking the water, IR refers to the ingestion rate of drinking water (L/day), and RfD_{oral} denotes the reference dose of a specific pollutant [mg/(kg × day)] through drinking the water. The calculation parameters used for health risk assessment in this study are listed in Table 1.

The total hazard quotient of noncarcinogenic risk of specific pollutants (i) (HQ_{total}) and overall noncarcinogenic health risks of multiple contaminants (1, 2, ..., i) (HI_{total}) through both dermal and drinking intake pathways were determined as follows:

$$HQ_{total,I} = HQ_{oral,i} + HQ_{dermal,i}$$
(8)

$$HI_{total} = HI_{oral} + HI_{dermal}$$
(9)

Exposure			Value	Composition	RfD _{oral}		
Parameter I	Infants	Children	Adult Females	Adult Males	composition	(mg/(kg \times day))	
EF (days/year)	365 ^a	365 ^a	365 ^a	365 ^a	NO ₃ -	1.6 ^d	
ED (years)	0.5 ^b	6 ^b	30 ^b	30 ^b	F	0.06 ^c	
IR (L/day)	0.65 ^b	1.5 ^b	2.66 ^b	3.62 ^b	Fe	0.7 ^a	
BW (kg)	6.94 ^b	25.9 ^b	64.0 ^b	73.0 ^b	Mn	0.14 ^a	
BH (cm)	62.1 ^b	117.0 ^b	163.0 ^b	165.3 ^b	Zn	0.3 ^e	
T (h/d)	0.4 ^b	0.4 ^b	0.4 ^b	0.4 ^b			
ABSgi	0.5 ^b	0.5 ^b	0.5 ^b	0.5 ^b			
EV (day)	1 ^a	1 ^a	1 ^a	1 ^a			
$CF(L/cm^3)$ (0.002 ^b	0.002 ^b	0.002 ^b	0.002 ^b			
K (cm/h) (0.001 ^b	0.001 ^b	0.001 ^b	0.001 ^b			

Table 1. Exposure parameters and RfD_{oral} used in the health risk assessment.

^a refer to [36]; ^b refer to [37]; ^c refer to [30]; ^d refer to [38]; ^e refer to [39].

3.3. Multivariate Statistical Analysis

Multivariate statistical analysis was carried out by descriptive statistical analysis, box plot, correlation analysis, and principal component analysis (PCA) using the SPSS software (IBM, Chicago, USA). The spatial distributions were obtained with the aid of the Kriging interpolation module of ArcGIS software (Esri, Redlands, USA). The descriptive statistical analysis and box plot were used to clearly illustrate variations in the physical-hydrochemical parameters of groundwaters in the study area. Correlation analysis was conducted to quantify the relation degree of two physical-hydrochemical parameters. A correlation coefficient close to +1 or -1 indicates strong positive or negative correlation between the two parameters, while coefficients close to 0 demonstrate a weak correlation [13]. PCA is a useful mathematical method to reduce the dimensionality of the dataset in order to identify the key mechanisms influencing/controlling groundwater chemistry without losing important information [40–42]. This method can transform the correlated observations to uncorrelated quantities (principal components) based on an orthogonal transformation. The principal component (PC) can be expressed as follows [41]:

$$z_{ij} = a_{i1}x_{1j} + a_{i2}x_2 + a_{i3}x_{3j} + \dots + a_{im}x_{mj}$$
⁽¹⁰⁾

where a represents the loading of component, z indicates the score of components, x denotes the measured value of a variable, *i* is the number of components, *j* signifies the number of samples, and m is the variables number.

4. Results and Discussion

4.1. Groundwater Hydrochemical Charecteristics

A statistical summary of the physicochemical analysis results for the groundwater in the study area is given in Table 2. The groundwaters have a slightly alkaline nature with a pH range of 7.3–8.1, averaging 7.7, which is well within the Chinese Guidelines [43]. The total hardness (TH) ranges between 86 mg/L and 414 mg/L, with an average of 216 mg/L. All groundwaters are within the maximum acceptable limits of 450 mg/L given by the Chinese Guideline [43]. The total dissolved solids (TDS) are in the range of 203–606 mg/L with an average of 316 mg/L. The relatively high TDS groundwaters were mainly distributed in the central basin in areas dominantly associated with agricultural lands, and some sporadic residential areas (Figure 3a). Groundwaters at all sites are fresh water according to the classification based on TDS (fresh: <1000 mg/L, slightly saline: 1000–3000 mg/L, moderately saline: 3000–10,000 mg/L, highly saline: 10,000–35,000 mg/L) suggested by the US Geological Survey [44]. The integrated classification of groundwater quality based on TDS and TH is demonstrated in Figure 4. It can be seen that all groundwaters belong to the hard freshwater category.

