Hydrochemical Characteristics and Water Quality Evaluation in Chaoyang District, Beijing

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Abstract. In this study, we used groundwater quality data from 17 sampling sites in Chaoyang District of Beijing, which was measured to analyze hydrochemical characteristics and water quality evaluation combined with Shukarev classification, single factor evaluation method, comprehensive evaluation method and fuzzy comprehensive evaluation method in different seasons in 2018. The results showed that there was little difference in chemical composition and groundwater quality in different seasons. The groundwater ions were mainly HCO3-, Ca2+, and Mg2+ in the western region, and the salinity of water was low. Na+ and Cl- appeared in the southwestern and eastern region, and the concentration of Na+ in May was lower than that in September. Although the single index evaluation method was one-sided, it could determine the main pollutants. Although the comprehensive evaluation method could reflect the water quality status, it greatly highlighted the pollution factors and overestimated the degree of water quality exceeding the standard to some extent. The fuzzy comprehensive evaluation method considered the weight of participating factors, which made the evaluation results more objective and reasonable. The four parameters of TH, Fe3+, NH4+-N and As3+ exceeded the standard, but they generally met the drinking water quality standard.

Keywords: Groundwater, Shukarev classification, Single index evaluation, Comprehensive evaluation, Fuzzy comprehensive evaluation

1. Introduction
Groundwater hydrochemistry and water quality evaluation are important research contents of hydrogeology [1]. Relevant research has great significance to reveal the hydrochemical characteristics of groundwater, and provides theoretical basis for the improvement, protection, sustainable and rational development utilization of groundwater environment [2]. In the past three decades, due to the rapid urbanization, the demand for various purposes water has increased rapidly in Beijing [3], which was accompanied by excessive exploitation of groundwater and water pollution caused by human factors [4, 5]. On the other hand, groundwater pollution is a very complex process, with the characteristics of long-term, lagging and concealment. If the groundwater is polluted and destroyed, it is very difficult to treat it and the cost of recovery is very high. Therefore, the basis of solving this problem is to adopt reasonable classification and evaluation methods [6, 7]. In this study, Shukarev classification method was used to analyze the chemical types of groundwater. At the same time, single
index evaluation method, comprehensive evaluation method and fuzzy comprehensive evaluation method \[8\] were used to analyze and compared groundwater quality in Chaoyang District of Beijing. The evaluation results of 17 monitoring sites showed that the overall water chemistry characteristics changed little in May and September. The area covered by Na\(^+\) concentration was reduced in southwest in September, and HCO\(_3\)-Ca-Mg type water also appeared in some eastern areas. The pollution degree of groundwater was relatively small in Chaoyang District, only the total hardness (TH) exceeded the standard during the dry and wet periods, and the overall water quality reached a good level.

2. Materials and Methods

2.1. Study Area

Chaoyang District is a transitional area from suburban suburbs to urban areas. It is located in the eastern part of Beijing with a length of about 30km and a width of about 18km. The specific geographic location is shown in figure 1(a). The whole area is low and flat, high in the northwest and low in the southeast. Chaoyang District is a resource-based water shortage area. The rivers are plain, with shallow riverbed and poor drainage. The most obvious feature is lack of stable water source, which is easy to form floods in rainy season. In non-rainy season, it undertakes the urban sewage discharge task. The river course has been polluted seriously \[9\], and the water body has poor self-purification capacity. The water quality is inferior to classification V for most rivers, and the water ecological environment is poor. The main lithology of the aeration zone is loess-valued clayey sand in this area \[10\], with relatively poor permeability coefficient. In the study area, the main lithology of vadose zone is clayey sandy soil with loess value, and the permeability coefficient is relatively poor. Therefore, it is difficult for surface pollutants to penetrate into the aquifer, and the ability to block, adsorb, and decompose pollutants entering the bottom layer is relatively strong, so groundwater protection conditions are better.

Groundwater is controlled by alluvial fans of various rivers and comes from underground Quaternary aquifer in Chaoyang District \[10\]. Most of them belong to calcium carbonate magnesium type water, which is suitable for agricultural and domestic water. Due to the excessive exploitation of groundwater in parts, there are three downward funnels in the groundwater level, which are Jiuxianqiao electronic industrial zone, Hongmiao textile industrial zone and Dajiaoting chemical industry zone. Atmospheric precipitation is the main recharge source of groundwater in the territory. The main replenishment methods are infiltration of natural precipitation, lateral recharge of groundwater in upstream area and leakage of agricultural irrigation.

