Research Article

Chemical Characteristics and Quality Assessment of Groundwater of Exploited Aquifers in Beijiao Water Source of Yinchuan, China: A Case Study for Drinking, Irrigation, and Industrial Purposes

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This work is aimed at reviewing the chemical characteristics and evaluation of the quality of exploited groundwater in Beijiao water source of Yinchuan. A coupled model based on osculating value method (OVM) and entropy is proposed to determine the suitability for drinking. Besides, phreatic water and confined water are evaluated for irrigation purposes and industrial purposes, respectively. Piper diagram shows different hydrochemical characteristics between aquifers, which can be explained by the control mechanisms revealed by Gibbs diagram. Chloroalkaline indices and ions relationship indicate that reverse ion exchanges occur in different aquifers. Based on the osculating values, 96% of the phreatic water samples are fit for human consumption, and the confined water can provide quality drinking water. Most of the phreatic water samples have no sodium hazard but have magnesium hazard. All the confined water samples generate mild foaming reaction, and 93% of them are mildly corrosive for boilers. An assessment by OVM without entropy is calculated. Similar results to the coupled model demonstrate that pure OVM is also objective and valid. The simple algorithm turns multicriteria decision-making problems into an integrated index which is just as useful to water quality assessment.

1. Introduction

Groundwater is a vital resource, especially in arid and semiarid areas. Sufficient groundwater with high quality is required to meet increasing domestic, agricultural, and industrial needs. Groundwater withdrawals exceeding naturally renewable storage bring about environmental problems, such as forming a cone of depression and extracting nonrenewable groundwater [1, 2]. The global groundwater crisis is exacerbated by water quality degradation which is closely related to human health [3]. Groundwater quality is determined not only by natural processes such as quality of recharge waters, groundwater velocity, aquifer lithology, and interaction with other types of aquifers, but also by anthropogenic activities such as industry, agriculture, pollution discharge, and water exploitation modifying the hydrological cycle [4, 5]. The increases of nitrate and sulfate in groundwater in agricultural region are largely attributed to leaching of chemical fertilizer. The irrational irrigation and development of intensive agriculture have resulted in salinization and alkalization of groundwater [6]. Industrial processes create a large amount of effluents and waste residues which are more likely to contain toxic substances. Without proper disposal, the contaminants may infiltrate into aquifers and generate severe pollution. Quantities of domestic waste dumps as well as inadequate discharge and disposal facilities have a significant impact on groundwater quality [7].

The rapid development of urbanization has been accompanied by enhanced public awareness and concern regarding protection of groundwater [8, 9]. Once groundwater is polluted, it is tough restoring its quality with respect to a long time of storage recovery cycle. Therefore, it is critical to monitor and assess the groundwater quality regularly. Numerous researchers across the world explored methods to reflect water quality status. The commonly used methods are Water Quality Index (WQI), improved WQIs (EWQI, FWQI) [10, 11], WQIs by institutions (OWQI, CWQI, CCME WQI, AWQI, and MWQI) [12, 13], fuzzy comprehensive assessment method [14], multivariate statistical method [15], matter element extension [16], and neural network [17]. In this study, the osculating value method is introduced for evaluating water quality for drinking purposes. The arithmetic with brief steps is simple and easy to calculate. It does not only classify water quality, but also gives the ranks. Integrated with Shannon entropy as weights, the results are more objective and reasonable.

The study area consists of urban (1/3) in the south and rural (2/3) in the center and north (Figure 1). Groundwater from 3 aquifers is being used for various purposes. The upper layer, phreatic water, as the only source of water supply in the rural area is exploited extensively by private individuals. Except for domestic demand, the phreatic water is used for irrigation as water supply source for farming during nonirrigation period and for vegetables in villagers' gardens all year round. The middle and lower layers, confined water, are exploited for municipal water supply network as domestic or industrial consumption. However, the water in the study area is faced with many threats. (1) As an agricultural region, the area has been irrigated using the water from Yellow River for over 2,000 years with a complicated canal system. Besides agricultural pollution, long-term flood irrigation leads to shallow buried depth of groundwater which is adverse to contamination prevention and induces salinization [18]. (2) The water supply wells (confined water) are located in bare sandy land; nowadays, the zone becomes a new urban district due to the rapid urbanization. The groundwater source protection zone was redesigned to the north so as to develop the city, yet the supply wells are not moved. As a result, the protection zone cannot play any role. The fast-growing population has a significant impact on quantity and quality of groundwater. (3) Over exploitation has led to cone of depression in the confined aquifer. The depression cone reduced hydraulic head of the confined aquifer, which causes the phreatic water to recharge confined water. Consequently, the environmentally sensitive phreatic water threatens the confined water quality.

The aims of this study were to understand the groundwater hydrochemistry, detect its control mechanisms, and evaluate the groundwater comprehensively. According to the usage of water, both kinds of groundwater were assessed for drinking purposes by osculating value method integrated with Shannon entropy as weights. In addition, the phreatic water was assessed for irrigation purposes regarding sodium hazard, residual sodium carbonate, and magnesium hazard, whereas the confined water was assessed for industrial use in consideration of effects of incrustation, foaming and corrosion. Before assessment, hydrochemical composition and its controlling factors were explored to get a better understanding of groundwater chemistry.

2. Study Area

The study region extends between latitude $38°28'$–$38°40'$N and longitude $106°02'$–$106°16'$E with altitude between 1105 and 1125 m above mean sea level. It covers an area of $242.6 km^2$ and is located in the northern suburb of Yinchuan city, Ningxia Hui Autonomous Region, northwestern China (Figure 1). The city is characterized by a temperate continental arid and semiarid climate with annual average precipitation of 186.94 mm. About 45% of the precipitation occurs in July and August. The monthly average temperature ranges from $-7.1°C$ in January to $24°C$ in July, with the annual mean value of $9.81°C$. The evaporation is intensive, with a range from 1194.0 to 1743.2 mm/a and an average value of 1586.3 mm/a.

The study region is a part of Yinchuan Plain which is bordered by Helan Mountains on the west and the Yellow River in the east. The landform in the study area consists mainly of proluvial clinoplain, proluvial-alluvial plain, and alluvial-lacustrine plain that distribute zonally from west to east. Small-scale aeolian dunes were deposited in the northeast and west. The Quaternary sediments are thick due to long-term settlement of the rift basin. Within a depth of 250 m, the aquifers are divided into phreatic aquifer, upper-confined aquifer, and lower confined aquifer from the surface down [19]. The aquitard composed of clayey sand and sandy clay between phreatic aquifer and upper-confined aquifer is continuous with a thickness of 10–20 m, while the aquitard between two layers of confined aquifers is not continuous with great variation in thickness, even no more than 1 m in some area [20]. As a consequence, there exists close hydraulic connection between the confined aquifers.

3. Materials and Methods

3.1. Sampling and Analysis. A total of 37 groundwater samples were collected during September 2013. Among them, 23 samples were phreatic groundwater collected from hand-pressed wells or pump wells in different villages, and the remaining 14 samples were collected from 7 pairs of water supply wells in the confined aquifers (Figure 1). The samples were stored in plastic bottles and brown glass. Before sampling, containers were rinsed with groundwater to be taken. After sampling, one plastic bottle was acidified with HNO_3, and all containers were sealed immediately. The sample in brown glass for determining the organic compounds was filled without air to avoid oxidation. Before loading, the sampled containers were labeled and packed into incubators. Samples were delivered to the laboratory of Ningxia Environmental Monitoring Center on the same day.