Index	Min	Max	Mean	SD *	Guideline	% of the Sample Exceeding the Chinese Guideline
pН	7.3	8.1	7.7	0.2	6.5-8.5 **	/
TH (mg/L)	86	414	216	65	450 **	/
TDS (mg/L)	203	606	316	86	1000 **	/
$Na^{+} + K^{+} (mg/L)$	5.3	165.0	28.9	37.3	200 ****	/
Ca^{2+} (mg/L)	20.0	89.2	53.4	16.0	75 ***	1.3%
Mg^{2+} (mg/L)	9.1	32.8	19.5	8.2	50 ***	/
Cl ⁻ (mg/L)	2.4	61.0	14.8	12.8	250 **	/
SO_4^{2-} (mg/L)	3.8	86.4	20.2	19.0	250 **	/
HCO_3^- (mg/L)	173	494	279	79	/	/
$NO_3-N(mg/L)$	0.04	21.80	5.01	5.11	10.0 ***	11.8%
NO_2 -N (mg/L)	0.01	0.09	0.01	0.02	1.0 **	/
NH_4 -N (mg/L)	0.02	0.40	0.12	0.16	0.5 **	/
F^{-} (mg/L)	0.12	1.17	0.39	0.22	1.0 **	2.6%
Fe (mg/L)	0.005	0.252	0.017	0.051	0.3 **	/
Mn (mg/L)	0.001	0.173	0.004	0.022	0.1 **	1.3%
Zn (mg/L)	0.001	1.12	0.032	0.134	1.0 **	1.3%

Table 2. Statistical analyses physicochemical parameters and drinking water standard.

* Standard Deviation; ** Chinese Guideline [43]; *** WHO Guideline [45]; **** refer to [46].

The dominant major cation ion is Ca^{2+} , with concentrations ranging from 20 mg/L to 89.2 mg/L, and an average of 53.4 mg/L. The concentrations of Na^++K^+ have a large range, i.e., 5.3–165 mg/L, averaging 28.9 mg/L. Among the major cations, Mg^{2+} has relative low concentrations, ranging from 9.1 mg/L to 32.8 mg/L, with an average of 19.5 mg/L. HCO_3^- is the dominant major anion ion, with concentrations ranging from 173 mg/L to 494 mg/L and an average of 279 mg/L, followed by SO_4^{2-} with 3.8 mg/L, 86.4 mg/L, and 20.2 mg/L as the minimum, maximum, and mean values, respectively. The Cl^- concentrations range from ~2.4 mg/L to 61 mg/L, with an average of ~14.8 mg/L. The concentrations of all major ions except Ca^{2+} are within the permissible limits, and about 1.3% of groundwater samples are found to slightly exceed the limit of 75 mg/L (Table 2). Overall, the abundance of major ions is in the order $Ca^{2+} > Na^+ + K^+ > Mg^{2+}$ for cations and $HCO_3^- > SO_4^{2-} > Cl^-$ for anions (Figure 5).



Figure 3. Spatial distribution of (a) TDS, (b) NO₃-N, (c) F, (d) Mn and (e) Zn in the study area.