Figure 1. (a) Schematic diagram of the location; (b) sampling point distribution of Chaoyang District.
2.2. Groundwater Sampling
In 2018, we have carried out groundwater quality evaluation and water quality influencing factors analysis in Chaoyang District during the high and low water periods [11], and determined the chemical composition of groundwater. During field sampling, due to closed or damaged monitoring wells, the scheduled monitoring wells were adjusted. 17 samples were collected for ion analysis in every season. As shown in figure 1(b), the sampling sites were evenly distributed on the spatial scale, which was conducive to spatial representation. A total of 39 routine parameters were tested for water samples. The parameters for water chemical analysis and water quality evaluation were COD, T-Hard, TDS, Cl, SO₄²⁻, Fe³⁺, Mn²⁺, Zn²⁺, Al³⁺, NH₃-N, NO₂⁻, NO₃⁻, As³⁺, Cr⁶⁺. The other 25 water quality parameters were not detected or lower than the minimum detection limit of water quality detection equipment.

2.3. Shukarev Classification
In this study, the groundwater chemical type classification method adopted Shukarev classification method [12], which was classified according to the six main ions Ca²⁺, Mg²⁺, Na⁺, HCO₃⁻, Cl⁻, SO₄²⁻ in groundwater. Anions and cations with a content greater than 25% milliequivalents were combined.

The implementation steps of Shukarev classification method are as follows: (1) In each well, the mass concentration of six ions is converted into equivalent concentration by using the formula. (2) Calculate the equivalent concentration percentage according to the equivalent concentration of each ion. (3) According to the equivalent concentration, draw the partition map of each ion and the partition map of each ion with 25% as the dividing line. In the partition map, take the sodium ion partition map as an example, the area larger than 25% is considered as Na⁺-type water, and other ions are similar. (4) The partition maps of the six ions are superimposed and calculated to obtain the partition map of the groundwater chemical composition in Chaoyang District. The rule of superposition calculation is: for example, if the ions with equivalent concentration exceeding 25% are Na⁺, Mg²⁺ and HCO₃⁻ in a certain area, then the chemical composition type of this area is HCO₃⁻-Na⁺-Mg type water.

2.4. Water Quality Evaluation Method
In order to ensure the safe use of water for residents and provide source water that meets the national water supply quality requirements. As a water supply source, groundwater must meet the relevant regulations of the national "Groundwater Quality Standard GB/T14848-2017" [13, 14]. At the same time, comprehensive evaluation method and fuzzy comprehensive evaluation method can reflect the actual situation of water quality more objectively.

2.4.1. Single Index Evaluation. Single index evaluation determines the groundwater quality category according to the limit range of the index value. When the index limit value is the same, the superior value is selected instead of the inferior value.

2.4.2. Comprehensive evaluation. Comprehensive evaluation uses actual measurement data and standard to compare and classify. The standard determines the comprehensive water quality category according to the worst category of single index evaluation results, and points out the parameter of the worst category.

2.4.3. Fuzzy Comprehensive Evaluation. Fuzzy comprehensive evaluation method is mainly based on the principle of fuzzy transformation, which describes the fuzzy limit of groundwater quality with membership degree [8]. It takes the construction of a reasonable membership function and weight matrix as the core to quantify some unclear boundaries factors in the groundwater quality evaluation. Compared with traditional evaluation methods, fuzzy comprehensive evaluation method is more suitable for the fuzziness of groundwater quality classification, and can reflect the actual situation of water quality more objectively. Therefore, for groundwater systems with complicated factors and uncertainty and randomness, the introduction of fuzzy mathematics concept meets the requirements of
groundwater quality evaluation. The overall evaluation process of fuzzy comprehensive evaluation method is shown in figure 2.

![Figure 2. Overall evaluation process of fuzzy comprehensive evaluation method.](image)

1. Establish factor set and evaluation set. Factor set is a set of factors that affect the evaluation level in the evaluated system. In the water quality evaluation, the selected water quality evaluation indexes form a factor set \( U = \{u_1, u_2, \ldots, u_n\} \), where \( u_i \) is the \( n \)-th type of evaluation index, and \( n \) is the number of evaluation indicators. Evaluation set refers to the set composed of all evaluation results. Generally, 5 quality evaluation levels are used in water quality evaluation, namely \( V = \{\text{I}, \text{II}, \text{III}, \text{IV}, \text{V}\} \).