A bulk chemical analysis was carried out for 65 parameters, including PH, total dissolved solid (TDS) as $CaCO_3$, total alkalinity (TA) as $CaCO_3$, total hardness (TH), major
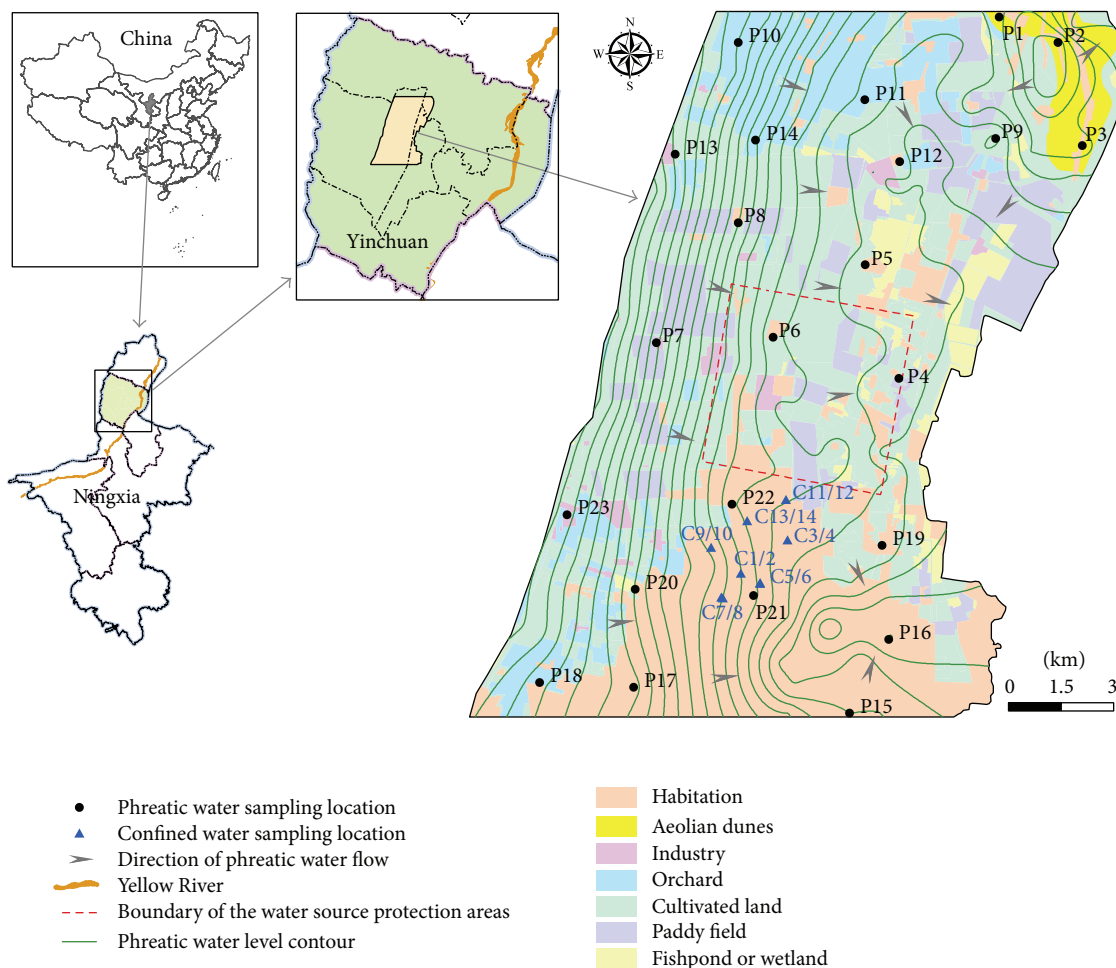
FIGURE 1: Location map of the study area showing the phreatic water level contour (interval of 1 m) and flow direction, land-use type, and sampling locations.

ions (K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, and SO_4^{2-}), nitrogen (NH_4^+-N, NO_3^--N, and NO_2^--N), fluoride (F^-), total phosphorus (TP), total cyanide, sulfide, selenium, arsenic, total coliforms (TC), total bacterial count (TBC), metal ions (Hg, Cr^{6+}, Cr, Cd, Cu, Fe, Mn, Ni, Pb, V, Zn, and Al), organic matters (phenol, volatile phenol, naphthalene, hexachlorocyclohexane (HCH), dichlorodiphenyl trichloroethane (DDT), carbon tetrachloride (CCl_4), olefins, alkanes, and benzene hydrocarbon).

3.2. Osculating Value Method.

The osculating value method is applied to solve multicriteria decision-making problems in system engineering. It has been used in scheme optimization, benefit evaluation, environmental assessment, and many other fields. The steps of osculating value method can be expressed as follows [21–24].

Step 1 (construction of the initial decision matrix). It is assumed that n indices of m samples are taken into evaluation.

An initial decision matrix **C** is constructed based on chemical analysis data:

$$\mathbf{C} = \begin{bmatrix} c_{11} & c_{12} & \cdots & c_{1n} \\ c_{21} & c_{22} & \cdots & c_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ c_{(m+p)1} & c_{(m+p)2} & \cdots & c_{(m+p)n} \end{bmatrix}, \qquad (1)$$

where c_{ij} is the concentration of jth index of ith sample ($i = 1, 2, \ldots, m$, and $j = 1, 2, \ldots, n$) and p is the number of rank in criterion. For $i > m$, c_{ij} is the concentration of each rank.

Step 2 (normalization of the matrix). Generally, multiple indices with different units and ranges are involved in calculation. The relationships among indices are complicated. Some indices are efficiency type (the higher the value, the better the performance), and some are cost type (the higher the value, the worse the performance). Therefore, the initial matrix is

standardized to get rid of discrepancies. The standardization treatment is expressed as follows:

$$r_{ij} = \begin{cases} \dfrac{c_{ij}}{\left[\sum_{i=1}^{m} c_{ij}^2\right]^{1/2}} & \text{efficiency type,} \\[3mm] -\dfrac{c_{ij}}{\left[\sum_{i=1}^{m} c_{ij}^2\right]^{1/2}} & \text{cost type.} \end{cases} \quad (2)$$

Standardized decision matrix is written as $\mathbf{R} = (r_{ij})_{(m+p)\times n}$.

Step 3 (determination of the optimum and inferior point sets). Let

$$r_j^+ = \max\left(r_{1j}, r_{2j}, \ldots, r_{(m+p)j}\right),$$
$$r_j^- = \min\left(r_{1j}, r_{2j}, \ldots, r_{(m+p)j}\right). \quad (3)$$

Then, the optimum point set is

$$\mathbf{G} = \left(r_1^+, r_2^+, \ldots, r_{(m+p)}^+\right). \quad (4)$$

And the inferior point set is

$$\mathbf{B} = \left(r_1^-, r_2^-, \ldots, r_{(m+p)}^-\right). \quad (5)$$

Step 4 (calculation of osculating value). The osculating value E_i can be calculated as follows:

$$E_i = \frac{d_i^+}{\min\left(d_i^+\right)} - \frac{d_i^-}{\max\left(d_i^-\right)}, \quad (6)$$

where

$$d_i^+ = \sqrt{\sum_{j=1}^{n} \omega_j \left(r_{ij} - r_j^+\right)^2},$$
$$d_i^- = \sqrt{\sum_{j=1}^{n} \omega_j \left(r_{ij} - r_j^-\right)^2}. \quad (7)$$

ω_j is the entropy weight of jth index, d_i^+ and d_i^- are the Euclidean distances to the optimum and inferior points, respectively. The values of E_i reflect the approach degree of sample points from extreme points. The smaller the value is, the sample point is further to optimum point and closer to inferior point, the better the groundwater quality is.

