



Article Chemical Characteristics and Controlling Factorsof Groundwater in Chahannur Basin

Zhiqiang Gong ¹, Xizhao Tian ¹, Lulu Fu ¹, Haobo Niu ², Zongze Xia ³, Zhiyuan Ma ¹, Jian Chen ^{2,*} and Yahong Zhou ³

- ¹ Hebei Key Laboratory of Geological Resources and Environment Monitoring and Protection, Hebei Geological Environment Monitoring Institute, Shijiazhuang 050021, China
- ² Center for Eco-Environment in Yangtze River Economic Belt, Chinese Academy of Environmental Planning, Beijing 100012, China
- ³ School of Water Resources and Environment, Hebei GEO University, Shijiazhuang 050031, China
- Correspondence: yeguiyun@163.com or xtsmog@163.com

Abstract: This paper studies the spatial distribution characteristics and controlling factors of groundwater chemistry in the Chahannur Basin. One hundred and seventy shallow groundwater samples (50 m shallow) are collected, and seven ions, pH, TDS, TH, iron, manganese, COD, barium and other indicators, are detected. Piper triplex graph, Gibbs model, ion ratio, analysis of variance and Kriging interpolation are used to carry out the research. The results show that bicarbonate water is the main water chemical type in the Chahannur Basin, in which bicarbonate water accounts for 65.23%, chloride water accounts for 15.15% and sulfate water accounts for 19.62%. Bicarbonate water is mainly distributed in the mountainous areas in the north and south of the basin, and the main controlling factor is rock weathering. Sulfate-type water is mainly distributed in the lower reaches of the northern mountains of the basin, and the main controlling factors are rock weathering and evaporation concentration. The chloride water is mainly distributed in the Chahannur Lake area and the shallow groundwater buried area in the central region of the basin. The main controlling factors are evaporation concentration and human influence. Na+ is mainly derived from atmospheric precipitation and rock salt leaching, Ca^{2+} and Mg^{2+} are mainly derived from carbonate minerals leaching, and silicate minerals leaching is less. The pH of groundwater in the basin ranges from 6.3 to 9.18, with an average value of 7.50. The TDS in the basin ranges from 227 to 22,700 mg/L, with an average of 1661 mg/L. Iron in the catchment ranges from 0.01 to 15.343 mg/L, with a mean of 0.837 mg/L. The manganese content in the basin ranges from 0.005 to 3.802 mg/L, with an average value of 0.254 mg/L. COD in the basin ranges from 0.71–32.72 mg/L, with an average value of 3.49 mg/L. Barium in the basin ranges from 0.005 to 0.312 mg/L, with an average of 0.075 mg/L. The research results provide basic scientific data support for groundwater hydrochemistry research in the Chahannur Basin and show that the types of water chemistry in the study area are complex and diverse, and although the distribution is still controlled by terrain and geological conditions, the area affected by human activities accounts for a high proportion, so attention should be paid to the impact of human activities on groundwater in this area.

Keywords: Chahannur Basin; chemical characteristics; controlling factors; groundwater

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The Chahannur Basin is located in Zhangjiakou City, covering an area of about 6757 km². The basin is home to a number of lakes, including the Chahannur Lake District. In recent years, due to the over-exploitation of groundwater, the water level has been dropping year by year, and then problems such as the gradual reduction in the area of Chahannur Lake and land desertification occur [1,2]. Therefore, it is extremely urgent to investigate the groundwater ecological environment geology in the Chahannur Basin [3,4].



