Research Article

Hydrogeochemical Features and Genesis of Confined Groundwater and Health Perspectives for Sustainable Development in Urban Hengshui, North China Plain

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Groundwater in confined aquifers is the preferred water resource worldwide, and its hydrochemical quality is the premise for sustainable development. A systematic hydrogeochemical research was conducted to get insight into the hydrochemical characteristics, genesis, and potential health threats of confined groundwater, based on analytical data of 45 groundwater samples collected from the urban area of Hengshui, Central North China Plain (NCP). The results showed most groundwater had desirable hydrochemical quality with a nearly neutral to slightly alkaline nature and dominantly soft-fresh Cl-Na face. Solute chemistry was governed by rock-water interaction including minerals dissolution and ion exchange, but out of the anthropogenic influences. All nitrogen pollutants and Zn were within the desirable limit, while F⁻, Mn, and Fe were beyond the desirable limit recommended by WHO in 28.9%, 15.6%, and 68.9% of samples. Overall chronic health risk from these toxic elements was identified in terms of various populations and mainly contributed by F⁻. Infants were more prone to the health risks of aqueous pollutants. Differential water supplies based on hydrochemical quality are recommended, and water improvement measures are suggested to be conducted aiming at the harmful fluoride in confined groundwater. The present research could provide valuable references for the health sustainability of confined groundwater utilization in sedimentary plains like NCP worldwide.

1. Introduction

The available freshwater is dominantly stored underground and accounts for approximately 96% of the total liquid freshwater on Earth [1]. Groundwater is a significant water source enabling the security of water and food and the key factor lifting the rural populations out of poverty over the world [2–5], especially in arid and semiarid regions with relative scarcity of surface water [6–10]. The availability of groundwater resources for the human community is limited not only by the water quantity but also by the hydrochemical quality [11, 12]. A full understanding of the hydrochemical features, mechanisms, and quality is the premise of effective management and sustainable development of groundwater resources in any region across the world [13, 14].

Groundwater chemistry is influenced or even governed by many factors including natural and anthropogenic ones [15, 16]. Generally, the natural groundwater chemistry is determined by the hydrochemical components of recharge water, lithology of aquifers along the groundwater flow path, residence time, groundwater hydrodynamic, and evaporation [17–21]. These factors are fundamental for the natural formation and evolution of groundwater chemical components [22–25], while anthropogenic factors from all aspects of human society including domestic, agricultural, and industrial activities can dramatically modify the composition of groundwater chemistry through direct pollutants input or indirect change of the hydrogeochemical conditions of natural mechanisms [26–31]. The driving forces from the human community to the evolution of groundwater

chemistry have more significant influences on the phreatic aquifers rather than the confined aquifers due to the protection of aquitards. In addition, evaporation usually has great effects on the salinity of phreatic groundwater, which would not occur in the confined aquifers [23, 32–34]. Thus, phreatic groundwater is found with poorer hydrochemical quality than confined groundwater [16, 35–39].

Attention has been concentratedly paid to the hydrochemistry and responsibilities for the poor quality of phreatic groundwater in the past decades [40–44] due to the frangibility of unconfined aquifers to the influences of external pollutions and extreme hydrological events. Great achievements have been obtained through these efforts on the understanding of hydrochemical features, evolutions, and mechanisms of shallow underground aquatic systems and effectively guided groundwater management globally [14, 44–47]. However, the confined groundwater is not lucky as the phreatic one. It is rarely concerned regarding the hydrogeochemical quality because it is regarded as the cleanest and best quality water beneath the traditional viewpoint. Although it is rare for confined groundwater affected by external factors on its hydrochemical quality, the potential poor quality as a result of the internal factors cannot be evaded [48]. Geogenic poor quality of groundwater has been one of the greatest threats to the water supply for human society and is widely reported in many regions across the world [48–54]. Thus, concerns on the hydrochemical quality and genesis are indispensable for confined groundwater if utilized for the human community.

The present research focuses on the hydrochemistry and health implication of confined water in large sedimentary plains. A subarea of the North China Plain (NCP), one of the global research hotspots of Anthropocene groundwater science, was investigated to provide references to the sustainable development of confined groundwater resources in other similar great sedimentary plains worldwide. The major aims of the present research were to (1) get insight into the hydrogeochemical features of confined groundwater, (2) reveal the mechanisms forming the hydrochemistry, (3) determine the toxic elements and their potential health threats, and (4) finally propose scientific management suggestions for the health sustainability of groundwater resources.

2. Study Area

The study area is located in the central area of the NCP (Figure 1). It lies between the latitude of 37°36′10″N-37°49′55″N and the longitude of 115°25′17″E-115°51′12″E and spreads over an area of 591 km^2. It represents semiarid continental monsoon conditions with an annual average temperature of 12.7°C. The average annual rainfall is approximately 500 mm where 75% occurs during the rainy season from June to September. The annual evaporation rate varies from ~1,300 mm to ~2,600 mm, approximating 3–5 times of the local rainfall. The land use type in this region is dominated by agricultural land, followed by urban land and industrial land.

Geologically, the study area belongs to the alluvial-lacustrine plain of the central NCP. The NCP is one of the largest sedimentary plains in the world and formed during the Cenozoic and Mesozoic era. This area is flat and descends slightly from the west towards the east with an elevation in the range of 22–27 m. Groundwater in this area mainly occurs in the Quaternary deposits with a thickness of more than 500 m [55]. This large Quaternary groundwater system provides the major quantity of water resource for the local development in various social-economic and ecological aspects.

The lithology of the Quaternary deposits varies from pebble to clay and silt, resulting in multiple aquifer groups vertically (Figure 2). The first continuous and stable aquitard is observed at the depth of 50–80 m below the ground surface. Generally, aquifers above this aquitard are defined as the phreatic aquifers, and those below this are identified as confined aquifers. Due to the wide distribution of saline water in phreatic aquifers [49], confined aquifers are regarded as the most potential aquifers supporting the development of the study area [33, 55]. The confined aquifers have a relatively poor water alternative ability and are mainly recharged and discharged through the lateral and vertical flow naturally.

Owing to the scarcity of surface water and high salinity of phreatic groundwater, water supply for various consumers of human society in this region mainly depends on the confined groundwater. Thus, human exploitation has become the main discharge form of the confined aquifers in the past decades [50]. In particular, agricultural irrigation, the largest water consumer, in recent decades has dominantly relied on confined groundwater [56], resulting in many groundwater depression cones in the confined aquifers as well as ground subsidence. These drastic changes of the hydraulic and geological environment also caused the evolution of the hydrogeochemical environment in confined aquifers and finally threatened the hydrochemical quality of groundwater [57], for example, the releasing of iodine into groundwater [58]. Thus, it is significantly necessary to perform targeted works to get insight into the hydrochemical quality, genesis, and potential quality issues of confined groundwater [59].