The method turns multiple indices into an integrated index. The groundwater quality can be obtained by the order of osculating value. The involvement of standard values in initial decision matrix helps to classify groundwater quality into different levels.

3.3. Entropy Theory. Entropy theory was developed by Shannon in 1948 [25]. Shannon entropy, as a measure of information, including disorder, dispersion, and diversification, can reduce the uncertainty of indices by predicting the output of a probabilistic event [26]. It is considered to be

an objective method to determine weights. The algorithm has been used in wide scientific fields, including hydrological and environmental sciences [27]. WQIs, TOPSIS, and many other water quality assessment methods were improved by integrating the entropy [28, 29]. The entropy weight can be calculated as follows [10, 26, 28].

Step 1 (construction of the initial matrix). Different from initial decision matrix of OVM, the initial matrix $\mathbf{C}'$ of entropy weight does not involve concentrations in criterion:

$$\mathbf{C}' = \begin{bmatrix} c_{11} & c_{12} & \cdots & c_{1n} \\ c_{21} & c_{22} & \cdots & c_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ c_{m1} & c_{m2} & \cdots & c_{mn} \end{bmatrix}, \quad (8)$$

where c_{ij} is the concentration of jth index of ith sample.

Step 2 (normalization of the matrix). The initial matrix is normalized by

$$y_{ij} = \begin{cases} \dfrac{c_{ij} - \left(c_{ij}\right)_{\min}}{\left(c_{ij}\right)_{\max} - \left(c_{ij}\right)_{\min}} & \text{efficiency type,} \\[3mm] \dfrac{\left(c_{ij}\right)_{\max} - c_{ij}}{\left(c_{ij}\right)_{\max} - \left(c_{ij}\right)_{\min}} & \text{cost type.} \end{cases} \quad (9)$$

Standardized matrix is written as $\mathbf{Y} = (y_{ij})_{m\times n}$.

Step 3 (calculation of information entropy). Let

$$P_{ij} = \frac{\left(y_{ij} + 10^{-4}\right)}{\sum_{i=1}^{m} \left(y_{ij} + 10^{-4}\right)},$$
$$e_j = -\frac{1}{\ln m} \sum_{i=1}^{m} P_{ij} \ln P_{ij}, \quad (10)$$

where e_j is the information entropy of jth index, 10^{-4} is a refined parameter to ensure the formula meaningful when y_{ij} is 0.

Step 4 (calculation of entropy weight). Let

$$\omega_j = \frac{1 - e_j}{\sum_{j=1}^{n} \left(1 - e_j\right)}, \quad (11)$$

where ω_j is the entropy weight of jth index.

4. Results and Discussion

4.1. Statistical Analysis. Statistical analysis of some parameters was carried out to describe the general physiochemical characteristics preliminarily, and the results are presented in Table 1. In order to find out whether it is suitable for drinking, the maximum values were compared with the acceptable limits which are the standards for drinking in Quality

Table 1: Statistics of groundwater quality parameters.

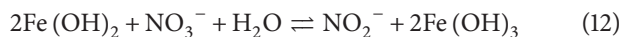| Parameter	Aquifer	Unit	Min	Max	Median	Mean	CV	Acceptable limits
pH	Unconfined	—	7.27	8.08	7.87	7.78	0.03	6.5–8.5
	Confined	—	7.89	8.24	8.21	8.15	0.01	
TDS	Unconfined	mg/L	255	1980	740	864.91	0.47	1000
	Confined	mg/L	224	267	246	246.57	0.05	
NH_4^+-N	Unconfined	mg/L	0.046	0.34	0.06	0.08	0.75	0.2
	Confined	mg/L	0.116	0.362	0.21	0.22	0.31	
TA	Unconfined	mg/L	149	701	336	334.78	0.36	—
	Confined	mg/L	188	251	203.5	206.29	0.08	
TH	Unconfined	mg/L	210	1089	531	512.35	0.39	450
	Confined	mg/L	179	222	194	197.50	0.07	
COD_{Mn}	Unconfined	mg/L	ND	2.1	1	1.03	0.44	3
	Confined	mg/L	ND	1	0.65	0.67	0.25	
NO_2^--N	Unconfined	mg/L	ND	0.211	ND	—	—	0.02
	Confined	mg/L	ND	ND	ND	ND	0	
Na^+	Unconfined	mg/L	42.6	371	157	178.8	0.47	200
	Confined	mg/L	26.7	61.5	32.4	34.37	0.26	
K^+	Unconfined	mg/L	4.29	42.1	7.01	10.24	0.84	—
	Confined	mg/L	3.13	8.94	5.48	5.73	0.38	
Mg^{2+}	Unconfined	mg/L	27.2	213	71.8	79.54	0.52	150
	Confined	mg/L	24.2	29.5	26.2	26.47	0.06	
Ca^{2+}	Unconfined	mg/L	39.9	163	87.8	88.03	0.35	200
	Confined	mg/L	32.7	69.3	38.5	41.89	0.21	
F^-	Unconfined	mg/L	0.14	1.82	0.38	0.57	0.84	1
	Confined	mg/L	0.27	0.43	0.34	0.34	0.14	
Cl^-	Unconfined	mg/L	62.5	335	147	177.35	0.45	250
	Confined	mg/L	55.5	75.7	64.85	64.48	0.09	
NO_3^--N	Unconfined	mg/L	1.99	26.2	6.53	8.51	0.94	20
	Confined	mg/L	0.87	2.63	1.22	1.45	0.40	
SO_4^{2+}	Unconfined	mg/L	47.6	466	279	264.45	0.49	250
	Confined	mg/L	30.5	47.8	36.5	37.64	0.13	
Fe	Unconfined	mg/L	ND	0.101	0.003	<0.012	—	—
	Confined	mg/L	0.078	0.25	0.183	0.15	0.33	
Mn	Unconfined	mg/L	ND	0.737	0.002	<0.050	—	—
	Confined	mg/L	0.036	0.077	0.065	0.06	0.17	
Se	Unconfined	mg/L	ND	1.76×10^{-3}	2.43×10^{-4}	—	—	0.01
	Confined	mg/L	ND	6.00×10^{-3}	ND	—	—	
Hg	Unconfined	mg/L	1.60×10^{-5}	1.85×10^{-4}	3.70×10^{-5}	6.38×10^{-5}	0.77	0.001
	Confined	mg/L	2.50×10^{-5}	1.84×10^{-4}	9.30×10^{-5}	9.64×10^{-5}	0.51	
As	Unconfined	mg/L	1.74×10^{-4}	1.35×10^{-3}	5.63×10^{-4}	5.99×10^{-4}	0.45	0.05
	Confined	mg/L	1.51×10^{-4}	1.28×10^{-3}	2.83×10^{-4}	3.89×10^{-4}	0.77	
TC	Unconfined	mpn/L	ND	2005	222	—	—	3
	Confined	mpn/L	ND	150	ND	—	—	
TBC	Unconfined	cfu/mL	0	102	20	30.8	1.1	100
	Confined	cfu/mL	0	12	0	1.14	2.82	

CV: coefficient of variation; ND: not detected.

Standard for Ground Water (QSGW) of China. For Na^+, Mg^{2+}, and Ca^{2+}, which are not included in QSGW, Guidelines for Drinking-water Quality by Word Health Organization (WHO) are used instead.