Nitrogen was detected in the groundwater in the study area. The concentrations of NO₃-N range from 0.04 mg/L to 21.8 mg/L, with an average of 5.01 mg/L, and about 11.8% of groundwater samples are found with NO₃-N beyond the permissible limit of 10 mg/L given by WHO [45]. High NO₃-N groundwaters are primarily distributed in residential areas ranging from Kangzhuang to Badaling Town, and some residential areas of the other major towns except Yanqing city (Figure 3b). Groundwaters at all sampling sites have low concentrations ranging, from 0.01 mg/L to 0.09 mg/L with an average of 0.01 mg/L for NO₂-N, and from 0.02 mg/L to 0.4 mg/L, with an average of 0.12 mg/L for NH₄-N. All groundwaters have acceptable concentrations of NO₂-N and NH₄-N according to the Chinese Guidelines [43]. The concentrations of F^- are observed to be slightly above the permissible limit of 1 mg/L given by Chinese Guideline at 2.6% of the sampling sites, showing a range of 0.12–1.17 mg/L and averaging 0.39 mg/L. For toxic metals, the concentrations are in the range of 0.004 mg/L, for Mn, and 0.001–1.12 mg/L, with an average of 0.032 mg/L, for Zn. The majority of sampling sites have low toxic metal contents, and only 1.3% of samples for Mn and 1.3% of samples for Zn are observed to be slightly

beyond the limits recommended in the Chinese Guideline. The high F^- , Zn, and Mn groundwaters are all sporadically distributed in the basin.



Figure 4. Scatter plots of TDS vs TH showing groundwater quality.



Figure 5. Piper diagram showing the chemical compositions of groundwaters in Yanqing basin.

4.2. Potential Health Risk Assessment

4.2.1. Spatial Distribution of the Total Health Risk

Groundwaters in the study area are found with the NO₃-N, F⁻, Mn, and Zn beyond the permissible limits of Chinese Guideline (Table 2). Their higher concentrations may pose health hazards to human beings. Noncarcinogenic risks to human health should be considered if exposed to high concentrations of NO₃-N, F⁻, Mn, and Zn in daily life recommended by USEPA [36]. Thus, these four chemical substances (NO₃-N, F⁻, Mn and Zn) are taken into account to identify their noncarcinogenic risks via

dermal and oral exposure pathways. Four population groups, i.e., infants, children, adult females, and adult males are considered. The assessment results are listed in Table 3.

Overall, human health risk may be posed by the harmful hydrochemical substances in groundwater according to the overall noncarcinogenic health risk (HI_{total}, i.e. HI of multiple potential harmful elements including NO₃-N, F⁻, Mn and Zn via both dermal and oral exposure pathways) assessment results. The HI_{total} values range from 0.42 to 6.14, with an average of 1.99, for infants, from 0.26 to 3.80, with an average of 1.23, for children, from 0.19 to 2.73, with an average of 0.89, for adult females, and from 0.22 to 3.25, with an average of 1.06, for adult males. According to the classification of noncarcinogenic risk based on HI values (Medium chronic risk: $1 \le \text{HI} < 4$, High chronic risk: $\text{HI} \ge 4$) [47], most groundwaters present medium or high chronic risk for infants, and only less than 25% showed low/negligible risks (HI < 1) which can be ignored (Figure 6). It also clearly shows that the percentage of groundwaters with high chronic risk is limited and only a handful of groundwaters have HI_{total} values greater than 4. The risk can be reduced or even eliminated if some appropriate measures are taken. All groundwaters at sampling sites are with total HI values less than 4 for other populations, implying low to medium chronic risk for children, adult females, and males. The total chronic risk via multiple pathways is in the order of infants > children > adult males > adult females (Figure 6).



Figure 6. Box plots of the overall noncarcinogenic health risks by multiple pathways.

The distribution of overall potential noncarcinogenic risks for various populations are demonstrated in Figure 7. It is clearly shown that the areas of potential chronic risks for various populations are in the order of infants > children > adult males > adult females (Figure 7), which coincide with the aforementioned statistic results (Figure 6). It can be seen that the areas of high potential noncarcinogenic risks for infants are concentrated adjacent to Zhangshanying, Kangzhuang, Badaling, Yongning, and some other sporadic area of the central basin (Figure 7a). For other populations, the high potential risks are mainly distributed adjacent to towns including Zhangshanying, Kangzhuang, Badaling, and Yongning (Figure 7b–d), which are also the highest potential risk areas for infants.