3. Material and Methods

3.1. Sampling and Analytical Techniques. In the present study, a total of 45 groundwater samples was collected from the confined aquifers across the study area (Figure 1(c)). All groundwaters were sampled from the boreholes at the depth of 150–700 m. The water in boreholes was pumped for more than three times of borehole volume before sampling to remove the stagnant water in the boreholes. In situ hydrochemical parameters, such as pH and electrical conductivity (EC), were monitored and sampling was conducted only after these parameters being stable. The sampled groundwaters were collected in the ultrapure water plastic buckets of 2.5 L which had been thoroughly rinsed with the target water three times before sampling. All groundwater samples were sent to the Laboratory for analysis with the aid
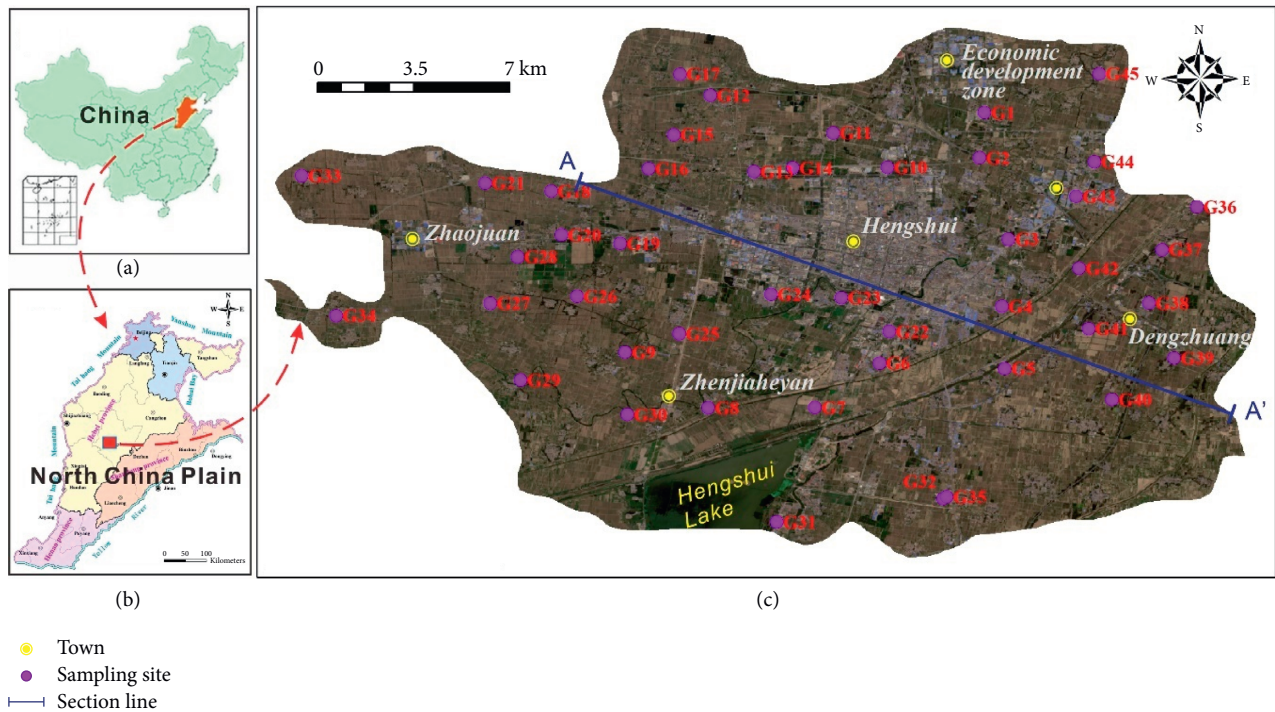
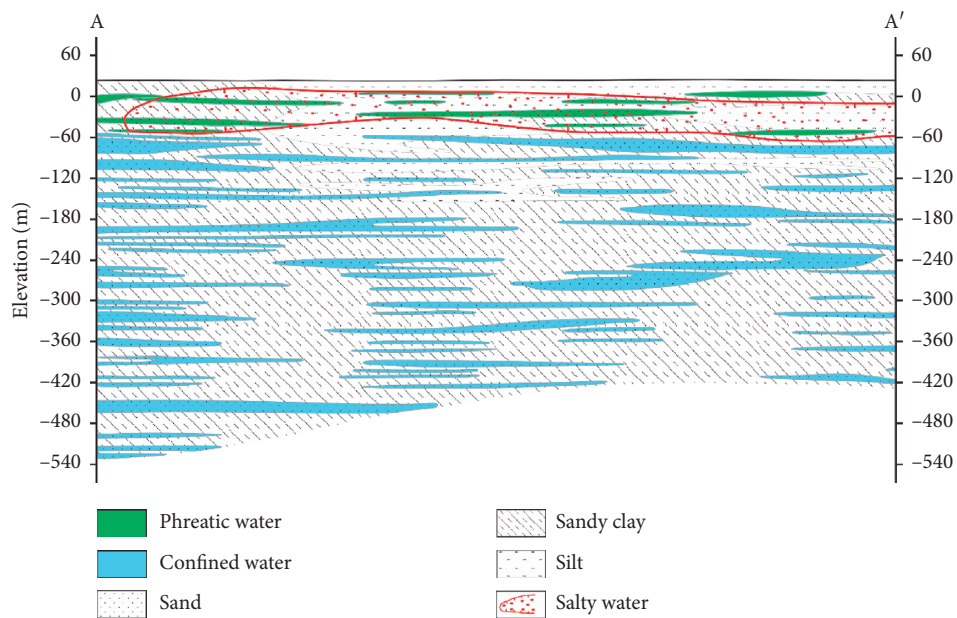FIGURE 1: Location of the study area and sampling sites.

FIGURE 2: The hydrogeological cross section along the A-A'.

of incubators which could keep the samples in the condition of 4°C temperature.

The in situ parameters like pH and EC were obtained at the field with the aid of a multiparameter device (Multi 350i/SET, Munich, Germany). The analysis of other chemical parameters was conducted in the Laboratory of Groundwater Sciences and Engineering of the Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences. Major cation ions (Ca^{2+}, Mg^{2+}, Na^+, K^+) and trace elements (Zn, Mn, Fe) were determined using inductively coupled plasma-mass spectrometry (Agilent 7500ce ICP-MS, Tokyo, Japan). Ammonia-nitrogen (NH_4^+) and anions including Cl^-, SO_4^{2-}, NO_3^-, NO_2^-, F^- were measured by ion chromatography (Shimadzu LC-10ADvp, Kyoto, Japan). HCO_3^- and total dissolved solids (TDS) were obtained with the aid of acid-base titration. Ionic charge

balance was conducted to verify the accuracy of chemical analyses. The results showed the charge balance errors of all samples were within the permissible limit of ±5%, demonstrating reasonably good measurement accuracy.

3.2. Human Health Risk Assessment. Contaminants in groundwater could potentially threaten the health of human beings if exposed to contaminated water. This potential health threat could be identified with the aid of a quantitative model, namely, the human health risk assessment model (HHRA model) established by the United States Environmental Protection Agency [60]. Generally, contaminants in water could pose threats through multiple pathways, such as drinking water intake, dermal contact, and inhalation. As reported by previous research, drinking water intake pathway has higher risks than other pathways regarding the high content of toxic elements in water [38, 39, 61, 62]. Thus, the pathway of drinking water intake should be paid significant attention regardless of age and gender.

The procedure of HHRA includes the following three steps:

Step 1: computation of the chronic daily intake dose of potential contaminants in target water:

$$CDI_i = \frac{(C_i \times IR \times EF \times ED)}{(BW \times AT)}, \quad (1)$$

$$AT = ED \times 365, \quad (2)$$

where CDI_i signifies the chronic daily intake dose of contaminant i; C_i indicates the content of contaminant i in target water; IR is the rate of water oral intake; EF represents the exposure frequency; ED and AT refer to exposure duration and average exposure time, respectively; BW signifies the mean body weight of the consumer.

Step 2: identification of the hazard quotient:

$$HQ_i = \frac{CDI_i}{RfD_i}, \quad (3)$$

where HQ_i expresses the probabilistic health risk posed by single contaminant i; RfD_i denotes the reference dose of contaminants i through the pathway of oral intake.

Step 3: synthetical assessment of the overall health risk:

$$HI = HQ_1 + HQ_2 + \ldots + HQ_i, \quad (4)$$

where HI is the overall potential health risk posed by multiple contaminants in drinking water.

The parameters used in the HHRA model in the present study are listed in Table 1.

4. Results and Discussion

4.1. Physicochemical Characteristics of Groundwater. The physicochemical parameters of confined groundwater in the study area were statistically demonstrated in the box plots of Figure 3. The desirable limit of various indices recommended by the WHO [65] and the Chinese guideline [66] was also presented.