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Eco-environmental geology is a discipline that studies and evaluates the impact and effect of geological environment changes on ecosystems and the correlation law between geological environment and ecological environment. It mainly investigates the upper lithosphere, and the research objects involve the lithosphere, soil sphere, hydrosphere, atmosphere and biosphere on the surface of the Earth [5]. Research directions include meteorological hydrology, dynamic change characteristics of groundwater level, dynamic change characteristics of groundwater hydrochemistry and water quality, recharge runoff and drainage conditions of groundwater, and soil salinization, desertification, ecological degradation and other disasters caused by groundwater environmental factors [6,7]. In recent years, more researchers have carried out some studies on groundwater level change, meteorological factors and ecological degradation risk in the Chahannur Basin. Wang Yixuan analyzed the changes of lake area in the Chahannur Basin and its response to climate. Summer precipitation and summer evaporation were the main factors affecting lake area in the wet season [8]. Chen Moyu studied the evolution characteristics of hydrological elements in the Chahannur Basin, and believed that the evaporation of groundwater showed an insignificant increase trend, while the runoff showed a significant decline trend throughout the year [9]. Li Yancang et al., made a quantitative assessment of the spatio-temporal evolution characteristics and driving factors of the groundwater level in the Chahannur Basin and concluded that the groundwater level in the study area was low in the middle and high in the periphery, and there was an obvious downward trend on the whole, especially in the recent 10 years. Groundwater extraction contributes the most to groundwater level, followed by precipitation and evaporation, and the least to runoff [10]. Chen Peng et al. carried out a study on the ecological degradation risk of the Chahannur Basin on the Bashang Plateau, and believed that the ecosystem of the Chahannur Basin was generally good, but due to poor resilience in local areas, the risk of ecological degradation was at a moderate level [11]. However, there is relatively little research on groundwater chemical characteristics in the Chahannur Basin. Therefore, the main purpose of this paper is to comprehensively study the groundwater chemical types and control factors in the inland of the Chahannur Basin, identify the dynamic evolution of groundwater chemical characteristics in the Chahannur Basin and provide basic data support for the ecological environment investigation in the Chahannur Basin.

2. Materials and Methods

2.1. Overview of the Study Area

The total area of the Chahannur Basin is about 6757 km². The elevation of the basin ranges from 1270 to 1561 m. The terrain is high around and low in the middle, and gullies are developed. The average annual rainfall is 364.1 mm, and the average annual temperature is 3.7 °C. The diving in the Chahannur Basin mainly consists of Quaternary loose rock pore diving and Neogene and Paleogene clastic rock fracture pore diving. The confined water mainly consists of pore-confined water of Quaternary loose rocks and fractured-pore-confined water of clastic rocks of Neogene, Paleogene and Cretaceous Lower series.

2.2. Sample Collection and Analysis

A total of 150 groups of groundwater hydrochemical samples are selected in this study, all of which are shallow groundwater (within 50 m). See Figure 1 for specific point locations.



Figure 1. Bitmap of hydrochemical sampling sites in the Chahannur Basin.

The sampling shall be conducted in strict accordance with the Technical Regulations for Groundwater Environmental Monitoring (HJ/T164-2020). Before sampling, water samples to be collected shall be moistened and washed in sampling bottles for three times. At the same time, the samples shall be filtered by 0.45 um microporous filter membrane, and then put into polyethylene bottles with a capacity of 1000 mL, sealed by sealing film and stored in cold storage at 4.0 °C. The scomponents of groundwater samples shall be tested by the Center for Groundwater, Mineral Water and Environment Monitoring, Ministry of Land and Resources (Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences) in accordance with the Standards for Groundwater Quality (GB/T 14848-2017). The main testing instruments include plasma emission spectrometer (iCAP6300,Thermo Fisher, Los Angeles, CA, USA), gas chromatography-mass spectrometry

(GC-MSQP2010plus, Yidian, Shanghai, China) and atomic absorption spectrophotometer (TAS-986, Yidian, Shanghai, China).

The detection limits of K⁺ and Na⁺ were 0.05 mg·L⁻¹ and 0.01 mg·L⁻¹, respectively, by flame atomic absorption spectrophotometry. Ca²⁺, Mg²⁺ and total hardness (CaCO₃) were determined by ethylenediamine tetraacetic acid disodium titration with a detection limit of 1.00 mg·L⁻¹. HCO₃⁻⁻ was determined by acid-base titration with a detection limit of 0.05 mg·L⁻¹. SO₄²⁻⁻ was determined by the barium sulfate turbidimetric method with a detection limit of 5.00 mg·L⁻¹. Cl⁻⁻ was determined by the silver nitrate volumetric method with a detection limit of 1.00 mg·L⁻¹. Cl⁻⁻ was determined by the silver nitrate volumetric method with a detection limit of 1.00 mg·L⁻¹. pH was determined by the glass electrode method; the detection limit was 0.01. The total dissolved solids (TDS) were measured gravimetrically using an electronic balance (MP8-1,Yidian, Shanghai, China). Iron was determined by spectrophotometry with the detection limit of 0.01 mg/L. The detection limit of barium was 0.005 mg/L by inductively coupled plasma mass spectrometry. COD was determined by the basic permanganate method, and the detection limit was 0.5 mg/L. The balance error of cion and cion of all tested samples was E < ±5% [12–15].