Among the 22 parameters considered of the phreatic samples, the maximum of 12 parameters consisting of TDS, TH, Na^+, Mg^{2+}, NH_4^+-N, NO_3^--N, NO_2^--N, Cl^-, SO_4^{2+}, F^-, TC, and TBC are beyond the acceptable limits. Fortunately,

the average concentrations of 8 parameters including TDS, Na^+, Mg^{2+}, NH_4^+-N, NO_3^--N, NO_2^--N, Cl^-, and F^- do not exceed the acceptable limits. The average concentrations of TH, NO_2^--N, and SO_4^{2+} are 512 mg/L, 0.023 mg/L, and 264 mg/L that are higher than acceptable limits 450 mg/L, 0.02 mg/L, and 250 mg/L, respectively. Whereas, the concentrations of NO_2^--N in 14 samples are below the detection limits of 0.003 mg/L, and the median of ND implied that only a few samples are polluted but severely.

The concentrations of parameters of the confined samples are lower than those of the phreatic samples obviously except NH_4^+-N, Fe, Mn, and Hg. Still, NH_4^+-N, and TC of some confined samples exceed the acceptable limits. And 10 of the 14 samples (71%) have exceeded NH_4^+-N. Ji [30] investigated the reasons for the high concentration of NH_4^+-N of the confined groundwater in Yinchuan. The source of NH_4^+ comes from chemical fertilizer, and anoxic condition caused by flood irrigation goes against nitrification which transforms NH_4^+ to NO_3^-. The NH_4^+ infiltrates into the confined aquifers by leakage recharge and encouraged by increased water head difference caused by overexploited confined water. It has been suggested that approximately 70% of recharge of upper-confined water comes from the phreatic aquifer [31]. The high Fe and Mn contents in the confined water, in general caused by geological environment [32], are another reason to be responsible for NH_4^+ pollution. As reducing agents, Fe and Mn are involved into redox reactions with oxidant NO_3^- in neutral or weak alkaline environment. The reactions are expressed as

$$2Fe(OH)_2 + NO_3^- + H_2O \rightleftharpoons NO_2^- + 2Fe(OH)_3 \qquad (12)$$

$$Mn(OH)_2 + NO_3^- \rightleftharpoons MnO_2 + NO_2^- + H_2O \qquad (13)$$

The reactions reduce NO_3^- and produce NO_2^- which is unstable. In the reaction processes, iron bacteria oxidize ferrous iron to ferric iron by using molecular oxygen and synthesize organic compounds using energy from the reactions, which consumes oxygen further [33]. The hypoxic environment inhibits nitrification, which accumulates NH_4^+. Ji [30] verified that there exist negative correlation between NO_3^- and Fe/Mn, nonlinear relationship between NO_2^- and Fe/Mn due to instability of NO_2^-, and positive correlation between NH_4^+ and Fe/Mn. Similar relationships were found in groundwater in Shunyi District, Beijing [34].

4.2. Groundwater Types. For the phreatic water samples, the cationic strength was observed as $Na^+ > Mg^{2+} > Ca^{2+} > K^+$ with percentages of 40.22%, 33.88%, 24.23%, and 1.66%, respectively. The percentages of $HCO_3^- > SO_4^{2-} > Cl^-$ are 40.40%, 30.58%, and 29.02%, respectively. The dominant elements of the confined water are quite different from that of the phreatic water. Cation dominances of the confined water were observed as $Mg^{2+} > Ca^{2+} > Na^+ > K^+$, and their percentages are 37.27%, 35.21%, 25.07%, and 2.45%, respectively. The percentages of $HCO_3^- > Cl^- > SO_4^{2-}$ were observed as 61.57%, 26.88%, and 11.55%, respectively. The main cations are Na^+, Mg^{2+}, and Ca^{2+} in the phreatic

water and confined water, respectively, and main anions are HCO_3^- in both types of water.

Piper trilinear diagram, which was conceived by Hill [35] and improved by Piper [36], is a widely used tool to understand the hydrochemical regime and facies classification of groundwater and surface water [37, 38]. Sample points with similar hydrochemistry tend to cluster together in the diagram. Hydrochemical facies were distinguished by equal 50% increments which are more helpful than equal 25% increments [39]. As shown in Figure 2, there are no dominant cations and anions for most phreatic water samples, except 6 samples that are dominated by Na^+ and discrepant 6 samples dominated by HCO_3^-. For samples from the confined aquifers, the anion chemistry is controlled by HCO_3^-, and the cation chemistry has no dominant ions. Except sample P10 identified as Na-HCO_3 type, all the other phreatic samples were classified into mixed type due to no cation-anion exceeding 50%. The diamond-shaped field showed that alkaline earths exceed alkalis and strong acids exceed weak acids for all confined water.

There is a huge difference in point distribution between the phreatic water and confined water in the diagram. The former has dispersed distribution, while the latter has concentrated distribution. This indicates that more complicated controlling factors exist in shallow groundwater than deep groundwater. The composition of elements implies weathering of carbonate minerals is the primary controlling factor. However, hydrochemistry of shallow groundwater is affected by evaporation considerably, because relative to the confined water, the phreatic water tends to have a higher proportion of $Na^+ + K^+$ and SO_4^{2-}, a lower proportion of Ca^{2+} and $HCO_3^- + CO_3^{2-}$ which are shown in the triangular field. This behavior is the consequence of $CaCO_3$ precipitation under evaporation that results in the phreatic water becomes alkaline. The similar hydrochemical proportions of samples from two layers of confined aquifers confirm the close hydraulic connection between them.

4.3. Ion Exchange. Water chemical composition changes during its travel or residence in the subsurface [40]. Aquifer materials are the sources of dissolved ions and encourage cation exchange and reverse ion exchange. In particular, for montmorillonite, it releases Na^+ or Ca^{2+} into groundwater to exchange Ca^{2+} or Na^+ [41]. In aquifer composed of unconsolidated deposits, a mass of clay minerals exist and adsorb cations in their pore space [42]. To get insight into the base exchange reaction between groundwater and its host environment, Schoeller [43] suggested two chloroalkaline indices CAI-I and CAI-II:

$$CAI\text{-}I = \frac{Cl^- - (Na^+ + K^+)}{Cl^-} \qquad (14)$$

$$CAI\text{-}II = \frac{Cl^- - (Na^+ + K^+)}{SO_4^{2-} + HCO_3^- + CO_3^{2-} + NO_3^-}. \qquad (15)$$