The pH of the sampling water had a range from 7.26 to 10.32 with an average of 8.14, indicating a nearly neutral to slightly alkaline nature of confined groundwater. As shown in Figure 3(a), most of the groundwaters were with a pH value within the desirable range of 6.5–8.5 recommended by WHO [65]. About 22.2% of the total samples were found out of the pH desirable range and with a slightly more alkaline feature. A relatively large variation of EC values was observed from the sampled groundwaters with the range from 693 μS/cm to 4,637 μS/cm averaging at 1,128 μS/cm. The TDS also showed a relatively wide range from 467 mg/L to 3,122 mg/L with an average of 681 mg/L. Thus, groundwater had a large variation of salinity in the study area. However, most of the sampled waters had relatively low EC and TDS values, and only a small portion of samples had the EC and TDS beyond 2000 μS/cm and 1000 mg/L, respectively (Figures 3(b) and 3(c)). The value of total hardness (TH) was in a wide range from 13 mg/L to 1,416 mg/L with an average of 121 mg/L. Groundwaters were dominantly with the TH value below the desirable limit of 450 mg/L and only 3 samples (6.7%) beyond this limit. According to the integrated water quality categories based on TDS and TH (Figure 4), confined groundwater in the study area was predominantly soft-fresh water. Four samples (8.9%) were observed falling in the moderately hard fresh category, one (2.2%) in the moderately hard brackish category and another (2.2%) in the hard brackish category. Only four groundwaters (8.9%) were under the very hard brackish category.

The solute chemistry of confined groundwater was dominated by Na^+ for cations (Figure 5) with a range from 162 mg/L to 591 mg/L and averaging at 203 mg/L. Ca^{2+} and Mg^{2+} ranked the second and third abundance in the major cations and varied from 4 mg/L to 221 mg/L and between 1 mg/L and 210 mg/L, respectively, with an average of 25 mg/L and 13 mg/L. K^+ was the least abundant ion in major cations and ranged from 0.41 mg/L to 8.88 mg/L with a mean of 1.12 mg/L. For all the major cations, only Mg^{2+} was found exceeding the desirable limit of 100 mg/L in three groundwater samples. It can be clearly seen from Figures 3(e)–3(h) that all these major cations of sampled groundwaters were concentrated in relatively low-value ranges, indicating desirable quality.

The major anions were dominated by Cl^-, followed by SO_4^{2-} and HCO_3^- (Figures 3(i)–3(k)). The concentration of these three anions was in the range of 108–1,353 mg/L for Cl^-, 109–659 mg/L for SO_4^{2-}, and 25–248 mg/L for HCO_3^-, with an average of 231 mg/L, 142 mg/L, and 113 mg/L, respectively. The portion of samples with Cl^- exceeding the desirable limit of 250 mg/L was large, accounting for approximately 42.2% of the total sampled waters (Figure 3(i)). For SO_4^{2-}, majority (88.9%) of the samples were observed within the desirable limit of 250 mg/L (Figure 3(j)). Thus, concerns on major anions should be focused on the relatively high content of Cl^-.

TABLE 1: The values of exposure parameters and RfD used in the HHAR model.

Exposure Parameter	Value				Contaminant	RfD_{oral} (mg/(kg × day))
	Infants	Children	Females	Males		
IR (L/day)	0.65[*]	1.5[*]	2.66[*]	3.62[*]	F^-	0.06[***]
EF (days/year)	365[**]	365[**]	365[*]	365[**]	Mn	0.14[**]
ED (years)	0.5[*]	6[*]	30[*]	30[*]	Fe	0.7[**]
BW (kg)	6.94[*]	25.9[*]	64.0[*]	73.0[*]		

[*]Zhai et al. [63]; [**]USEPA [60]; [***]Zhang et al. [64].

Overall, groundwaters in the confined aquifers were predominantly of the Cl-Na type, with a few of the Mixed Cl-Mg·Ca type (2.2%) and Cl-Ca type (2.2%) (Figure 5). Generally, the relatively salty hydrochemical faces of groundwater like Cl-Na type are potentially formed by the natural hydrochemical evolution, or external salinity contamination input like seawater intrusion and anthropogenic pollutants input [9, 23]. Given the far away location from sea and poor water alternative ability in vertical, natural hydrochemical evolution was highly possible responsible for the salty Cl-Na type of confined groundwater in the study area. Those relatively fresh hydrochemical facies, that is, Mixed Cl-Mg·Ca type and Cl-Ca type, were the results of groundwater chemical evolution at different stages.

Some minor elements like nitrogen, F^-, Zn, Mn, and Fe were detected to get insight into their contents in the confined groundwater and potential effects on safe water utilization. Nitrogen including NO_3^-, NO_2^-, and NH_4^+ was all below the desirable limits (Figures 3(l)–3(n)), suggesting safe contents. Zn in all sampled groundwaters was also observed within the desirable limit of 1 mg/L. However, F^-, Mn, and Fe were found beyond the desirable limits in some samples. The content of F^- varied from 0.40 mg/L to 1.97 mg/L, with an average of 0.74 mg/L. About 28.9% of samples were detected exceeding the desirable limit of 1 mg/L. The concentrations of Mn and Fe in groundwater were in the range of 0.001–0.361 mg/L and 0.02–30.96 mg/L, respectively, with an average of 0.014 mg/L and 1.09 mg/L. It can be clearly seen that only a small portion (15.6%) of samples had the Mn exceeding the desirable limit of 0.1 mg/L (Figure 3(q)), while high Fe groundwaters were widely distributed in the study area and 68.9% of the sampled groundwaters were observed beyond the desirable limit of 0.3 mg/L (Figure 3(r)). Thus, attention should be paid to the high F^-, Mn, and Fe in confined water as their negative health effects on human beings.

4.2. Mechanisms Governing Groundwater Solute Chemistry. To reveal the mechanisms controlling groundwater solute chemistry in confined aquifers of the study area, hydrochemical diagrams, correlation matrix, and hydrogeochemical simulation were introduced in the present study. Generally, the hydrochemical compositions of natural water were dominantly governed by three mechanisms, namely, precipitation, rock, and evaporation dominance, which could be visibly revealed by the Gibbs diagrams. As shown in Figure 6, all sampled confined groundwaters were situated in the rock dominance of Gibbs diagrams,

suggesting the solute chemistry of confined groundwater was naturally controlled by the rock-water interactions.

Besides the natural process, human activities are important external factors potentially regulating the hydrochemical composition of water. Nitrogen is an important indicator of pollution from the human community. As demonstrated in Figures 3(l)–3(n), all confined groundwaters in the study area had relatively low concentrations of nitrogen (including NO_3^-, NO_2^-, and NH_4^+). Generally, the NO_3^- concentration in natural conditions is below 10 mg/L, and water with NO_3^- concentration below this natural limit is regarded as not influenced by human society. It can be clearly seen that almost all sampled groundwaters were dominantly with the NO_3^- concentration below 10 mg/L except for three samples slightly exceeding this natural limit, confirming nearly no anthropogenic pollutants inputted into the confined aquifers in the study area. Thus, the hydrochemistry of confined groundwater was only governed by the natural mechanism of rock-water interactions.

Various rocks can potentially be involved in the natural rock-water interactions during the groundwater circulation period. To constrain the potential contributed rocks, the end-member diagrams constructed by the ratio of Ca^{2+}/Na^+ versus Mg^{2+}/Na^+ and HCO_3^-/Na^+ were performed in the present study. Rocks involved in natural rock-water interactions can be revealed from three end-members of rock types, that is, carbonates, silicates, and evaporites [17, 43, 67]. As demonstrated in Figure 7, the sampled groundwaters were plotted in the dominance from the evaporites to the silicates, suggesting that the chemical solutes in the confined groundwater originated from the dissolution of evaporates and silicates. However, no sample was found located in the carbonates dominance, implying few contribution of carbonate minerals to groundwater chemistry.