2.3. Analysis Method

The chemical composition of groundwater is controlled by many factors such as topography, landform, meteorological hydrology, geological structure, changes in hydrogeological conditions and human activities. A Piper three-line diagram was used to characterize the chemical types of groundwater. The Gibbs model and ion ratio method were used to discuss the main controlling factors of groundwater hydrochemistry.

The Kriging interpolation method was used to describe the spatial distribution and variation of pH, TDS, TH, Cl⁻, SO₄^{2–} Na⁺, K⁺, Fe, Mn, COD, barium and other indexes. In addition, statistical analysis of variance was used to analyze the possibility of ions being affected by human activities, so as to preliminarily judge the regions heavily affected by human activities based on the distribution of ions with high values. In statistics, variance is used to describe the degree to which a random variable is discrete from its mathematical expectation (mean). If the values of a groundwater chemical composition are concentrated, the variance is small, indicating that the groundwater chemical composition is mainly affected by natural processes. On the contrary, the value of the chemical composition of groundwater is relatively dispersed, so the variance is large, indicating that the chemical composition of groundwater is mainly affected by human activities [16–21].

The first consideration of a Kriging interpolation is the variation distribution of spatial attributes in spatial position. Determine the range of distances that affect the value of a point to be interpolated, and then use the sampling points within this range to estimate the attribute value of the point to be interpolated. According to the different spatial location of samples and the different degree of correlation between samples, different weights were assigned to each sample grade, and a sliding weighted average was carried out to estimate the average grade of the central block. The graph of ion concentration distribution in this paper uses a circular function embedded in ArcGIS software.

The variance of a discrete random variable is expressed as follows:

$$\sigma^2 = \frac{1}{n} \sum_{i=1}^n \left(X_i - \overline{X} \right)^2$$

where σ^2 is the sample variance, *n* is the number of samples, X_i is the value for each sample and \overline{X} is the average of the values of all samples.

Because the absolute range of the variable (the chemical composition of groundwater) may vary greatly, comparisons cannot be made with the difference alone. Therefore, it is first defined as the ratio of each variable of the sample to the mean value of that variable. That is, $V_i = \frac{X_i}{X}$. Since the mean value of the comparison coefficient is 1, each variable is converted to another variable with the same mean value (the comparison coefficient), and the variance of the comparison coefficient of each variable is calculated for comparison.

3. Results and Discussion

3.1. Chemical Types of Groundwater in the Watershed

The hydrochemical type of groundwater in the basin is mainly bicarbonate-type water, but there is less chloride-type water and sulfate-type water in the central and northeastern mountains of the basin. The main anions in groundwater are HCO_3^- , Cl^- and SO_4^{2-} , among which HCO_3 , Cl and SO_4 account for 60.4%, 21.8% and 17.8%, respectively. The cations are mainly Ca^{2+} and Na^+ . The bicarbonate water is mainly HCO_3 -Ca·Mg water. Chloride-type water is mainly Cl-Na·Mg-type water. SO_4 ·Cl-Ca·Mg water is the main type of sulfate water. Bicarbonate water is mainly distributed in the north and south of the basin and the groundwater recharge runoff area of the basin. Chloride-type and sulfate-type water are mainly distributed in the lake area and the northeastern part of the basin and the groundwater discharge area of the basin. See the Figures 2 and 3 below for details.

3.2. Cause Analysis of Hydrochemical Types

The formation mechanism of groundwater chemical components is mainly controlled by atmospheric rainfall, rock weathering, evaporation-concentration (concentration caused by evaporation) and mixing [22–26]. Figure 4a,b shows that most of the ion contents of groundwater sampling points fall in the middle of the Gibbs diagram, indicating that rock weathering is the main controlling factor of groundwater chemical components in the study area. However, some sampling points (about 40%) exhibited a tendency to shift to the upper right region, indicating that evaporation-concentration also has a certain impact on the chemical components of groundwater in the study area.



Figure 2. Piper trilinear diagram of the chemical types of groundwater in the Chahannur Basin.