Population	Indexes	Dermal Contact Pathway				Dr	inking W	ater Pathw	ay	Multiple Pathways (Oral + Dermal)				
1 of minition		Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD	
	HQ _{NO3-N}	0.00	0.05	0.01	0.01	0.01	5.65	1.30	1.33	0.01	5.7	1.31	1.34	
Infants	HQ _F	0.00	0.05	0.01	0.01	0.19	1.83	0.60	0.34	0.19	5.35	0.67	0.64	
	HQ _{Mn}	0.00	0.00	0.00	0.00	0.00	0.12	0.00	0.02	0.00	0.12	0.00	0.02	
	HQ _{Zn}	0.00	0.00	0.00	0.00	0.00	0.35	0.01	0.04	0.00	0.35	0.01	0.04	
	HI	0.00	0.05	0.02	0.01	0.42	6.08	1.98	1.29	0.42	6.14	1.99	1.36	
	HQ _{NO3-N}	0.00	0.03	0.01	0.01	0.01	3.49	0.80	0.82	0.01	3.53	0.81	0.83	
Children	HQ _F	0.00	0.03	0.00	0.00	0.12	1.13	0.37	0.21	0.12	3.31	0.41	0.40	
	HQ _{Mn}	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0.01	0.00	0.07	0.00	0.01	
	HQ _{Zn}	0.00	0.00	0.00	0.00	0.00	0.22	0.01	0.03	0.00	0.22	0.01	0.03	
	HI	0.00	0.04	0.01	0.01	0.26	3.76	1.19	0.80	0.26	3.8	1.23	0.84	
	HQ _{NO3-N}	0.00	0.03	0.01	0.01	0.00	2.51	0.58	0.59	0.00	2.53	0.58	0.59	
	HQ _F	0.00	0.02	0.00	0.00	0.08	0.81	0.27	0.15	0.08	2.38	0.30	0.29	
Females	HQ _{Mn}	0.00	0.00	0.00	0.00	0.00	0.05	0.00	0.01	0.00	0.05	0.00	0.01	
	HQ _{Zn}	0.00	0.00	0.00	0.00	0.00	0.16	0.00	0.02	0.00	0.16	0.00	0.02	
	HI	0.00	0.03	0.01	0.01	0.19	2.7	0.86	0.57	0.19	2.73	0.89	0.60	
	HQ _{NO3-N}	0.00	0.02	0.01	0.01	0.01	2.99	0.69	0.7	0.01	2.53	0.58	0.59	
	HQ _F	0.00	0.02	0.00	0.01	0.10	0.97	0.32	0.18	0.1	2.83	0.35	0.34	
Males	HQ _{Mn}	0.00	0.00	0.00	0.00	0.00	0.06	0.00	0.01	0.00	0.06	0.00	0.01	
	HQ _{Zn}	0.00	0.00	0.00	0.00	0.00	0.19	0.01	0.02	0.00	0.19	0.01	0.02	
	HI	0.00	0.03	0.01	0.01	0.22	3.22	1.02	0.68	0.22	3.25	1.06	0.71	

Table 3. Statistics of health risks assessment results through drinking and dermal contact.

HQ denotes the hazard quotient of noncarcinogenic risk by a specified contaminant; HI signifies overall noncarcinogenic health risks of multiple contaminants.



Figure 7. Spatial distribution of the overall noncarcinogenic health risks by multiple pathways for (a) infants, (b) children, (c) adult females and (d) adult males.

4.2.2. Discrepancy of Health Risk through Various Exposure Pathways

Risks from different exposure pathways were identified and are presented in Figure 8. It can be clearly seen that the total health risks through dermal contact pathway for infants, children, adult females, and males are far below the permissible limit of 1, implying the total health risks potentially posed by NO₃-N, F, Mn and Zn via dermal exposure are very low, and would not likely threaten the health of local residents (Figure 8a). In contrast, the total health risks via oral pathway for various populations are greater than 1 at some sampling sites, indicating the existence of potential health impacts on humans (Figure 8b). Thus, the overall noncarcinogenic health risks demonstrated in Figure 6 are dominantly through the oral pathway (Figure 8).



Figure 8. Box plots of the overall noncarcinogenic health risks via (a) dermal and (b) oral pathway.

For the oral pathway, the HI (HI_{oral}, i.e. HI of oral pathway) values are in the range of 0.42–6.08 for infants, 0.26–3.76 for children, 0.19–2.70 for adult females, and 0.22–3.22 for adult males, with an average of 1.98, 1.19, 0.86, and 1.02, respectively (Table 3). The total potential health risks for various populations

via oral pathway (HI_{oral}) are in the order of infants > children > adult males > adult females (Figure 8b), which is consistent with the overall health risk (HI_{total}) order demonstrated in Figure 6.