The correlation matrix was introduced to further determine the contributions of evaporates and silicates to the hydrochemical components of confined aquifers. Significantly positive relations were observed between Na^+ and Cl^-, with the correlation coefficient of 0.96, implying the dissolution of halite (formula (1)) was one of the dominant processes controlling groundwater chemistry. This evidenced the aforementioned natural genesis of the salty hydrochemical face of Cl-Na in confined aquifers. Ca^{2+} also showed a significant positive relation to SO_4^{2-}, suggesting the sulfate minerals dissolution (formulas (2) and (3)) dominantly contributed to the hydrochemical compositions in confined aquifers of the study area. These hydrochemical processes were evidenced by the saturation indexes (SI)
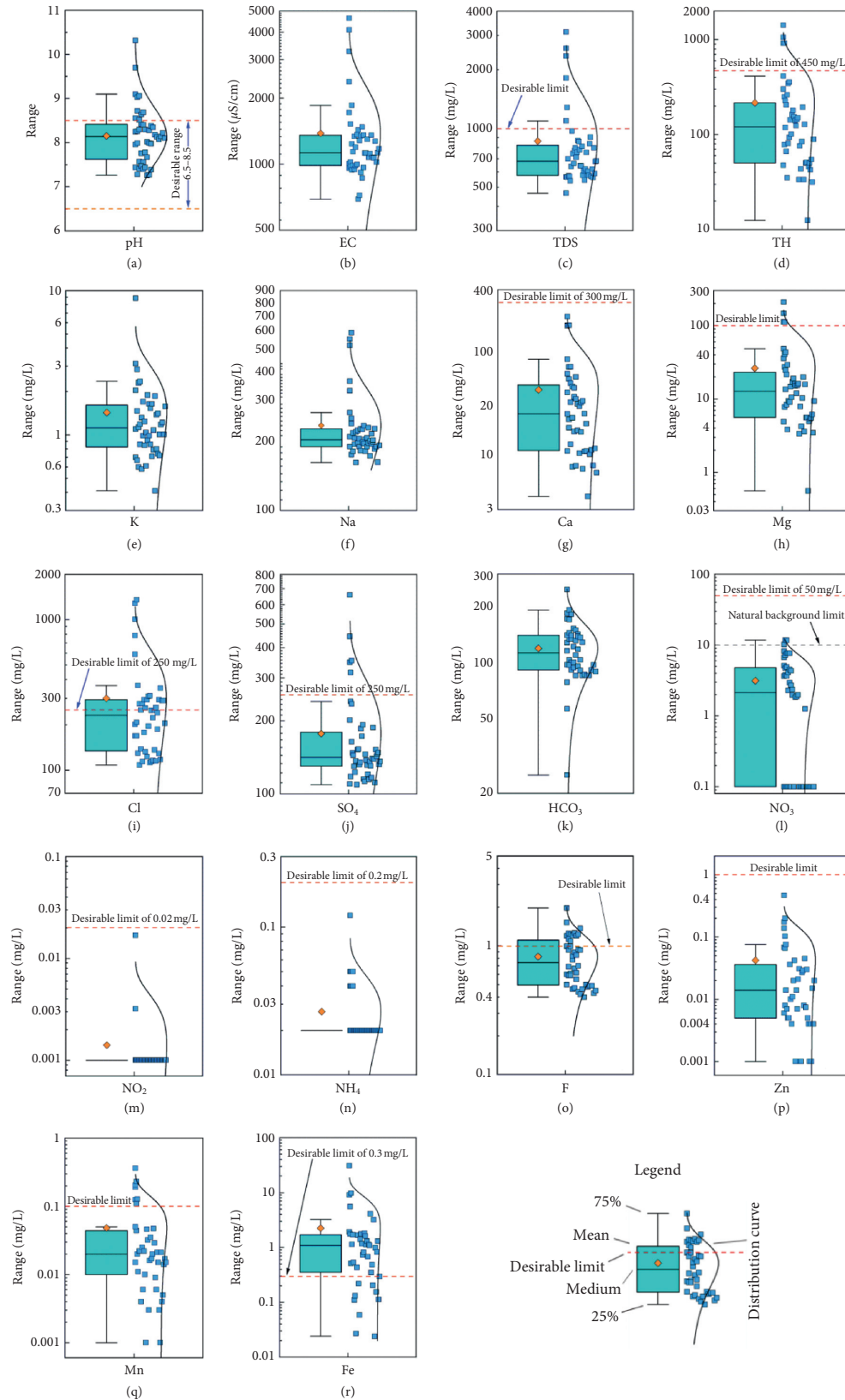
Figure 3: Box plots of physicochemical parameters of groundwater in the study area.

presented in Figure 8(a) that all sampled groundwaters were with unsaturated status (SI < 0) of halite, anhydrite, and gypsum minerals. Additionally, the dissolution of silicates (formula (4)) was another dominant process contributing the major ions to groundwater, which was also demonstrated in Figure 7. The results of hydrochemical simulations
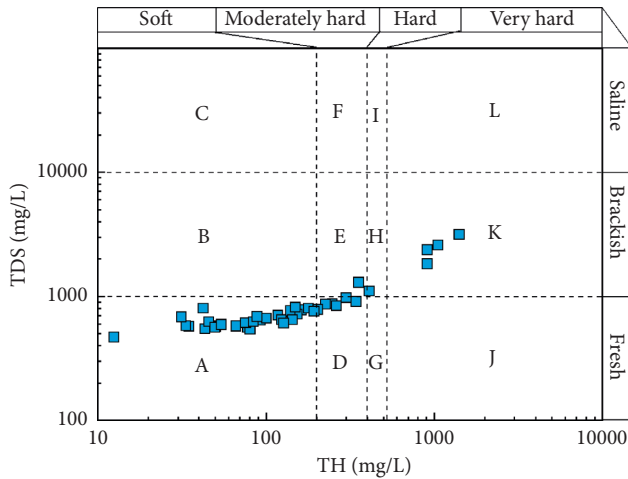
FIGURE 4: Scatter plots of total hardness (TH) versus total dissolved solids (TDS) showing the quality of groundwater.
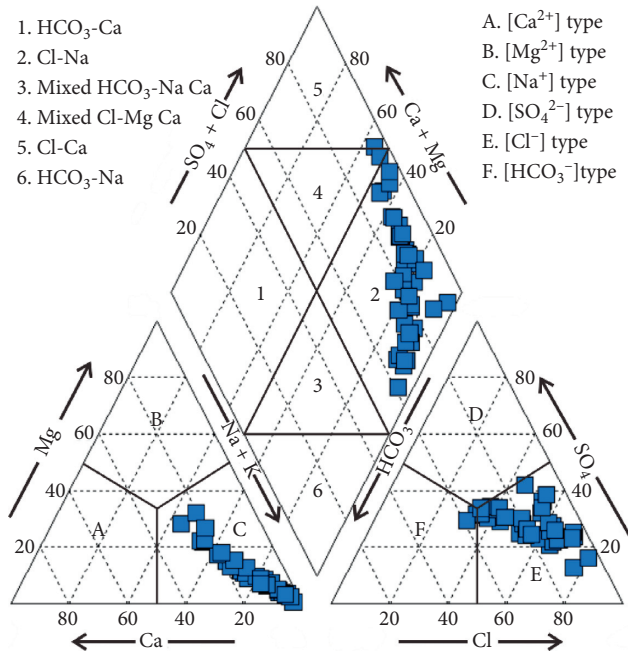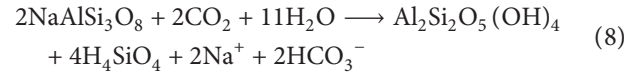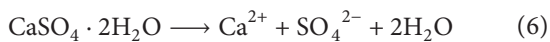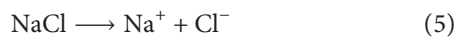

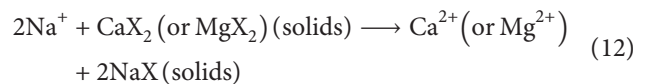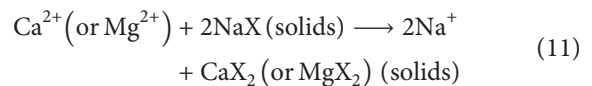FIGURE 5: Piper diagrams demonstrating the hydrochemical compositions of groundwater in the study area.

also showed that all fluoride-bearing, Fe-bearing, and Mn-bearing minerals were in the status of unsaturation (Figure 8(b)), suggesting the potential natural releasing of F^-, Mn, and Fe into groundwater from the aquifers' medium if these minerals exist. This was the reason for the relatively high contents of F^-, Mn, and Fe in some sampling groundwaters of the study area (Figures 3(o), 3(q), and 3(r)):

$$NaCl \longrightarrow Na^+ + Cl^- \tag{5}$$

$$CaSO_4 \cdot 2H_2O \longrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O \tag{6}$$

$$CaSO_4 \longrightarrow Ca^{2+} + SO_4^{2-} \tag{7}$$

$$2NaAlSi_3O_8 + 2CO_2 + 11H_2O \longrightarrow Al_2Si_2O_5(OH)_4 \\ + 4H_4SiO_4 + 2Na^+ + 2HCO_3^- \tag{8}$$