Figure 3. Zoning map of the chemical types of shallow groundwater in the Chahannur Basin.

 Na^+ and K^+ in groundwater mainly come from atmospheric precipitation and rock salt dissolution. Without the influence of human activities, rock salt dissolution is the main source of Na^+ and Cl^- in groundwater, and the ratio of their concentrations (milliequivalents per liter, mEq/L) is generally around 1. As shown in Figure 5a, the ratio of the concentration of Na^+ to that of Cl^- in the groundwater of the Chahannur Basin is about 1, indicating that Na^+ in the groundwater of the Chahannur Basin mainly comes from atmospheric precipitation and rock salt dissolution.

The ratio of the concentration of Ca^{2+} to that of Mg^{2+} can reflect the dissolution of carbonate minerals such as calcite and dolomite. If the ratio is close to 1, it indicates that dolomite has dissolved to a large extent. If the ratio increases, it may be because of calcite dissolution. When the ratio is greater than 2, it indicates silicate mineral dissolution. The diagram of the relationship between Ca^{2+} and Mg^{2+} in groundwater samples (Figure 5b) shows that a small part of the groundwater samples is located above the 2:1 line, indicating that Ca^{2+} and Mg^{2+} in the groundwater partly originate from the dissolution of silicate minerals; furthermore, most of the samples are located above the 1:1 line, indicating that Ca^{2+} and Mg^{2+} in groundwater are mainly derived from the dissolution of carbonate minerals such as dolomite and calcite.



Figure 4. Analysis of chemical origin of groundwater. (a) Na/(Na+Ca), (b) Cl/(Cl+HCO₃).



Figure 5. Relationships between (a) Na⁺/Cl⁻, (b) Ca²⁺/Mg²⁺, (c) Ca²⁺/Mg²⁺ versus HCO₃⁻/SO₄²⁻, and (d) Ca²⁺/Mg²⁺—HCO₃⁻/SO₄²⁻ versus Na⁺/Cl⁻ in the groundwater of the Chahannur Basin.

The ratio of $c(Ca^{2+} + Mg^{2+})/c(HCO_3^- + SO_4^{2-})$ was used to characterize the dissolution of carbonate minerals and sulfate minerals in the groundwater system. As shown in Figure 5c, the sample points are mainly located near the 1:1 line, indicating both carbonate dissolution and silicate dissolution. At the same time, the ratio of the sample points is slightly offset on the 1:1 line, indicating that the SO_4^{2-} sources and the Ca^{2+} and Mg^{2+} sources are slightly different. Sulfate may originate from the participation of sulfuric acid in the dissolution of carbonate rocks and the dissolution of gypsum. Most of the sample points tend to be above the 1:1 line, indicating that the Ca^{2+} and Mg^{2+} ions in the groundwater in the study area are derived mainly from the dissolution of carbonate minerals and partly from the dissolution of silicate minerals.

To further understand the main sources of groundwater ions in the basin, the relationship between $c(Ca^{2+} + Mg^{2+} - HCO_3^- - SO_4^{2-})$ and $c(Na^+ - Cl^-)$ (meq/L) was used to characterize the degree of the effect of ion exchange on the samples. The groundwater sample points in the Chahannur Basin (Figure 5d) showed a positive correlation between the two, indicating that there was ion exchange in the region. The Na⁺ ions in the groundwater replaced the Ca²⁺ and Mg²⁺ ions in the aeration zone and the aquifer medium; this increased the concentrations of Ca²⁺ and Mg²⁺ in the groundwater, thereby increasing the hardness of the groundwater.

In conclusion, Na⁺ in groundwater of the Chahannur Basin mainly comes from atmospheric precipitation and halite dissolution. Ca²⁺ and Mg²⁺ are mainly derived from the dissolution of carbonate minerals such as dolomite and calcite, while silicate minerals are less dissolved. There is ion exchange in the region. Na+ in the groundwater replaces Ca²⁺ and Mg²⁺ in the vadic zone and water-bearing medium, which increases the concentration of Ca²⁺ and Mg²⁺ in the groundwater, thus increasing the groundwater hardness.

3.3. Spatial Distribution Characteristics of Groundwater Indexes in Watershed

This section characterized the spatial distribution of pH, TDS, COD, Na, SO_4^{2-} , Fe, Mn and Ba plasma, preliminarily analyzed the variation rule of ion concentration in groundwater and the influencing reasons and evaluated each ion according to the standard of "Groundwater Quality" (GB/T 14848-2017). For details, see the following Table 1.