2. Determination of weight factors. In the evaluation of groundwater quality, considering the difference of each single index, the effect on groundwater quality will be different, which is not only related to the measured data, but also related to the allowable concentration of each index in a certain application. When the measured data are the same, the allowable concentration content is high and the standard is low, which has little impact on groundwater quality. Therefore, weight calculation is required. Generally, the weighted method of detection index concentration exceeding the standard is adopted.

3. Calculate the membership matrix \( R \). In the current water quality standards, most of the index quality categories are based on the progress value of the index from small to large or from large to small, that is, unidirectional distribution. Therefore, the descending half trapezoidal distribution method is often used in groundwater quality evaluation, and the membership function \( Y_{ij} \) of the detection indicators to all levels of water is as follows.

The membership function of classification I water, namely \( j=1 \):

\[
Y_{ij} = \begin{cases} 
1 & X_{ki} < C_{i1} \\
\frac{C_{i2} - X_{ki}}{C_{i2} - C_{i1}} & C_{i1} \leq X_{ki} \leq C_{i2} \\
0 & X_{ki} > C_{i2}
\end{cases}
\]  

(1)
The membership function of water from level II to m-1, namely \( j=2, 3, \ldots, m-1 \):

\[
Y_{ij} = \begin{cases} 
1 - \frac{C_{ij} - X_{ki}}{C_{ij} - C_{ij-1}} & C_{ij-1} \leq X_{ki} \leq C_{ij} \\
0 & X_{ki} > C_{ij-1}, X_{ki} > C_{ij+1} \\
\frac{C_{ij+1} - X_{ki}}{C_{ij+1} - C_{ij}} & C_{ij} < X_{ki} \leq C_{ij+1} 
\end{cases}
\]

(2)

The membership function of m level water, namely \( j=m \):

\[
Y_{ij} = \begin{cases} 
0 & X_{ki} < C_{im-1} \\
1 - \frac{C_{im} - X_{ki}}{C_{im} - C_{im-1}} & C_{im-1} \leq X_{ki} \leq C_{im} \\
1 & X_{ki} > C_{im} 
\end{cases}
\]

(3)

Where: \( n \) is the number of participating indicators; The water quality evaluation standard is divided into five levels, \( X_{ki} \) is the measured value of a monitoring index \( i \) in the \( k \)-th monitoring site; \( C_{ij} \) is the \( j \)-level standard concentration of the \( i \)-th participating index.

(4) Determine the fuzzy evaluation matrix. After determining the weight matrix \( A \) and the membership matrix \( R \), the convolution method can be used for compound operation. Each monitoring point will get a \( 1 \times 5 \) order fuzzy evaluation matrix, and then normalize the results. According to the principle of maximum membership degree, we can determine the final water quality grade.

3. Results and Discussion

3.1. Hydrochemical Characteristics of Groundwater

The hydrochemical types of groundwater were varied in Chaoyang District. In May and September, the groundwater chemical composition distribution areas were mainly \( \text{HCO}_3^-\text{-Cl-\text{Ca-Mg}} \) type water, \( \text{HCO}_3^-\text{-Na-\text{Ca-Mg}} \) type water and \( \text{HCO}_3^-\text{-Na-\text{Ca}} \) type water in the whole region, which were located in the south, west, most of the middle east and east respectively. In addition, \( \text{HCO}_3^-\text{-Na} \) type water was mainly distributed in the northeast and east, and \( \text{HCO}_3^-\text{-Cl-\text{Na-\text{Ca-Mg}}} \) type water also occupied a small area correspondingly. The content of \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \) decreased from west to east gradually, while the content of \( \text{Na}^+ \) ion increased gradually. It showed that the salinity of water quality increased from west to east, but the overall groundwater quality was still well, and the groundwater quality in most areas met the requirements.

In May and September, there was little change in the overall hydrochemical characteristics, and the difference mainly occurred in the downstream area. Compared with May, the area covered by \( \text{Na}^+ \) concentration has decreased in parts of the southwestern in September, and \( \text{HCO}_3^-\text{-Ca-Mg} \) type water also appeared in some eastern areas, possibly due to the dilution effect of rainfall. The specific distribution is shown in figure 3.
The chemical composition of groundwater was mainly influenced by hydrogeochemistry and human activities in Chaoyang District. The terrain of Chaoyang District inclined slowly from northwest to southeast, and the aquifer developed from single phreatic aquifer to multi-layer phreatic-confined aquifer from northwest to southeast. From the perspective of zoning, it came from the underground runoff of granite area in the upstream area. The leaching effect was strong, and the water salinity was low. As the runoff reached the midstream and downstream area, the salinity increased, gypsum was dissolved in carbonate rocks at the same time. The less soluble salts saturated and precipitated gradually. The content of soluble salts such as NaCl increased in the groundwater, the concentration of Cl\(^{-}\) and Na\(^{+}\) increased in the water.