Ions exchange is a common rock-water interaction occurring in aquifers, especially that with fine mediums. As demonstrated in Figure 2, there occurs many fine aquifers' mediums in the study area, which could potentially provide the sources of ions for the ions exchange processes. The chloro-alkaline indices, which could be expressed by CAI-1 (formula (5)) and CAI-2 (formula (6)), were introduced to determine whether the ions exchange processes occurred and contributed to the hydrochemical compositions of groundwater. Generally, if one water having all the two chloro-alkaline indices below 0, indicating cation-exchange reaction (formula (7)) occurred; while, if reverse cation-exchange reaction (formula (8)) occurs, all chloro-alkaline indices would be positive. As shown in Figure 9(a), most (88.9%) of sampled groundwaters were with negative chloro-alkaline indices, implying a cation-exchange reaction occurred there. The rest of the sampling groundwaters (G6, G29, G31, G39, G44) were found with positive negative chloro-alkaline indices, suggesting reverse cation-exchange reaction for these waters. These processes were examined using the relationship between $Na^+ + K^+ + Cl^-$ and $Ca^{2+} + Mg^{2+} - HCO_3^- - SO_4^{2-}$. Generally, if the cation-exchange reaction is the dominant process in the aquifers, groundwater should be plotted in the lower right dominance and along the $Y = -X$ line. If the reverse cation-exchange reaction is the predominant hydrochemical mechanism in the aquifer, water should be situated in the upper left dominance of the diagram and along the $Y = -X$ line. The bivariate diagram presented in Figure 9(b) evidenced the cation-exchange reaction for most groundwaters and reverse cation-exchange reaction for groundwaters of G6, G29, G31, G39, and G44:

$$CAI - 1 = \frac{Cl^- - (Na^+ + K^+)}{Cl^-} \tag{9}$$

$$CAI - 2 = \frac{Cl^- - (Na^+ + K^+)}{HCO_3^- + SO_4^{2-} + CO_3^- + NO_3^-} \tag{10}$$

$$Ca^{2+}(or\ Mg^{2+}) + 2NaX\ (solids) \longrightarrow 2Na^+ \\ + CaX_2\ (or\ MgX_2)\ (solids) \tag{11}$$

$$2Na^+ + CaX_2\ (or\ MgX_2)\ (solids) \longrightarrow Ca^{2+}(or\ Mg^{2+}) \\ + 2NaX\ (solids) \tag{12}$$

The correlation matrix (Table 2) also demonstrated that the EC, TH, and TDS had a significant positive relation to the ions of Na^+, Ca^{2+}, Mg^{2+}, and Cl^-. Besides these four ions, the TH and TDS were also observed with significant positive relations to SO_4^{2-}. This evidenced that the hydrogeochemical processes discussed above predominantly contributed to the mineralization of confined groundwater in the study area. Overall, the solute chemistry of confined groundwater was dominantly controlled by the natural dissolution of evaporates (halite and sulfate) and silicates, cation-exchange
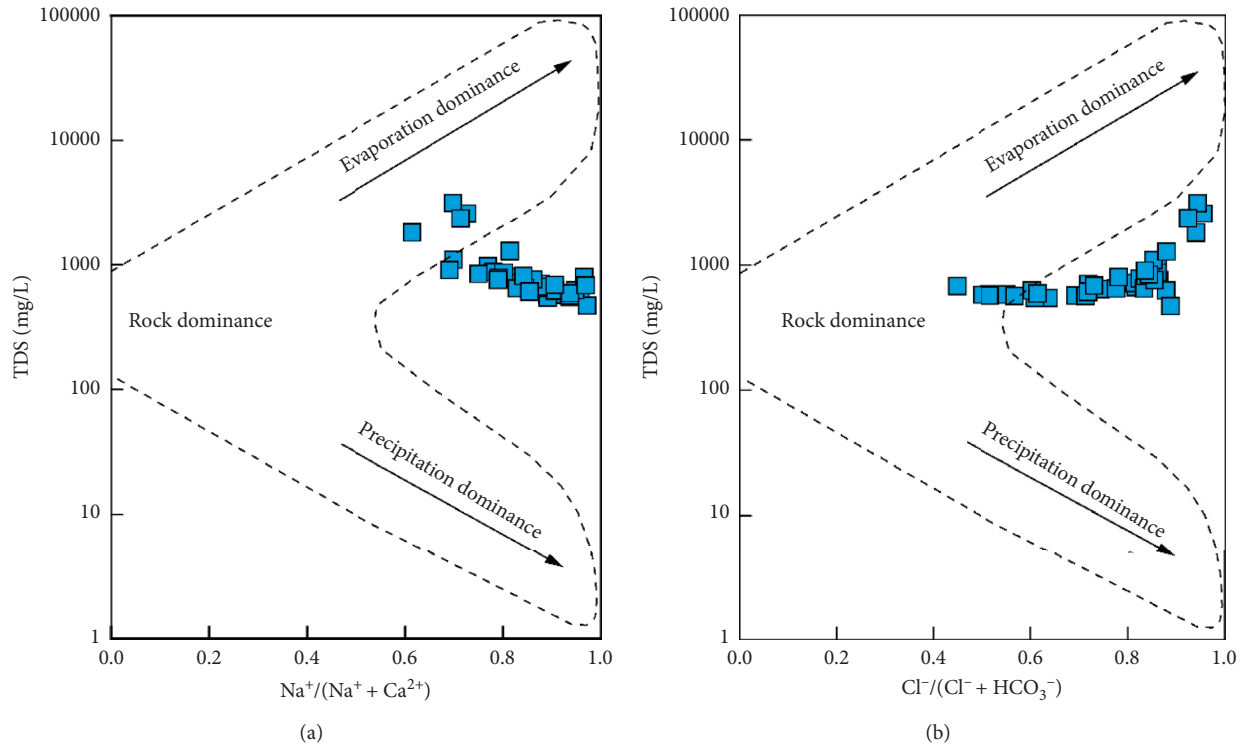
FIGURE 6: Gibbs diagrams demonstrating the natural mechanisms governing groundwater chemistry.
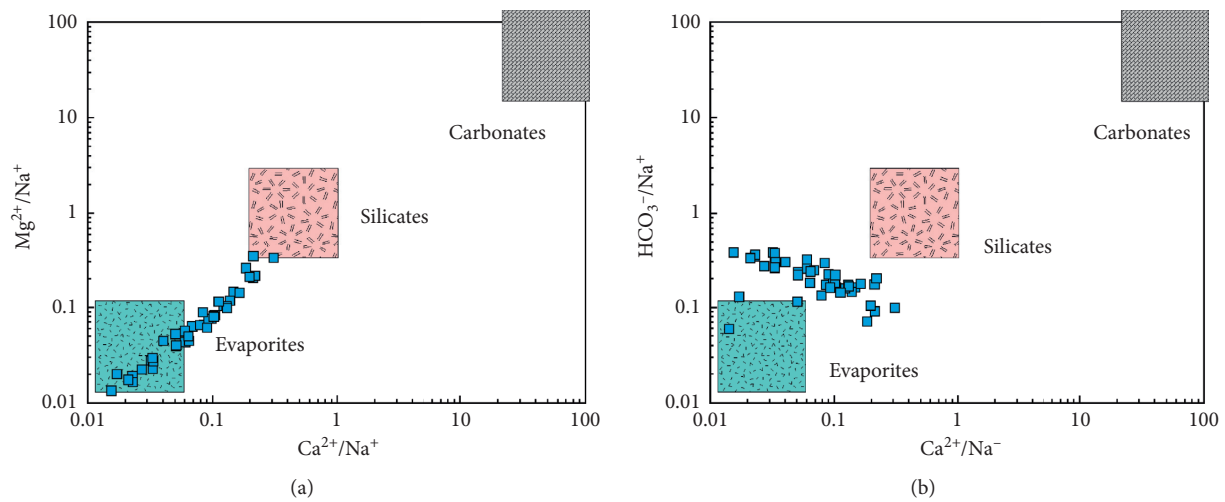
FIGURE 7: Scatter plots of (a) Na-normalized Ca versus Mg and (b) Na-normalized Ca versus HCO_3.

reaction. The ions releasing from fluoride-bearing, Fe-bearing, and Mn-bearing minerals contributed to the exceeding of F^-, Mn, and Fe in groundwater. Additionally, reverse cation-exchange reaction was also an important process influencing the hydrochemistry of confined groundwater at some sampling locations. However, the hydrogeochemical compositions of confined groundwater were nearly out of the influence of anthropogenic factors.