Index	Ι	II	III	IV	V
pH		6.5-8.5		5.5-6.5; 8.5-9.0	<5.5 or > 9.0
TH (mg/L)	≤ 150	\leq 300	≤ 450	≤ 650	>650
TDS (mg/L)	\leq 300	\leq 500	≤ 1000	≤ 2000	>2000
COD (mg/L)	≤ 1.0	≤ 2.0	≤3.0	≤10.0	>10.0
Na (mg/L)	≤ 100	≤ 150	≤ 200	≤ 400	>400
CI^{-} (mg/L)	≤ 50	≤ 150	≤ 250	\leq 350	>350
SO ₄ ²⁻ (mg/L)	≤ 50	≤ 150	≤ 250	\leq 350	>350
Fe (mg/L)	≤ 0.1	≤ 0.2	≤0.3	≤ 2.0	>2.0
Mn (mg/L)	≤ 0.05	≤ 0.05	≤ 0.1	≤1.5	>1.5
Ba (mg/L)	≤ 0.01	≤ 0.10	≤ 0.7	≤ 4.00	>4.00

Table 1. Groundwater quality evaluation criteria.

Spatial distribution characteristics of pH

pH value is an important index of groundwater environmental characteristics and is closely related to the chemical composition of groundwater. The groundwater pH in the basin ranges from 6.3 to 9.18, with an average of 7.50. On the whole, the neutral and weakly acidic groundwater accounts for a large proportion within the basin, and only a few points have a high pH, which is located near Daqinggou. Generally speaking, the groundwater is weakly alkaline, and the drainage area in the inland basin is relatively weak acidic, indicating that the drainage area in the inland basin is affected by human activities. According to the standard of "Groundwater Quality" (GB/T 14848-2017), the pH of groundwater in the whole area meets the Class III water standard. See the table below for the pH evaluation criteria.as shown in Figure 6a.



(c)

Figure 6. Spatial distributions of (a) pH, (b) TDS, (c) TH and (d) COD in the Chahannur Basin.

Spatial distribution characteristics of TDS

Total dissolved solids (TDS) reflect the comprehensive effects of hydrogeochemistry and human activities on groundwater chemistry. The highest TDS value was 22,700 mg/L in the Chahannur Lake area. The TDS value in groundwater showed a decreasing trend from the lake area to the south, north and east. The TDS in the basin ranged from 227 to

22,700 mg/L, with an average of 1661 mg/L. Due to the drought in the Chahannur Basin, the Chahannur Lake area is located in the drainage area of the whole basin [1]. Therefore, evaporation and concentration and man-made action lead to the increase in TDS in the lake area and its surrounding areas. According to the standard of Groundwater Quality (GB/T 14848-2017), the proportion of the area with groundwater TDS meeting the standard of Class III and Class IV water is large, and the whole area is in a high TDS environment, as shown in Figure 6b.

Spatial distribution characteristics of total hardness (TH)

As shown in Figure 6c, the total hardness of groundwater in the study area is relatively high on the whole, with TH value ranging from 85.58 to 3390 mg/L, with an average value of 723.56 mg/L, and it gradually increases from the edge of the basin to the center of the lake area. The groundwater with low hardness is mainly distributed in a small range of hills and mountains at the edge of the basin. The lake district in the middle of the basin and its surrounding areas are used as groundwater runoff and excreta discharge areas. The total hardness of groundwater is extremely high, up to about 1400 mg/L, far exceeding the standard of Class V water, and the area of this area accounts for a large proportion.

Spatial distribution characteristics of chemical oxygen demand (COD)

According to Figure 6d, there are differences in the oxygen consumption concentration of the water in different regions of the study area. The overall oxygen consumption concentration is general, showing a banded pattern of decreasing gradually from the middle to the south to the north. COD in the basin ranges from 0.71–32.72 mg/L, with an average value of 3.49 mg/L. Based on the analysis of oxygen consumption concentration, it can be seen that the proportion of Class II and Class III water is the largest in the study area. Only in the lake area in the middle of the basin did Class V water with high oxygen-consumption concentration appear, and the highest oxygen consumption concentration was about 32.72 mg/L.