4.2.3. Health Risk from Nitrogen, Fluoride, and Toxic metals

In order to further reveal the risk of each contaminant, the hazard quotients (HQ) of NO₃-N, F^- , Mn, and Zn were determined. As discussed in Section 4.2.2, the health risk via the dermal contact pathway is negligible. Thus, only oral exposure is discussed here.

As demonstrated in Table 3 and Figure 9, the HQ values of NO₃-N via the oral pathway are in a range of 0.01–5.65 for infants, 0.01–3.49 for children, 0.01–2.51 for adult females, and 0.01–2.99 for adult males, with an average of 1.30, 0.80, 0.58, and 0.69, respectively. This implies that NO₃-N contamination groundwater at some sampling sites presents a potential threat to all populations, as some HQ values exceeding the permissible limit (HQ = 1). The HQ values of F⁻ via theoral pathway are in a range of 0.19–1.83, with an average of 0.60, for infants, 0.12–1.13, with an average of 0.37, for children, and less than 1 for both adult females and adult males, indicating that F⁻ could pose potential health threats to infants and children, but not to adults. The maximum HQ values of Mn and Zn substances in groundwater via the oral pathway are far below the permissible limit of 1 for all populations, suggesting that the effect of these toxic metals on human health are negligible, although groundwaters at some local sites showed slightly higher concentrations. Therefore, the potential health risks are primarily posed by NO₃-N and F⁻, rather than Mn and Zn substances. Infants were shown to be the most susceptible population to harmful substances in groundwater, followed by children, adult males, and adult females (Figure 9).



Figure 9. Box plots of the hazard quotient of noncarcinogenic risk due to (**a**) NO₃-N, (**b**) F^- , (**c**) Mn, and (**d**) Zn through oral pathway.

The distributions of HQ of NO₃-N and F^- via the oral pathway for various populations are further revealed in Figures 10 and 11. As shown in Figure 10, many towns in the basin like Zhangshanying, Kangzhuang, Badaling, Shenjiaying, and Yongning presented relatively high noncarcinogenic risk of NO₃-N. The distributions of NO₃-N risk for various populations (Figure 10) were consistent with the overall noncarcinogenic risk distribution (Figure 7). As the chronic health risk of F^- for adults

was low and negligible (Figure 9b), only F^- risks for minors (infants and children) were examined in terms of their spatial distribution (Figure 11). It can be seen that the F^- hazard risk to infant health is sporadically distributed around Jingzhuang, Dayushu, and Yanqing, while for children, the same risk applies to only a small area located to the southeast of Jingzhuang. In terms of a single risk-causing substance, NO₃-N poses a greater threat to various populations than F^- ; indeed, the overall potential noncarcinogenic health risks in the basin are dominantly due to by NO₃-N. Thus, extra attentions should be paid to NO₃-N contaminants in groundwater. F^- hazard risk also should be examined for the minors (i.e. infants and children) in high F^- content groundwater areas.



Figure 10. Spatial distribution of the hazard quotient of noncarcinogenic risk due to nitrate through the oral pathway for (**a**) infants, (**b**) children, (**c**) adult females, and (**d**) adult males.



Figure 11. Spatial distribution of the hazard quotient of noncarcinogenic risk due to fluoride through the oral pathway for (**a**) infants and (**b**) children.

4.3. Source Analysis and Implication for Sustainable Water Management

As shown in Figure 3, the high TDS groundwaters are mainly distributed in the central basin. Some other sporadic areas are also observed with relative high TDS groundwaters. The distribution

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of high nitrate-nitrogen groundwaters is very similar to the relative high TDS groundwaters areas besides the central basin (Figure 3a,b). The linear relationship between various chemical parameters (presented in Table 4) shows that NO_3^- has a high correlation coefficient with TDS (r = 0.83), implying that NO_3^- and TDS are from same source(s). NO_3^- is a common contamination in groundwater and below 10 mg/L (~2.3 mg/L for NO_3 -N) in natural conditions. Groundwater with NO_3^- exceeding this limit is generally influenced by the anthropogenic input of nitrogen [21]. This suggests that the relatively high TDS in the sporadic areas of the basin is caused by anthropogenic activities. In addition, it can be seen that the high NO_3^- groundwaters are dominantly distributed in the residential areas of basin (Figures 1 and 3b), indicating domestic sources like effluents and septic tanks. The high TDS groundwaters in the central basin are located in agricultural areas (Figure 1; Figure 3a), implying a relationship with agricultural practices. Meanwhile, no high nitrogen groundwater is found in these areas, suggesting the absence of direct external inputs. The high TDS is possibly from the leaching from the vadose zone due to the infiltration of agricultural irrigation water.