If Ca^{2+} or Mg^{2+} in groundwater is exchanged with Na^+ or K^+ in the host rocks, both of the two indices are negative, whereas a reverse ion exchange gives positive indices [44, 45].
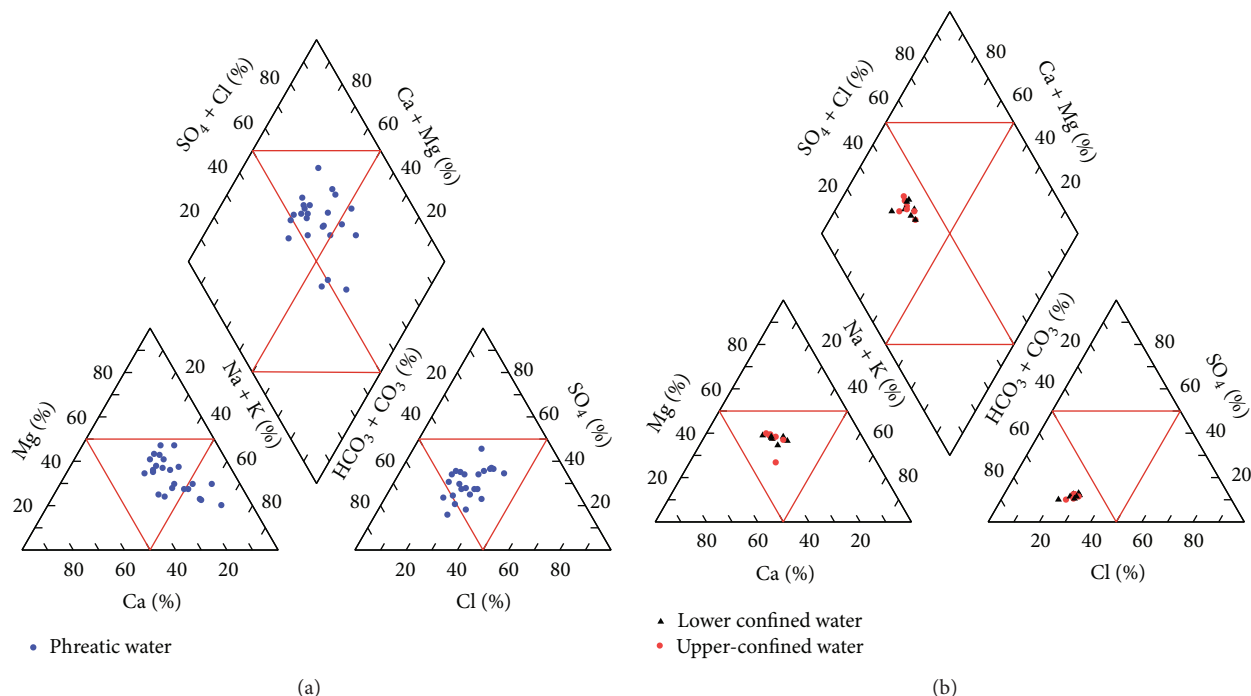
(a)

(b)

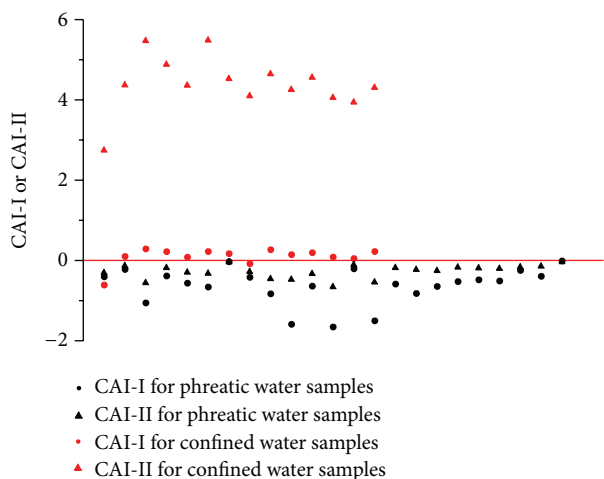FIGURE 2: The piper diagrams for the phreatic water samples (a) and the confined water samples (b).

FIGURE 3: Chloroalkaline indices (CAI-I and CAI-II) for the phreatic water samples and the confined water samples.

FIGURE 4: Scatter plot for SO_4 + HCO_3 versus Ca + Mg.

Figure 3 showed both indices are negative for all the phreatic water samples and positive for most confined water samples except for CAI-I of samples C1 and C8. The opposite signs for the phreatic and confined water indicate contrary ion exchange processes take place in the two types of water. This potentially explains the relative abundance of Na^+ in the phreatic water and the abundance of alkaline earth, especially Mg^{2+}, in the confined water.

In the water environment dominated by the dissolutions of calcite, dolomite, and gypsum, the relationship between (Ca^{2+} + Mg^{2+}) and (SO_4^{2-} + HCO_3^-) is close to 1 : 1 [46, 47].

The ion exchange known as direct tends to shift the points because of the excess of (SO_4^{2-} + HCO_3^-) over (Ca^{2+} + Mg^{2+}). Whereas the reverse ion exchange shifts the points to the left due to increased Ca^{2+} and/or Mg^{2+} released by rocks [47, 48]. Figure 4 showed 78% of the phreatic water samples are below the 1 : 1 line due to a deficiency of Ca^{2+} and Mg^{2+}. As
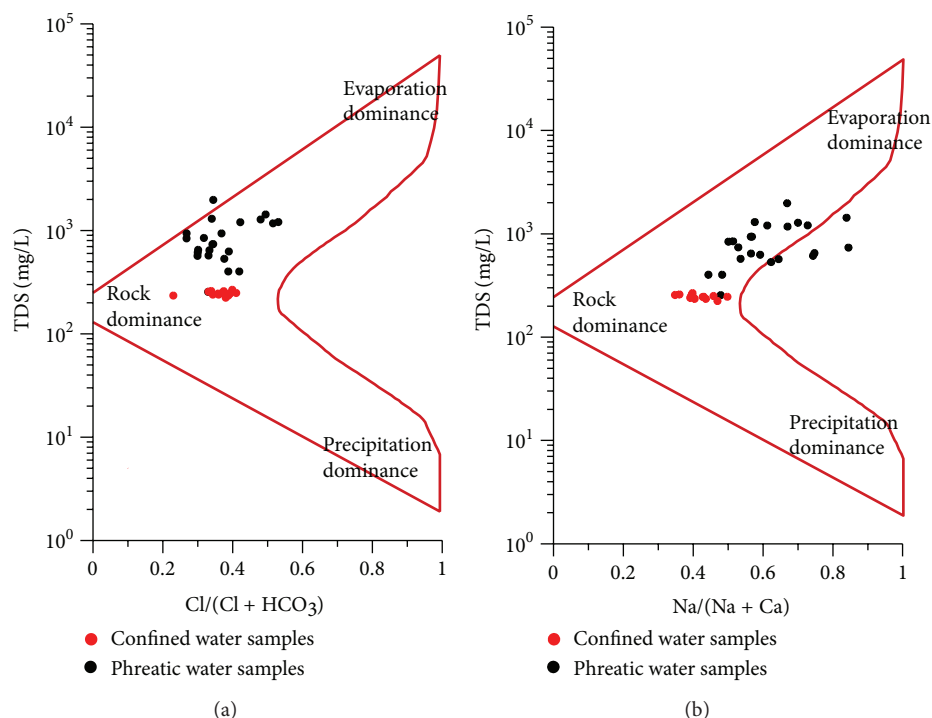
(a)

(b)

Figure 5: Gibbs diagram showing TDS versus (a) $Cl/(Cl + HCO_3)$ and (b) $Na/(Na + Ca)$.

a result, Na^+ must balance the excessive anions. The abundant Na^+ is evidence of the ion exchange process. And 86% of the confined water samples fall above the 1 : 1 line which indicates the reverse ion exchange dominancy.

Gibbs diagram is used to detect mechanisms that control the hydrochemical components in surface water [49] and groundwater [47, 50]. The values of TDS are plotted against ratios of dominant cations [$Na/(Na + Ca)$] or anions [$Cl/(Cl + HCO_3)$] [51]. The diagram is divided into three zones representing different controlling mechanisms which are evaporation, rock, and precipitation (rainfall) dominance from top to bottom. The chemical analyses of phreatic and confined water samples were plotted in the Gibbs diagram (Figure 5). It showed all the confined water samples fall in the rock dominance zone entirely which is compatible with storage conditions. Whereas, the phreatic water samples falling in the zone between evaporation and rock dominance demonstrate a mixed controlling mechanism. Evaporation results in increased TDS relative to the confined water with relation to high ratios of dominant cations and anions, especially sodium ions, due to $CaCO_3$ precipitate caused by the combination of Ca^{2+} and HCO_3^-. Huge quantities of irrigation return flow elevated groundwater level, hence increases evaporation and induce salinization.