(a)

(b)

FIGURE 8: Saturation index of selected minerals in groundwater of the study area.

(a)

(b)

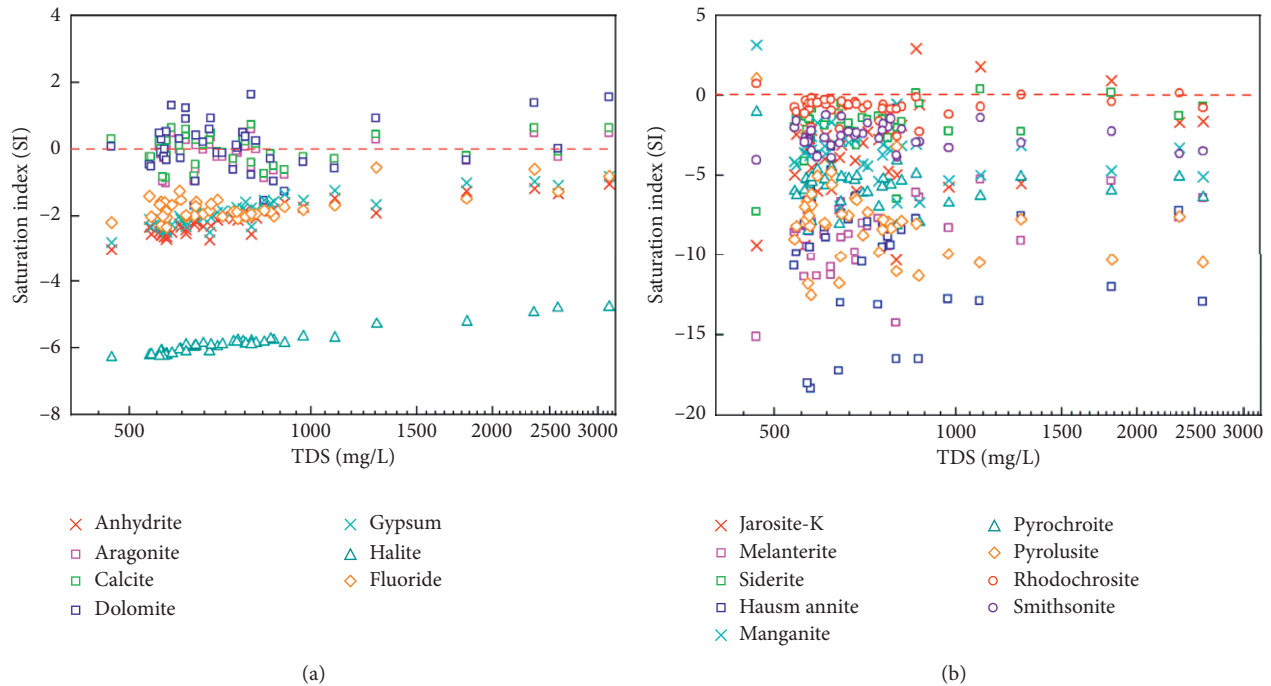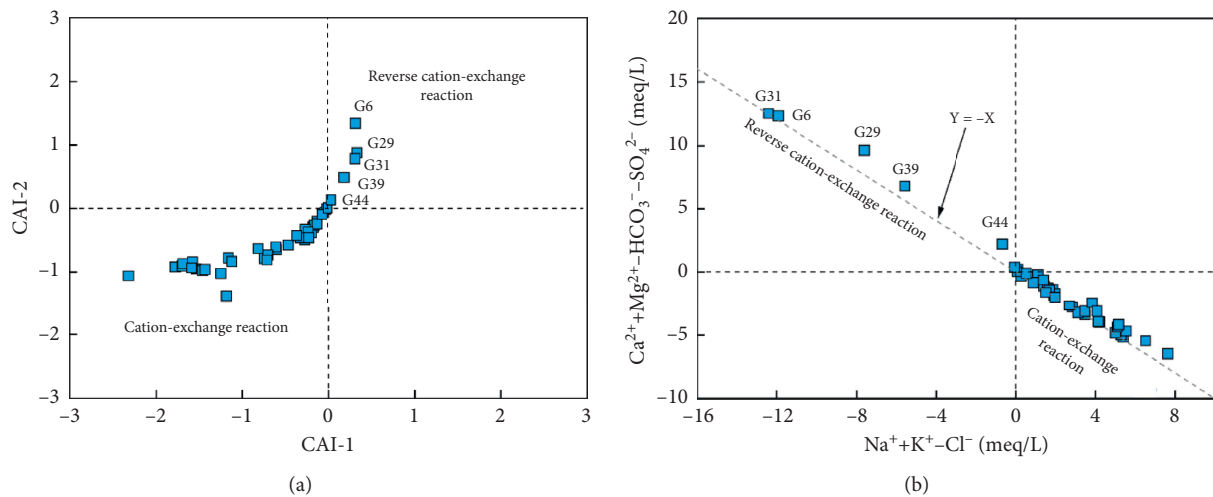FIGURE 9: Scatter plots of (a) chloro-alkaline indices CAI-1 versus CAI-2 and (b) $Na^+ + K^+ - Cl^-$ versus $Ca^{2+} + Mg^{2+} - HCO_3^- - SO_4^{2-}$.

4.3. Potential Health Threats and Responsible Contaminants.

As discussed above, the F^-, Mn, and Fe were detected with relatively high contents in groundwater and may pose negative effects on human health. The human health risk assessment model (HHRA model) was introduced to reveal the potential negative effects of these contaminants on human health.

According to the assessment results, the HI values were in the range of 0.67–4.99 for infants, 0.42–3.08 for children, 0.30–2.21 for adult females and 0.36–2.64 for adult males, averaging at 1.60, 0.99, 0.71, and 0.85, respectively. It can be clearly seen that the overall health risks for various populations were in the order of infants>children>males>females (Figure 10(a)). Similar results were also reported by many researchers [68–70]. The health risk can be classified into three categories, that is, low risk, medium risk, and high risk. Generally, an HI value less than 1 suggests the water with low and negligible health risk [71]. An HI value in the range of 1–4 is regarded as a medium health risk, and high health risk is implied if the HI value is beyond 4 [55, 72]. Thus, all populations were at health risk to some degree. Specifically, the potential health risk for infants varied from low to high risk category (Figure 10(a)), with 24.4% in the low chronic risk category, 73.4% in the medium

TABLE 2: Linear relationship (R2) between various chemical parameters of groundwater in the study area.

Index	pH	EC	TH	TDS	K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	NO_3^-	NO_2^-	NH_4^+	F^-	Zn	Mn	Fe
pH	1																	
EC	−0.26	1																
TH	−0.36	0.93*	1															
TDS	−0.28	0.97*	0.98*	1														
K^+	0.45	−0.05	−0.06	−0.01	1													
Na^+	−0.17	0.95*	0.91*	0.97*	0.02	1												
Ca^{2+}	−0.40	0.92*	0.99*	0.97*	−0.07	0.89*	1											
Mg^{2+}	−0.33	0.94*	0.99*	0.99*	−0.06	0.92*	0.97*	1										
Cl^-	−0.30	0.97*	0.98*	0.99*	−0.03	0.96*	0.96*	0.97*	1									
SO_4^{2-}	−0.24	0.81	0.93*	0.93*	0.08	0.86*	0.90*	0.93*	0.87*	1								
HCO_3^-	−0.10	−0.12	−0.12	−0.05	−0.41	0.06	−0.16	−0.08	−0.14	−0.01	1							
NO_3^-	−0.30	−0.24	−0.12	−0.18	0.12	−0.27	−0.07	−0.15	−0.15	−0.15	−0.42	1						
NO_2^-	0.34	−0.03	−0.10	−0.03	0.87*	0.04	−0.12	−0.09	−0.08	0.08	−0.08	−0.14	1					
NH_4^+	−0.07	−0.11	−0.14	−0.14	−0.01	−0.13	−0.14	−0.13	−0.14	−0.12	0.01	0.14	0.05	1				
F^-	0.36	0.09	0.04	0.13	−0.06	0.27	0.01	0.07	0.09	0.10	0.50*	−0.62*	0.16	−0.15	1			
Zn	−0.14	0.07	0.05	−0.01	−0.04	−0.09	0.09	0.03	-0.03	0.11	−0.13	0.07	−0.08	−0.11	−0.20	1		
Mn	−0.01	0.67*	0.48	0.44	−0.03	0.40	0.54*	0.43	0.45	0.36	−0.23	−0.25	−0.10	0.01	0.10	0.18	1	
Fe	0.11	0.01	−0.03	−0.05	0.02	−0.06	−0.01	−0.04	−0.05	−0.02	−0.14	−0.01	−0.07	0.20	−0.15	0.06	0.46	1