F⁻, Mn, and Zn in groundwater are found with relative low concentrations in most of the basin (Figure 3c–e). Only a few sampling sites are showed high F⁻/Mn/Zn. As shown in Table 4, a strong negative correlation (r = -0.57) exists between F⁻ and HCO₃⁻. Additionally, Mg²⁺ is shown to have a negative correlation with F⁻. This suggests that F⁻ is strongly related to reverse ion exchange processes in the aquifers [34]. F⁻ also shows a positive correlation with pH, i.e., alkalinity, indicating that F⁻ in fluoride-bearing minerals like biotite and muscovite was replaced by OH⁻ ligands in groundwater [34,48,49]. Mn showed a strong positive correlation with pH (r = 0.57) and F⁻ (r = 0.62), implying similar origins (water-rock interaction). All the absolute values of correlation coefficients for F⁻/Mn and TDS/NO₃⁻ are below 0.5, confirming that the high levels of F⁻ and Mn in groundwater are from geogenic sources rather than anthropogenic ones. The Zn in groundwaters has no significant relation with other elements (Table 4). However, areas having high Zn groundwaters are also shown to have relatively high NO₃⁻ (Figure 3b,e), implying that the high levels Zn are due to anthropogenic activities.

The result of the PCA analysis is presented in Figure 12. The first two principal components (PC) are extracted, and account for 51.19% of the total variance. The first principal component (PC1) explains 31.08% of the total variance in the groundwater chemical dataset. PC1 has a clear positive loading on TH, TDS, Cl⁻, NO₃⁻, and a negative loading on pH, F⁻, and Mn. As discussed, high TDS and NO₃⁻ in groundwater is associated with anthropogenic activities, and high F⁻ and pH (alkalinity) is related to natural origins. Thus, positive PC1 value can be attributed to anthropogenic sources, and negative PC1 values represent the natural processes. PC2 shows clear a positive loading on Na⁺ + K⁺, and a negative loading on Ca²⁺ and Mg²⁺, indicating cation-exchange and reverse cation-exchange processes, respectively. This confirms the aforementioned mechanism for the formation of F⁻.

Overall, groundwater sources in the study area are potentially threatened by high NO₃⁻, F⁻, Mn, and Zn, and especially by NO₃⁻ and F⁻. The high NO₃⁻ in groundwater is attributed to anthropogenic sources like domestic effluents and septic tanks in urban areas. The capital city Yanqing did not show high NO₃⁻. This is ascribed to the advanced administration measures and strict controls in the city on potential waste sources. Thus, the high NO₃-N risk areas should adopt measures to protect groundwater from the anthropogenic nitrogen input. The high Zn in groundwater is also related to anthropogenic activities. Although it is sporadic and relatively low, attention should to paid to it in future water resource administration. The TDS of groundwater is found to be elevated not only in urban areas due to the urban anthropogenic waste input, but also in the rural areas due to the leaching of agricultural irrigation water. Scientific and rational irrigation methods like dropping and sprinkling are encouraged in the agricultural practices, as opposed to flooding irrigation. The F⁻ and Mn in the groundwater in the study area originate from geogenic sources. These two substances are sporadically distributed and slightly beyond the permissible limits. Mn would not pose hazards to human health; however, high F⁻ levels in the study area may threaten the health of minor, and treatment is necessary if the water is to be used for long-term drinking purposes.