4.4. Water Quality for Drinking Purposes. Quality Standard for Ground Water (QSGW) of China was chosen as evaluation criterion. The core indices (TDS, TH, COD_{Mn}, NH_4^+-N, NO_3^--N, NO_2^--N, Cl^-, SO_4^{2+}, and F^-) and some other indices (Se, Hg, As, TC, and TBC) included in QSGW were

opted for assessment. A separate calculation of osculating value based on entropy was processed for the phreatic groundwater and confined groundwater, on account of disparities in physiochemical characteristic, source, and storage condition. The results are present in Tables 2 and 3. Four groups of criteria (S1, S2, S3, and S4) in QSGW classified groundwater quality into five ranks.

Ranking of the phreatic water samples (Table 2) showed that 4 samples are excellent quality water (rank 1), 1 sample belongs to good quality water (rank 2), 17 samples are classified in medium quality category (rank 3), and 1 sample is poor quality water (rank 4). Groundwater in ranks 1, 2, and 3 is suitable for drinking according to QSGW of China. Except for sample P4 with osculating value of 5.29 that is just greater than the standard value of rank 3 of 5.13, all the other phreatic samples are appropriate for human consumption.

Ranking of the confined water samples (Table 3) revealed that 12 samples had the good quality (rank 2) and 2 samples had the medium quality (rank 3). This indicates that mixing water from supply wells can provide quality drinking water.

The majority of the phreatic samples (73.9%) belong to rank 3, while most confined samples (85.7%) are rank 2. A level worse than the confined water to the phreatic water is consistent with their characteristics. The results suggest that the phreatic water has been adversely affected by human activities, such as increased nitrogen caused by infiltration of fertilizers and pesticides in the Yellow River irrigated agricultural region, and high numbers of coliforms and bacterial counts due to backwardness of toilet, waste disposal, and other sanitation in the rural area. In spite of

Table 2: Assessment results of osculating values method with entropy and without entropy for the phreatic water samples.

Sample number	OVM with entropy		OVM without entropy	
	Osculating value	Rank	Osculating value	Rank
P1	2.43	3	2.17	3
P2	0.29	1	0.48	1
P3	0.4	1	0.58	1
P4	5.29	4	4.95	3
P5	0	1	0	1
P6	1.61	3	1.64	3
P7	1.56	3	1.6	3
P8	0.35	1	0.48	1
P9	3.67	3	3.7	3
P10	1.42	3	1.45	3
P11	2.34	3	2.16	3
P12	0.72	2	0.94	2
P13	1.69	3	0.99	2
P14	1.11	3	2.19	3
P15	3.76	3	3.19	3
P16	4.35	3	4.2	3
P17	2.78	3	2.62	3
P18	1.07	3	1.02	2
P19	3.83	3	3.13	3
P20	3.09	3	2.23	3
P21	2.42	3	2.33	3
P22	1.43	3	1.44	3
P23	2.27	3	1.5	3
S1	0.47		0.73	
S2	1.05		1.26	
S3	5.13		5.99	
S4	13.18		16.06	

Table 3: Assessment results of osculating values method with entropy and without entropy for the confined water samples.

Sample number	OVM with entropy		OVM without entropy	
	Osculating value	Rank	Osculating value	Rank
C1	0.23	2	0.01	1
C2	2.49	3	2.16	3
C3	1.03	2	0.74	2
C4	1.22	2	0.93	2
C5	4.11	3	4.54	3
C6	0.61	2	0.31	2
C7	0.77	2	0.48	2
C8	2.00	2	1.66	2
C9	0.88	2	0.67	2
C10	0.26	2	0.13	2
C11	1.43	2	1.14	2
C12	1.13	2	0.86	2
C13	1.63	2	1.35	2
C14	1.06	2	0.79	2
S1	0.02		0.06	
S2	2.39		1.82	
S3	9.07		7.04	
S4	17.55		16.97	

pure osculating value method is also reasonable and useful. The method is applicable to other countries and criteria by exchanging QSGW of China in the initial decision matrix for other standard values. An assessment without standard values is also feasible; thus, a score and rank can be obtained for each sample.

drinkable of the phreatic water, it is urgent to concern and improve the groundwater quality because osculating values of some phreatic samples are close to the critical value of drinkable.

Contour map of osculating value with entropy for the phreatic water was interpolated by kriging with Gaussian variogram model (Figure 6). The osculating value contour map showed inconsistency with the phreatic water level contour in the west, even opposition in some regions. The rank 4 region is downstream of the phreatic water, and it is the center of a small town with a population of high density but poor sanitation. The northeast corner (rank 1) of the study area is small-scale aeolian dunes where land is wasteland or poor farmland. These are also evidence that anthropogenic activities are responsible for groundwater pollution.

The results assessed by osculating value without entropy were also listed in Tables 2 and 3 for comparison. The comparison reveals that entropy has a minor influence on the ranks. Only 3 phreatic samples and 1 confined sample have different ranks. And the different ranks just have one level change. This demonstrates pure osculating value method is objective which is a great advantage of the algorithm. The

4.5. Water Quality for Irrigation Purposes

4.5.1. Sodium Hazard.
Sodium is the mainly concerned parameter when assessing the suitability of groundwater for irrigation. Groundwater with high concentration of sodium ions is undesirable to irrigate crops. In Na-enriched groundwater, Mg^{2+} and Ca^{2+} will be released from soil into groundwater, while Na^+ will be adsorbed onto the soil resulting from the cation exchange processes. On the contrary, Na^+ will be released from cation exchange sites and Ca^{2+} ions are adsorbed in groundwater that is rich in Ca^{2+} [52]. Overburdened sodium ions in the soil affect the behavior of the colloidal fraction and lead to soil aggregates to disperse that result in decrease of soil permeability, and hardening of the soil affects plough and seedling emergence [53–55]. In addition, saline and alkaline soils, which are harmful to plant growth, are formed by combining sodium with chloride and carbonate, respectively [41].

Sodium adsorption ratio (SAR), used by the United States Salinity Laboratory, was used as the primary indicator for evaluating irrigation [56, 57]. The sodium percentage (Na%) expressed as a ratio of Na^+ and K^+ concentration to Na^+,
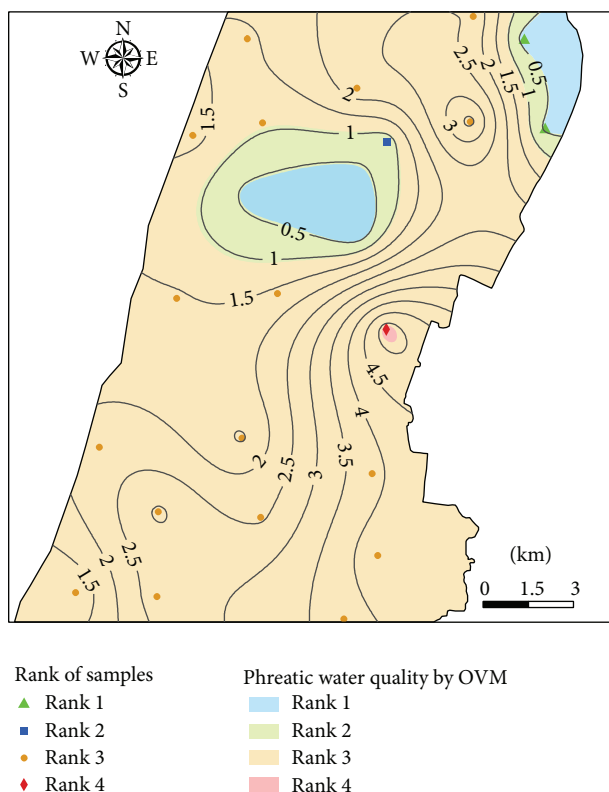
FIGURE 6: Contour map of osculating value and classification of the phreatic water quality by OVM with entropy.