• Spatial distribution characteristics of chloride (Cl⁻)

Cl⁻ is easily dissolved, is not ingested by plants and bacteria, is not adsorbed on the surface of soil particles and is the most stable ion in groundwater. Therefore, Cl⁻ is the main anion in high-TDS water, so Cl⁻ will increase with the increase in TDS, and the distribution law of Cl⁻ is consistent with the distribution law of TDS. The concentration of chloride in groundwater in the study area is relatively high on the whole, and it gradually increases from the edge of the basin to the center of the basin. Groundwater with low chloride concentration is mainly distributed in hills and mountains on the edge of the basin. The lake area in the middle of the basin, as the groundwater discharge area of the study area, has a very high chloride concentration, up to about 7000 mg/L, far exceeding the chloride standard of Class V water. The groundwater in other areas outside the lake area mostly meets the chloride standard of Class II water, as shown in Figure 7a.

• Spatial distribution characteristics of sulfate (SO₄²⁻)

The concentration of sulfate in the lower water of the basin increased gradually from the edge to the center of the basin. The sulfate concentration is not high on the whole, except in the lakes in the middle of the basin. The lake district in the middle of the basin, as the groundwater discharge area of the study area, has a maximum concentration of about 2000 mg/L, far exceeding the standard of Class V water. However, in other areas outside the lake area, the sulfate content in groundwater mostly meets the Class II water standard (50–150 mg/L), and the sulfate concentration is mostly 50–150 mg/L, as shown in Figure 7b.



(a)

Figure 7. Spatial distributions of (a) Cl- and (b) SO_4^{2-} in the Chahannur Basin.

Spatial distribution characteristics of sodium (Na⁺)

As can be seen from Figure 8a, the concentration of Na⁺ in groundwater in the study area is relatively high on the whole and gradually increases from the edge of the basin to the center of the basin, which is similar to the distribution characteristics of chloride. Groundwater with low Na⁺ concentration is mainly distributed in hills and mountains on the edge of the basin. As the groundwater discharge area of the study area, the lake area in the middle of the basin has a very high concentration of Na⁺, up to about 7000 mg/L, far exceeding the standard of Class V water. In other areas outside the lake area, Na⁺ concentration in groundwater is mostly in Class I and Class II water standards.

Spatial distribution characteristics of iron (Fe)

As shown in Figure 8b, The concentration of iron ions in the water in different areas of the study area was significantly different, showing a trend of decreasing from the high concentration in the Chahannur Lake area to the surrounding area. Iron in the catchment ranges from 0.01 to 15.343 mg/L, with a mean of 0.837 mg/L. The groundwater with high concentration of iron ions is mainly distributed in the lake district in the middle of the basin, with the highest concentration of 15.343 mg/L, which exceeds the standard of Class V water. The groundwater with low concentration of iron ions is mainly distributed in hills, mountains and plateaus at the edge of the river basin, and the concentration of iron ions in the groundwater is mostly 0–0.1 mg/L, belonging to the Class I water standard.

Spatial distribution characteristics of manganese (Mn)

As shown in Figure 8c, there are obvious differences in the concentration of manganese ions in groundwater in the study area, and the overall concentration is not high, showing a ribbon-like pattern gradually decreasing from the middle to the south to the north. Manganese in the catchment ranges from 0.005 to 3.802 mg/L, with a mean of 0.254 mg/L. That is, the groundwater with high concentration of manganese ions is located in and around the Chahanzhur Lake area, where the concentration of manganese ions is 0.11-3.802 mg/L, which is the standard of Class IV water, while the concentration of manganese ions in other areas is mostly the standard of Class I water.



Figure 8. Spatial distributions of (a) Na⁺, (b) Fe, (c) Mn²⁺ and (d) Ba²⁺ in Chahannur Basin.

• Spatial distribution characteristics of barium (Ba²⁺)

As can be seen from Figure 8d, the content of barium ions in groundwater in the whole study area is not high. Barium ions in the basin range from 0.005-0.312 mg/L, with an average value of 0.075 mg/L. On the whole, Class I and Class II water are dominant, and Ba2+ concentration is relatively high only in Daheisha Town and Caosiyao Town.

The mean, median and outlier values of pH, TDS, TH, COD, Cl^- , SO_4^{2-} , Na^+ , Fe, Mn^{2+} , Ba^{2+} are shown in Figure 9.