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

chronic risk category, and 2.2% in the high risk category. For children, adult females, and males, the potential overall health risks only fell in the low risk and medium risk category, and no high risk was observed (Figure 10(a)). Most of the sampled waters had the HI value below 1 for these three populations, accounting for 60.0%, 91.1%, and 66.7% of the total sampled waters, respectively, suggesting negligible health risk in most of the area (Figure 11(b)–11(d)). Spatially, the potential health risk is distributed in the northern area surrounding the sampling site of G17 and the eastern area, as well as some sporadic areas adjacent to sampling sites like G22 and G4 (Figure 11).

For further illustrating the responsibility of each exceeding contaminant for the potential health risk, the HQ values of various contaminants for all populations are statistically presented in Figures 10(b)–10(d) with the aid of box plots. It can be seen that the HQ values of Mn for various populations were all below the permissible limit of 1 (Figure 10(c)), indicating negligible health threats from Mn in groundwater. For Fe in groundwater, the HQ values were dominantly (accounting for more than 90% of the sampled waters) below 1, and only very limited samples had the HQ value beyond the desirable limit of 1 (Figure 10(d)). For infants, one sample (2.2%) and two samples (4.4%) were found with high potential health risk and medium potential health risk from Fe in groundwater, respectively. Only one sample (2.2%), that is, G17, was observed with potential health threats to children, adult females, and males, and all ranked in the medium risk category. However, the potential health hazards of F^- were relatively higher than those of Mn and Fe in groundwater for all populations (Figures 10(b)–10(d)). Out of the sampled groundwater, 57.8%, 26.7%, 4.4%, and 17.8% were under the category of medium potential health risks to infants, children, adult females, and males, respectively, in terms of F^- in groundwater (Figure 10(b)). The statistic distribution of HQ posed by F^- was very similar to that of HI of multiple contaminants (Figures 10(a) and 10(b)). All these indicated the exceeding F^- in groundwater had higher responsibilities to the overall potential health risk than other contaminants in the study area.

4.4. Implication for Sustainable Water Management.

As discussed above, groundwater is essential for the development of various aspects in the North China Plain. Confined groundwater is more precious for the middle and lower reaches of the North China Plain due to the widespread distribution of salty water in the shallow aquifers. Thus, it is significantly crucial to realize the sustainable management of groundwater resources in confined aquifers although existing some potentially toxic elements in the water.

Most of the confined groundwater is fresh and soft in the study area, suggesting desirable water quality for the utilization by the human community in terms of the major solute chemistry. Although the quality of confined groundwater was not affected by the anthropogenic factors, the natural toxic elements including F^-, Mn, and Fe exceeded the desirable limit for drinking purpose and would potentially pose threats to human society. Thus, these potential toxic elements should be paid attention to when the water is utilized as a domestic water resource. However, not all confined groundwater in the study area causes health threats to human beings, the attention should be concentratedly focused on the areas with potential threats by toxic elements. As aforementioned, the overall potential health threats mainly exist in the northern area surrounding the sampling site of G17 and the eastern area, as well as some sporadic areas adjacent to sampling sites like G22 and G4. Thus, other areas are safe for the utilization of confined groundwater resource.

For the potential risk areas mentioned above, the degree of health threats is different for various populations. Infants are more prone to the toxic elements in groundwater, and
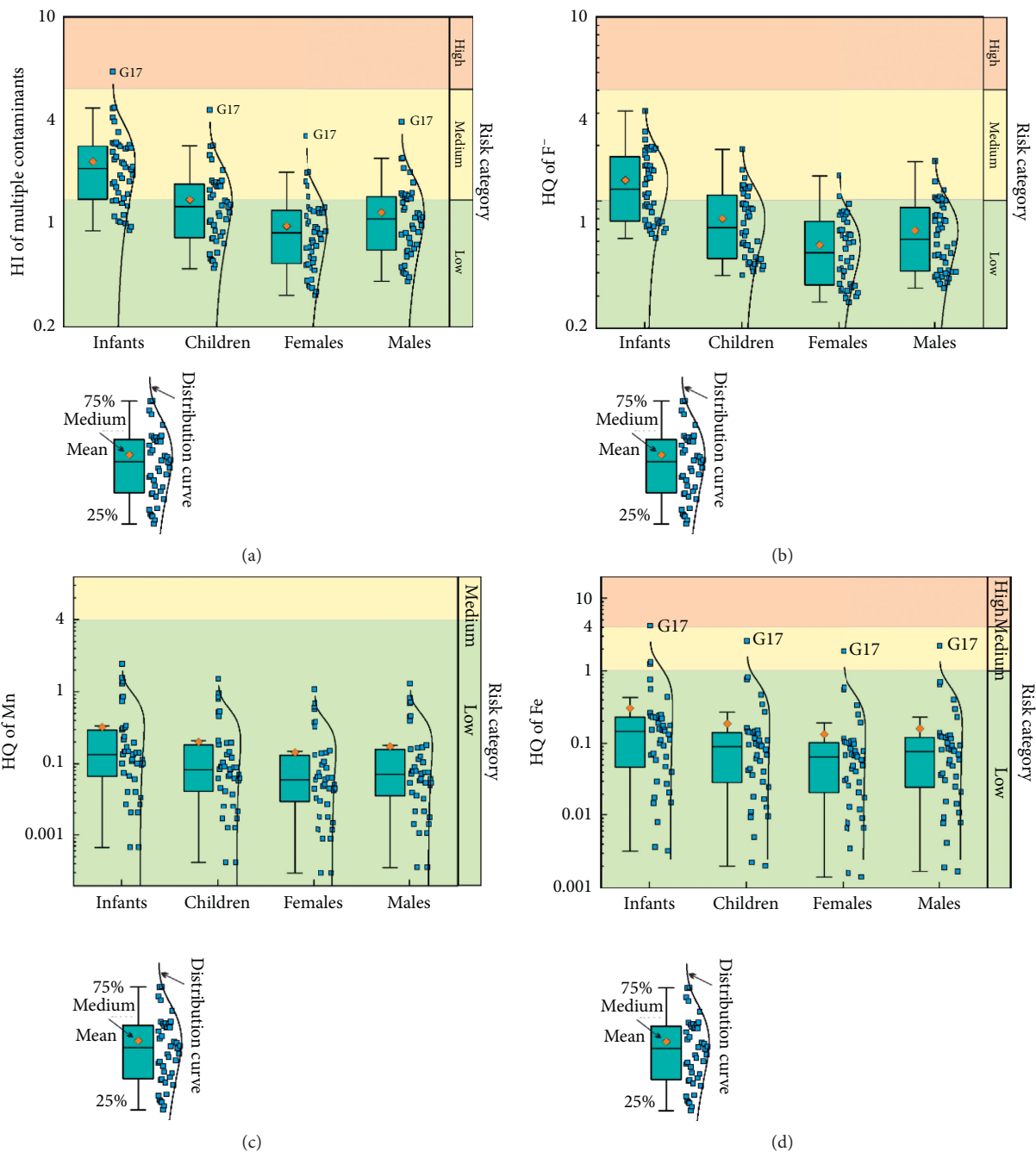
FIGURE 10: Box plots of (a) the overall noncarcinogenic health risk due to multiple contaminants and the hazard quotient of the noncarcinogenic health risk posed by a single contaminant of (b) F⁻, (c) Mn, and (d) Fe.