On the other hand, with the growth of social productivity and population, human activities have become the most important factor affecting the chemical composition of groundwater in this area. The eastern part of Chaoyang District is densely populated. The waste which produced by human production and life polluted the groundwater environment seriously, which changed the chemical composition of groundwater.

3.2. Single Index Evaluation and Comprehensive Evaluation Results
The single index evaluation results (figure 4) showed that: in the dry season, the over-standard rate of T-Hard reached 17.6%, and the over-standard rate of NH\(_3\)-N and As\(^{3+}\) were 5.9%. During the wet season, the T-Hard and Fe exceeded the standard rate were both 17.6%, and other parameters were not exceeding the standard. The comprehensive evaluation results showed that the water quality samples exceeded the standard rate of 23.5% during the dry season and 35.3% during the wet season. All the samples that exceeded the standard reached IV water standard. Although the contents of the groundwater main components changed to a certain extent in dry and wet seasons, the difference was small.
Based on the historical industrial layout and pollution source investigation, we analyzed the natural and human factors of groundwater pollution. (1) Due to the concentrated over-exploitation of groundwater in some areas, the groundwater level has a falling funnel, which resulted in the deterioration of groundwater quality. (2) Long term use of sewage to irrigate farmland polluted a large range of groundwater. (3) The main rivers flowing through Chaoyang District had insufficient stable water sources. Affected by atmospheric precipitation, there were many flood disasters during the rainy season. Also, urban sewage had been accepted, and the water quality was polluted seriously.

T-Hard was one of the most significant factors that exceed the standard of shallow groundwater quality in Chaoyang District, and it played an important role in groundwater quality evaluation. There were two main reasons for the high T-Hard concentration of groundwater. One was the pollution caused by urbanization and the unreasonable development and utilization of groundwater. On the other hand, a series of hydrogeochemical interactions between groundwater and vadose zone and its surrounding rock were caused by excessive exploitation of groundwater.

3.3. Fuzzy Comprehensive Evaluation Method Results

First, determine the factor set U= \{COD_{Mn}, \text{T-Hard}, \text{TDS}, \text{Cl}^-, \text{SO}_4^{2-}, \text{Fe}^{3+}, \text{Mn}^{2+}, \text{Zn}^{2+}, \text{Al}^{3+}, \text{NH}_3-N, \text{NO}_2-N, \text{NO}_3-N, \text{As}^{3+}\}; evaluation set S= \{\text{I, II, III, IV, V}\}. Taking the monitoring data (1 point) of Dongba Township in the dry season in 2018 as an example, we should calculate the weight of each participating index, and the resulting weight row vector was W= (1.061, 0.619, 0.535, 0.478, 0.054, 0.016, 0.091, 0.048, 0.090, 0.028, 0.000, 0.075, 0.045, 0.075). According to the weight value of each participating index, the membership matrix was calculated as follows.
Multiplied the weight vector $W$ and the membership matrix $R$, and obtained the comprehensive evaluation matrix $B_{1\times 6} = \{0.255, 0.306, 0.413, 0.026, 0\}$ through compound operation, that is, the probability of water quality classification I, II, III, IV and V was 0.255, 0.306, 0.413, 0.026 and 0, respectively. According to the principle of maximum membership degree, the groundwater quality was classified as classification III. In the same way, the membership degree and final water quality evaluation results of other monitoring wells could be obtained by the above method, and the evaluation results are shown in figure 5.

The results showed that all the water quality samples were evaluated as classification I ~ III water, and the overall performance was well. The main difference between fuzzy comprehensive evaluation and the above evaluation method was that fuzzy comprehensive evaluation not only gave proper attention to the excessive pollutants, but also reduced the influence of abnormal values on the evaluation results, so the results were more accurate. Although the single index evaluation is one-sided, it can determine the main pollutants and reflect the over standard situation and distribution range of single index directly. Although the comprehensive evaluation overestimates the degree of water pollution to a certain extent, it can directly reflect the indicators of serious pollution in water quality. Grasping the pollutants exceeding the standard in time can contribute to the prevention of groundwater quality. Therefore, the comparative analysis of the three methods can reflect the groundwater quality more objectively in Chaoyang District, and all of them have certain applicability.