Figure 9. Box diagram of chemical composition of groundwater.

3.4. Source Determination of Groundwater Chemical Components

The factors controlling the formation of the chemical composition of groundwater include two aspects, one is the influence of natural conditions (such as water-rock interaction), and the other is the influence of human activities. Under natural conditions, in a complete regional groundwater flow system, the TDS value of the recharge area is small. With the increase in runoff channels, the water-rock interaction time also increases, and the groundwater TDS value increases. Therefore, the TDS value of the runoff area is larger than that of the recharge area, and the TDS value of the discharge area is the largest.

The influence of human activities on the chemical composition of groundwater is different from that of natural conditions. Because the way and intensity of human activities cannot have uniform influence on groundwater, the influence of human activities on the chemical composition of groundwater is more random than that of natural conditions. Therefore, the content of groundwater components mainly affected by human activities tends to vary in a wide range; that is, it shows great volatility [27,28].

Based on the different characteristics of the influence of natural conditions and human activities on the chemical composition of groundwater, the method of variance contrast analysis was used to distinguish the formation of the chemical components of groundwater that were mainly influenced by the evolution of natural conditions or human activities and to compare the degree of each component affected by human activities. According to the data obtained in this study, variance σ i2 was calculated for the contrast coefficient of groundwater chemical components, and the results are shown in Table 2 [29–37].

As can be seen from Table 2, σ^2 of manganese and iron has exceeded 10 in the variance of the contrast coefficients of each component in all sample points, indicating that these ions are most strongly influenced by human activities. σ^2 values of TDS, potassium, sodium, chloride, sulfate, oxygen consumption and boron are higher (>1), indicating that these ions are also affected by human activities. Low σ^2 values for pH, calcium, magnesium, bicarbonate and total hardness indicate that these indicators are mainly controlled by natural water chemical evolution and are less influenced by human activities [38–44].

Component	TDS	pН	Potassium	Sodium	Boron
Lining coefficient	1.74	0.02	6.39	4.69	2.32
Component	bicarbonate	chloride	Magnesium	manganese	Oxygen consumption
Lining coefficient	0.59	4.79	1.03	15.13	1.17
Component	Total hardness	iron	Calcium		
Lining coefficient	0.60	12.37	0.54		

Table 2. Variance table of groundwater chemical composition contrast coefficient.

Based on the spatial distribution characteristics of groundwater chemical indexes in the basin, it can be concluded that the concentration of TDS ions in the Chahannur Lake area and its surrounding areas is higher than that in other areas, showing a trend of gradual increase from the edge of the Basin to the center of the lake area. Based on the analysis of groundwater chemical components, it can be seen that TDS ions are also affected by human activities. Theoretically, in the same hydrogeological unit, the variation of TDS value from recharge area to discharge area is small, and the variation of TDS concentration in the Chahannur Lake area and its surrounding areas are greatly influenced by human activities [45–49].

4. Conclusions

- (1) The spatial distribution law of pH, TDS, TH, Cl⁻, SO₄²⁻, Na⁺, iron, manganese, COD, barium and other indicators is described, which provides basic data support for the groundwater ecological environment research in the Chahannur Basin.
- (2) The plasma concentrations of TDS, TH, Cl, Na and COD are high in the Chahannur Lake area and its surrounding areas, which are strongly influenced by human activities.
- (3) The hydrochemical type of groundwater in the basin is mainly bicarbonate-type water, but there is less chloride-type water and sulfate-type water in the central and northeastern mountains of the basin. The bicarbonate-type water is mainly affected by the natural conditions of rock weathering, while the chloride-type water and sulfate-type water in the central and northeast are mainly affected by human influence and evaporation and concentration.
- (4) Na⁺ in the basin groundwater is mainly derived from the dissolution of atmospheric precipitation and rock salt, Ca²⁺ and Mg²⁺ ions are mainly derived from the dissolution of carbonate minerals, and silicate minerals are less dissolved. The concentrations of Ca²⁺ and Mg²⁺ in groundwater in and around the lake area were increased because of anthropogenic influences and high ion exchange intensity in the basin.

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Data Availability Statement: All the data in this paper are from the monitoring data of Hebei Geological Environment Monitoring Institute, and the data are reliable.

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