K^+, Ca^{2+}, and Mg^{2+} concentration is another indicator used widely [58]:

$$SAR = \frac{Na^+}{\sqrt{(Ca^{2+} + Mg^{2+})/2}} \qquad (16)$$

$$Na\% = \frac{Na^+ + K^+}{Na^+ + K^+ + Ca^{2+} + Mg^{2+}} \times 100, \qquad (17)$$

where the concentrations of all ions are in meq/L. **Figure 7(a)** showed SAR of the phreatic water in the study area fall within the range between 1.27 and 6.73, all much smaller than the safe value 9 with no structural deterioration [59, 60]. It means that all the water samples meet the general requirements for irrigation. However, the values of Na% are in the range of 29.2–67.5, beyond the permissible limits of 60 partially (**Figure 7(b)**). In fact, Na% of sample P12 is 67.5, while the rest of samples within the permissible limits. The results indicated that sample P12 is unsuitable for irrigation because of sodium hazard.

4.5.2. Residual Sodium Carbonate. Generally, water loses after irrigation because of evaporation and evapotranspiration. Hence, the concentration of soil solution is elevated which causes the precipitation of Ca^{2+} and Mg^{2+} combined with CO_3^{2-} and HCO_3^- [61]. Meanwhile, the percentage of Na^+ arises and high Na^+ content increases the SAR and exchangeable Na^+ of soil solution [62]. If the concentration

of carbonates is greater than that of alkaline earths, $NaHCO_3$ which can affect soil structure will be formed by combining Na^+ with the rest of carbonates after precipitation [63]. Residual sodium carbonate (RSC) expresses as the concentration of carbonates minus the concentration of alkaline earths [41, 64]:

$$RSC = (HCO_3^- + CO_3^{2-}) - (Ca^{2+} + Mg^{2+})$$
$$= TA - (OH^- + Ca^{2+} + Mg^{2+}), \qquad (18)$$

where TA represents the concentration of total alkalinity (as $CaCO_3$) and the concentrations of all parameters are expressed in meq/L. The concentration of OH^- is less than 10^{-3} meq/L which can be ignored compared to the values of other parameters, when PH is within the range of 6 and 8 [64]. Irrigation water was classified based on RSC values of less than 1.25, 1.25–2.5, and greater than 2.5 as suitable, marginal, and unsuitable, respectively [65]. As per the data, the values of RSC range from −9.9 to 1.5, and 2 samples (P10 and P12) fall into the marginal range, while others fall into the suitable range (**Figure 7(c)**). This indicates that sodium hazard caused by exceeded carbonates is light.

4.5.3. Magnesium Hazard. A high level of Mg^{2+} in the soil can be expected to result in alkaline which damages soil structure and affects crop yields. Normally, irrigation water of high concentration of Mg^{2+} makes soils release Na^+ and exchange Mg^{2+} in the water [63]. In the study area, the equilibrium of cation exchange processes is as the above case which is proved by CAI-I and CAI-II. So, magnesium ratio (MR) was carried out to evaluate the magnesium hazard proposed by Szaboles and Darab [66]:

$$MR = \frac{Mg^{2+}}{Ca^{2+} + Mg^{2+}} \times 100, \qquad (19)$$

where all ionic concentrations are expressed in meq/L. If MR is more than 50, the water is considered to be harmful to soil and affects the crop yields. The values of MR in the study area vary from 42.1 to 73.1. It is found that 21 samples of all the 23 phreatic water samples (91.3%) exceed the permissible limit of MR (**Figure 7(d)**). Only sample P6 and P7 have no magnesium hazard with magnesium ratios of 42.1 and 49.6, respectively, which are closed to the limit.

4.6. Water Quality for Industrial Purposes. Water used for industry is one of the important parts of urban water supply. Its requirements of water quality are very different from drinking and irrigation purposes, even altered in various industries [67]. Each industry has its own standards for water. Boiler water is quite common and requires high quality water. Generally, they suffer from three effects of incrustation, foaming and corrosion which are caused by adverse chemical reaction under the condition of high temperature and high pressure [9, 68].

4.6.1. Incrustation. Boiler scale attached to the boiler wall is adverse to heat transfer, hence wastes fuel, even melts
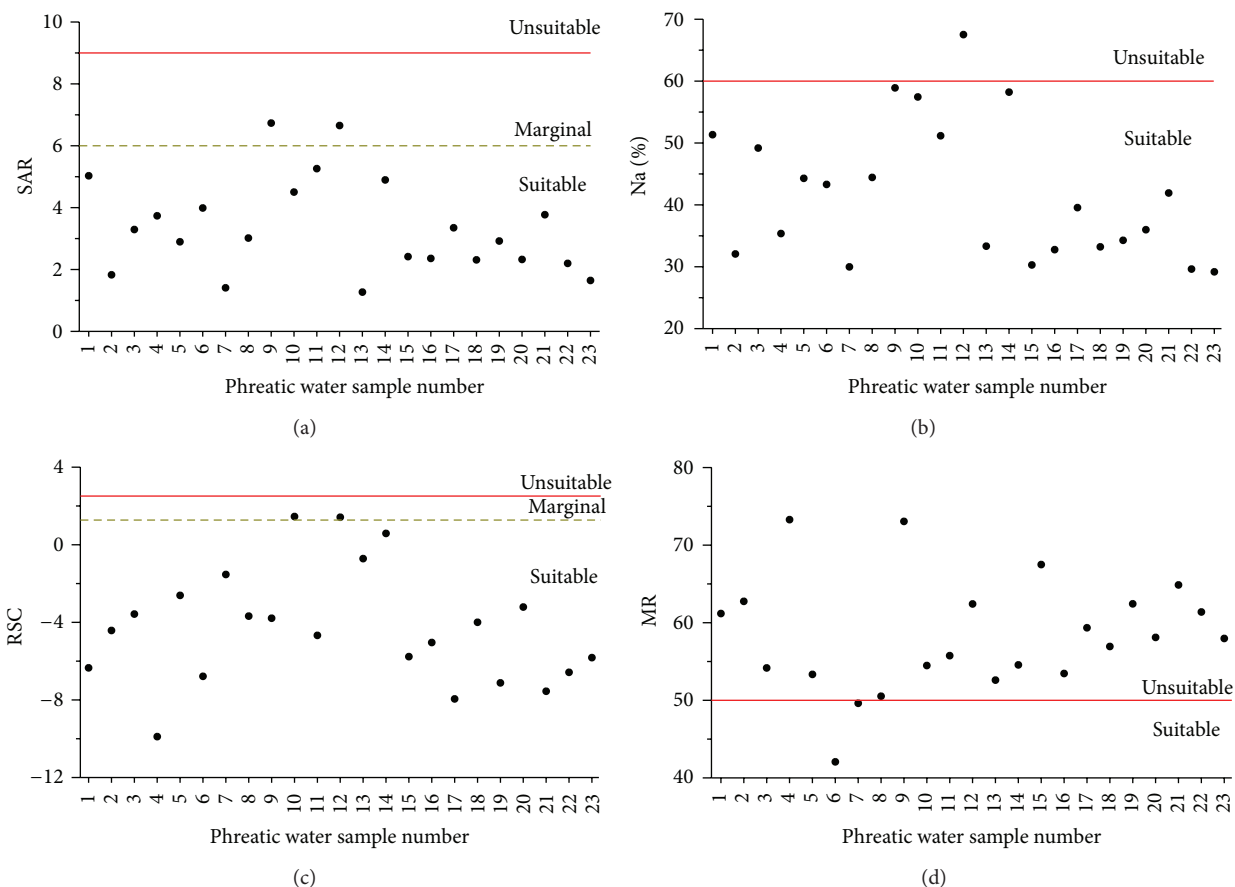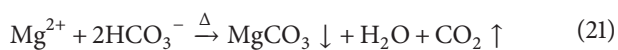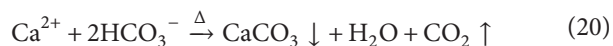
Figure 7: (a) SAR, (b) Na%, (c) RSC, and (d) MR for the phreatic water samples.