the threats to children, adult females, and males are much less. Given the preciousness of confined groundwater resource, differential water supplies based on the potential health risk to various populations are recommended in the study area. Additionally, water quality improvement should be implemented in the potential risk area. Although Mn and Fe are exceeding the desirable limit for water ingestion, their threats to human health are very limited and can be ignored. However, the health threat from the exceeding F⁻ in groundwater is significant. Considering the economic feasibility, the water improvement measures should be carried out aiming at exceeding F⁻ rather than other ions.
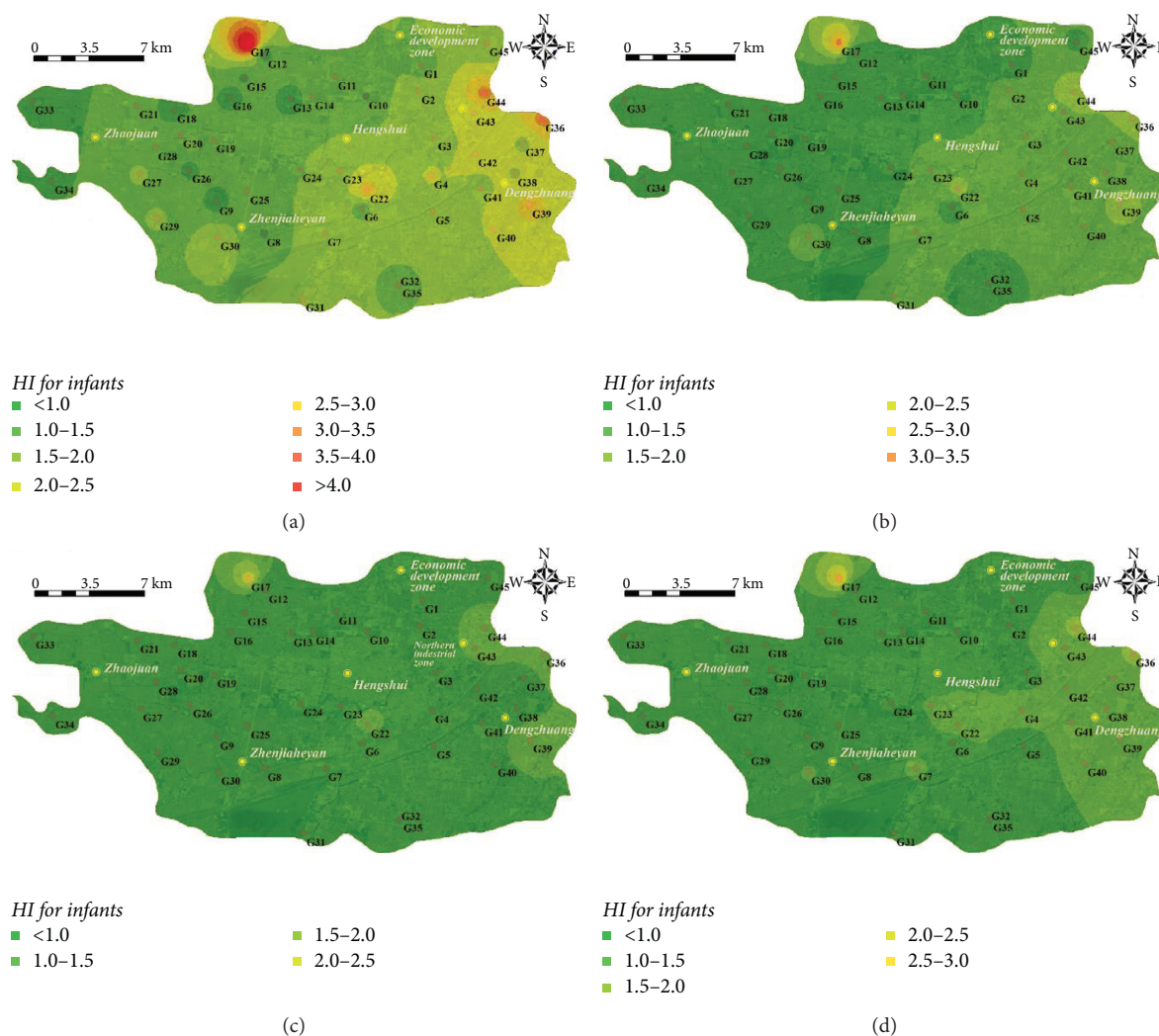
HI for infants
- ■ <1.0
- ■ 1.0–1.5
- ■ 1.5–2.0
- ■ 2.0–2.5
- ■ 2.5–3.0
- ■ 3.0–3.5
- ■ 3.5–4.0
- ■ >4.0

(a)

HI for infants
- ■ <1.0
- ■ 1.0–1.5
- ■ 1.5–2.0
- ■ 2.0–2.5
- ■ 2.5–3.0
- ■ 3.0–3.5

(b)

HI for infants
- ■ <1.0
- ■ 1.0–1.5
- ■ 1.5–2.0
- ■ 2.0–2.5

(c)

HI for infants
- ■ <1.0
- ■ 1.0–1.5
- ■ 1.5–2.0
- ■ 2.0–2.5
- ■ 2.5–3.0

(d)

FIGURE 11: Distribution of the overall noncarcinogenic health risk to (a) infants, (b) children, (c) females, and (d) males.

5. Conclusions

Confined groundwater is the preferred water resource worldwide, especially in arid and semiarid regions with scarce surface water and poor quality of phreatic water. Hydrochemistry is the premise of available and sustainable confined groundwater and should be concerned preferentially. The urban area of Hengshui, North China Plain, was taken as the study area to get insight into the hydrochemistry and health perspective of confined groundwater in large sedimentary plains. The main findings are as follows:

(1) Confined groundwater was of nearly neutral to slightly alkaline nature in the study area. Groundwater was predominantly soft-fresh water with average TH and TDS of 121 mg/L and 681 mg/L, respectively, and only a few samples in harder fresh or brackish categories. Hydrochemical facies were dominantly identified as Cl-Na type, with a few of the Mixed Cl-Mg·Ca type (2.2%) and Cl-Ca type (2.2%). The majority of the groundwater samples had the major ions within the desirable limit of WHO, except

for 6.7%, 11.1%, and 42.2% of Mg^{2+}, SO_4^{2-}, and Cl^-, respectively. Nitrogen (including NO_3^-, NO_2^-, and NH_4^+) and Zn were in a low and safe content, while F^-, Mn, and Fe were found exceeding the recommended limit of WHO in 28.9%, 15.6%, and 68.9% of the sampled groundwaters, respectively.

(2) The solute chemistry of confined groundwater was governed by the natural rock-water interactions and out of the effects of anthropogenic activities. The major hydrochemical composition and mineralization were dominantly contributed by the dissolution of evaporates (halite and sulfate) and silicates, cation-exchange reaction. Reverse cation-exchange reaction also controlled the major chemistry in sporadic samples. The exceeding content of toxic elements of F^-, Mn, and Fe was a result of ions releasing of fluoride-bearing, Fe-bearing, and Mn-bearing minerals.

(3) The overall chronic health risk posed by multiple contaminants was in the order of infants>children>males>females. The high health risk was only

potentially existing for infants. Majority of groundwater samples had the potential health risk negligible to children (60.0%), adult females (91.1%), and males (66.7%), but 73.4% of the sampled groundwater were with potential medium chronic health threats to infants. The exceeding F^- was highly responsible for the potential health risk to residents. The exceeding Fe in a few water samples can also pose health threats to some degree, while the potential risk from Mn was very low and negligible.

(4) Most of the confined groundwaters had desirable hydrochemical quality for drinking purpose, but attention should also be paid to the exceeding geogenic toxic elements of F^-, Mn, and Fe. The potential chronic health risk was dominantly posed by F^- rather than Mn and Fe and at different levels. Differential water supplies based on the potential health risk to various populations are recommended. Water improvement measures should be conducted to eliminate the health threat from exceeding F^-, especially to the infants.

Data Availability

The data used to support the findings of the present study will be provided upon request by the corresponding author.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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