4. Conclusions
We used Shukarev classification method to study the hydrochemical characteristics of groundwater in Chaoyang District. The groundwater dominated by low-salinity hydrochemical types. From the spatial
point of view, the Na⁺ content in the eastern region was higher than that in the western region. From the temporal point of view, the area covered by Na⁺ concentration in parts of the southwest and east in September decreased compared with that in May. In general, the water quality was well and needed to be paid more attention in the future.

By using single index evaluation, comprehensive evaluation and fuzzy comprehensive evaluation, the groundwater quality was compared and analyzed in Chaoyang District of Beijing. The results showed that the groundwater quality was mainly classification I ~ III water, and the overall condition was well. The main pollution indicators were T-Hard and Fe³⁺. Single index evaluation is simple and clear, which can directly judge the relationship between environmental quality and evaluation standards. Comprehensive evaluation was to determine the comprehensive water quality category according to the worst category of single index evaluation results, which might not reflect the water quality status objectively. Fuzzy comprehensive evaluation method adopted the weighting method of pollutant concentration exceeding the standard to determine the weight, and considered the excessive pollutants while reducing the influence of the maximum value on the evaluation result. Therefore, the evaluation results were more objective.

Acknowledgments
This work was supported by the National Key Research and Development Program of China (Grant No. 2016YFC0401401), the National Natural Science Foundation of China (Grant Nos. 51739011 & 51879274), and the Research Fund of the State Key Laboratory of Simulation and Regulation of Water Cycle in River Basin (Grant No. SKL2020ZY03).

References
[1] Wang X 2011 Fundamentals of Hydrogeology 6th Edition Beijing: Geological Publishing House. (In Chinese)
[2] Adams S, Titus R, Pietersen K, Tredoux G and Harris C 2001 Hydrochemical characteristics of aquifers near Sutherland in the Western Karoo, South Africa Journal of Hydrology 241(1).
[3] Zhai Y, Wang J, Teng Y and Zuo R 2013 Hydrogeochemical and isotopic evidence of groundwater evolution and recharge in aquifers in Beijing Plain, China Environmental Earth Sciences 69(7).
[4] Kazi T G, Arain M B, Jamali M K, Jalbani N, Afridi H I, Sarfraz R A, Baig J A, Shah A Q 2009 Assessment of water quality of polluted lake using multivariate statistical techniques: a case study Ecotoxicology and Environmental Safety 72(2).
[5] Pazand K, Hezarkhani A, Ghanbari Y and Aghavali N 2012 Groundwater geochemistry in the Meshkinshahr basin of Ardabil province in Iran Environmental Earth Sciences 65(3).
[6] Foster S D, Hirata R and Howard K W F 2011 Groundwater use in developing cities: policy issues arising from current trends Hydrogeology Journal 19(2).
[7] Wang S 2013 Groundwater quality and its suitability for drinking and agricultural use in the Yanqi Basin of Xinjiang Province Northwest China Environmental Monitoring and Assessment 185(9).
[8] Guo Y, Wei J, Gui H, Zhang Z and Hu M 2020 Evaluation of changes in groundwater quality caused by a water inrush event in Taoyuan coal mine, China Environmental Earth Sciences 79: 528.
[9] Yang Z S, Dou Y B and Wang Z Q 2010 Analysis on the reasons of the decline of ground water level in the primary water supply source area of Beijing and the countermeasures China Water Resources 19: 52–54. (In Chinese)
[10] Zhou Y, Dong D, Liu J and Li W 2013 Upgrading a regional groundwater level monitoring network for Beijing Plain, China Geoscience Frontiers 4(01): 127-138.
[11] Luo Z, Zhao S, Wu J, Zhang Y, Liu P and Jia R 2019 The influence of ecological restoration projects on groundwater in Yongding River Basin in Beijing, China Water Supply 19(8).
[12] Karmann I, Cruz F W, Viana O and Burns S J 2007 Climate influence on geochemistry parameters of waters from Santana–Pérolas cave system, Brazil Chemical Geology 244(1-2).

[13] Li Y F, Song G H, Wu Y G, Wan W F, Zhang M S, Xu Y, et al. 2009 Evaluation of water quality and protection strategies of water resources in arid–semiarid climates: a case study in the Yuxi River Valley of Northern Shanxi Province, China Environmental Geology 57(8).

[14] Li Q, Zhou J L, Zhou Y Z, Bai C Y, Tao H F, Jia R L, et al. 2014 Variation of groundwater hydrochemical characteristics in the plain area of the Tarim Basin, Xinjiang Region, China Environmental Earth Sciences 72(1).