boiler or causes an explosion. It is formed by precipitation of calcium salt, magnesium salt, SiO_2, Al_2O_3, and suspended solids dissolved in water. When water boils, precipitation reactions take place and form $CaCO_3$, $Mg(OH)_2$, $CaSO_4$, $CaSiO_3$, $MgSiO_3$, CaO, and so forth which are insoluble compounds. Some common reactions can be expressed as follows [68]:

$$Ca^{2+} + 2HCO_3^- \xrightarrow{\Delta} CaCO_3 \downarrow + H_2O + CO_2 \uparrow \quad (20)$$

$$Mg^{2+} + 2HCO_3^- \xrightarrow{\Delta} MgCO_3 \downarrow + H_2O + CO_2 \uparrow \quad (21)$$

$$MgCO_3 + 2H_2O \longrightarrow Mg(OH)_2 \downarrow + H_2O + CO_2 \uparrow \quad (22)$$

Three parameters can be adopted to decide the properties of incrustation. The concentrations of TH, HCO_3^-, and SO_4^{2-} are greater than 300 mg/L, 400 mg/L and 100 mg/L, respectively, may cause incrustation [63]. As per the data of 14 confined groundwater samples, TH, HCO_3^-, and SO_4^{2-} are in the range of 179–222 mg/L, 167–365 mg/L, and 30.5–47.8 mg/L. All the parameters are within the limits, this showed that no worry about incrustation.

4.6.2. Foaming. Water bubbled up to the surface when boiled. While bubbles cannot break open in time, thick and unstable bubbles are formed. Too many bubbles elevate the water table resulting in boilers not working. This is a result of the saponification reaction related to sodium (Na), potassium (K), grease, and suspended solids [69]. The foaming coefficient is a measure of foaming action:

$$F = 62 \times Na^+ + 78 \times K^+, \quad (23)$$

where the concentrations of sodium and potassium are expressed in meq/L. The water of no foaming action is $F < 60$, and that of foaming action is $F > 200$. While F is in the range of 60–200, the water is marginal. As per the data of 14 samples, the values of F range from 78.88 to 182.01, which all belong to marginal range. It means that locomotive water boiler needs to be refreshed at least two or three days. As for no foaming action water, refreshing once a week is required.

4.6.3. Corrosion. Corrosive actions extremely damage the boiler, notably under high steam pressure. It eats metal through replacement reaction, even bring about explosion accidents. It was reported that 119 boilers exploded caused by corrosion at least once during 1956 and 1970 in 640 investigative boilers in the USA [68]. Corrosive actions are influenced by many factors, such as H^+, O_2, H_2S, CO_2, Fe_2S_3, organic matters. The corrosive coefficient is an indicator that reflects the intensity of corrosion.

For acidic water, the corrosive coefficient is expressed as

$$K = 1.008 \left(\text{H}^+ + \text{Al}^{3+} + \text{Fe}^{2+} + \text{Mg}^{2+} - \text{CO}_3{}^{2-} \right. \\ \left. - \text{HCO}_3{}^- \right). \tag{24}$$

For alkaline water, the corrosive coefficient is expressed as

$$K = 1.008 \left(\text{Mg}^{2+} - \text{HCO}_3{}^- \right), \tag{25}$$

where all ionic concentrations are expressed in meq/L. When $K > 0$, the water is corrosive. For $K < 0$, if $K + 0.0503\text{Ca}^{2+} < 0$, the water is not corrosive; otherwise, the water is mildly corrosive, where Ca^{2+} is expressed in mg/L. As per the data, all the confined water samples are alkaline water ($7.89 < \text{pH} < 8.24$), and the values of K vary from -3.71 to -0.60 which are all negative. The values of $K + 0.0503\text{Ca}^{2+}$ range from -0.22 to 1.50. The results show that sample C1 is not corrosive, while others are mildly corrosive.

5. Conclusions

Three aquifers in Yinchuan northern suburb which are exploited and utilized by human were investigated to evaluate the groundwater quality for drinking, irrigation, and industrial purposes.

Statistical analysis showed the quality of the confined water samples is better than the phreatic water samples'. Nevertheless, the concentration of $\text{NH}_4{}^+$-N of the confined water exceeds drinkable limits generally, which is conspicuous and abnormal. This can attribute to multiple reasons, such as fertilizer leakage, flood irrigation, over exploitation, and redox reactions.

The Piper diagram revealed different chemical composition between the phreatic water and confined water, which implied different controlling factors. The phreatic water is mixed type, whereas the confined water has dominant anion of $\text{HCO}_3{}^-$ and no dominant cations. The triangular field in the diagram implied CaCO_3 precipitation caused by evaporation results in alkalization for the phreatic water. The phreatic water has negative values of CAI-I and CAI-II, which has positive values for most confined water. This indicated that Ca^{2+} or Mg^{2+} in the phreatic water is exchanged with Na^+ or K^+ in the host rocks, and a reverse ion exchange proceeds in the confined water. The relationship between $(\text{Ca}^{2+} + \text{Mg}^{2+})$ and $(\text{SO}_4{}^{2-} + \text{HCO}_3{}^-)$ verified the different ion exchanges. Gibbs diagrams showed different controlling mechanisms of chemical components apparently. The confined water is entirely rock dominance, including ion exchange and precipitation/dissolution. The phreatic water is controlled by water-rock interaction and evaporation. Due to long-term flood irrigation, the shallow buried depth of groundwater greatly enhanced the evaporation.

The osculating value method with entropy was used to assess groundwater quality for drinking purpose. About 17%, 4%, 74%, and 4% of the phreatic samples have excellent, good, medium, and poor quality, respectively, and about 86% and 14% of the confined samples belong to good and medium quality water, respectively. The results stated that all the water samples, except for one phreatic sample, are fit for human consumption, and the confined aquifers can provide quality drinking water. In spite of this, groundwater is polluted by human in terms of high nitrogen content, coliforms and bacterial contamination, and inconsistent osculating value contour. The comparison between OVM with and without entropy showed that OVM without entropy is also objective and valid. Hence, OVM is an excellent algorithm for groundwater quality assessment.

The calculation of SAR, Na%, RSC, and MR of the phreatic water indicated that most phreatic water has no sodium hazard but has magnesium hazard which can give rise to alkaline and damage soil structure. Thus, the phreatic water is not appropriate for irrigation.

Industrial suitability of the confined water was evaluated in terms of incrustation, foaming, and corrosion. The results showed that all the confined water samples have no incrustation harm to boilers, but they can generate mild foaming reaction, and most of them are mildly corrosive. For the sake of security, boiler water needs to be refreshed every couple of days.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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