Index	pН	TH	TDS	Na ⁺ +K ⁺	Ca ²⁺	Mg ²⁺	Cl-	SO4 ²⁻	HCO ₃ -	NO ₃ -	NO ₂ -	NH ₄ +	F -	Mn	Zn
pН	1														
TH	-0.54 *	1													
TDS	-0.45	0.96 *	1												
Na ⁺ + K ⁺	-0.17	0.24	0.18	1											
Ca ²⁺	-0.02	0.02	-0.01	-0.66 *	1										
Mg ²⁺	-0.31	0.39	0.33	-0.44	0.78 *	1									
Cl-	-0.36	0.86 *	0.94 *	0.03	0.05	0.30	1								
SO_4^{2-}	0.10	0.44	0.59 *	0.16	-0.14	-0.20	0.56 *	1							
HCO ₃ ⁻	-0.44	0.45	0.32	0.69 *	0.03	0.25	0.12	-0.03	1						
NO ₃ ⁻	-0.38	0.79 *	0.83 *	0.12	-0.08	0.18	0.89 *	0.46	0.09	1					
NO_2^-	-0.42	0.00	-0.05	-0.14	0.23	0.41	-0.18	-0.13	0.14	-0.21	1				
NH_4^+	-0.19	0.30	0.23	0.94 *	-0.54 *	-0.31	0.10	0.13	0.70 *	0.17	-0.07	1			
F ⁻	0.48	-0.49	-0.31	-0.20	-0.20	-0.46	-0.28	0.41	-0.57 *	-0.27	-0.02	-0.27	1		
Mn	0.57 *	-0.29	-0.11	-0.02	-0.05	-0.14	-0.11	0.39	-0.15	-0.32	-0.10	-0.09	0.62 *	1	
Zn	-0.27	0.18	0.13	0.36	-0.24	-0.31	0.03	0.22	0.19	0.19	-0.13	0.25	-0.07	-0.17	1

Table 4. Linear relationship between various chemical parameters of groundwater in the study area.

* significant relation (absolute value of correlation coefficient >0.5).



Figure 12. Plots of principal components loadings of interrelationships among various hydrogeochemical parameters.

5. Conclusions

Groundwater is a crucial water resource in arid and semiarid regions. In this study, groundwater contaminations and the associated health risks for various populations were investigated in a typical semiarid basin of north China, and the contaminations sources were discussed in order to propose measures to reduce the risks. The following conclusions were drawn:

- (1) The groundwater in the basin is slightly alkaline, hard fresh water. The abundance of major ions in groundwater is in the order of $Ca^{2+} > Na^+ + K^+ > Mg^{2+}$ for cations and $HCO_3^- > SO_4^{2-} > Cl^-$ for anions. NO₃-N, F⁻, Mn, and Zn were found to be beyond the permissible limits at some sampling sites. Groundwaters exceeding the limits of NO₃-N, F⁻, Mn and Zn accounted for 11.8%, 2.6%, 1.3%, and 1.3% in all the sampled sites, respectively, with maximum concentrations of 21.8 mg/L, 1.17 mg/L, 0.17 mg/L and 1.12 mg/L.
- (2) Groundwater NO₃-N and F⁻ contaminants may pose potential health risks to local residents. The risks due to Mn and Zn in the study area are low and negligible. The dermal exposure of high nitrate and fluoride contaminations in groundwater would not threated health, but oral exposure pathway should be further studied, as high potential risks be may posed. The health risks for all populations are primarily posed by NO₃-N contamination. Adults are only at risk of NO₃-N contaminants in groundwater, while minors are susceptible to both NO₃-N and F⁻ contaminants. The total potential noncarcinogenic risks for various populations are in the order of infants > children > adult males > adult females.
- (3) High NO₃-N groundwaters are dominantly distributed in residential areas, and were attributed to the anthropogenic sources. The inputs of anthropogenic sources in these urban areas also elevate the TDS values of groundwater. Advanced and strict administration measures are recommended to protect groundwaters from contamination due to anthropogenic activities. The elevation of TDS in groundwater is also associated with the leaching of irrigation water in agricultural areas. Rational irrigation practices like dropping and sprinkling are encouraged to replace the older flooding method. The high Zn in groundwaters is also related to anthropogenic activities, and should be studied by future water resource administrations. F⁻ and Mn contaminants in groundwater originate from geogenic sources. Treatment of groundwaters with high levels of F⁻ contaminants is necessary if the waters are to be used for long-term drinking purposes, especially regarding infants and children. The effects of Mn contamination in groundwater is limited and can be ignored.

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