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Research on Chemical Types and Genetic Mechanism of Groundwater in Yiluo Basin

Xiaohui LU[1], Yushu HU and Mingxuan CUI
College of Earth Science and Engineer, Hohai University, Nanjing, Jiangsu, China

Abstract. Groundwater and its geological functions are closely related to human life and economic construction. The quality of groundwater is of great significance for maintaining the development of the national economy and the daily life of residents in the region. Understanding the chemical characteristics and genesis mechanism of groundwater in a certain area is helpful to provide important basis for the sustainable development of groundwater resources in this area. This study is mainly aimed at the Yiluo Basin, a piedmont basin in the western part of Henan Province. According to the chemical composition of shallow groundwater, the study area was systematically analyzed by using ionic scale coefficient, Piper three-line diagram, Kriging interpolation method and Shukarev classification. Finally, the hydrogeochemical simulation software PHREEQC was used to study the reverse hydrogeochemical simulation of fluoride ions in groundwater, and the simulation results were analyzed and discussed, revealing the existence state of ions in shallow groundwater.

Keywords. Groundwater chemistry, Yiluo Basin, Shukarev classification, Piper's three-line diagram, PHREEQC

1. Introduction

The total amount of groundwater resources in my country is about $8.7\times10^{11}m^3$, however, China's urban shallow groundwater is polluted as high as 70%, leading to serious water stress and water safety problems in many places. Most areas of the Yiluo Basin use groundwater as the main water supply source.

There are relatively many domestic and foreign studies on the chemical characteristics of groundwater. For example, in 2014, Sun [1] systematically studied the formation and evolution mechanism of shallow groundwater in Guanzhong Basin by using graphical method, mathematical statistics method and PHREEQC simulation on the basis of analyzing the hydrochemical data. In 2018, Ali [2] and others conducted a hydrochemical study on parts of the Benderhan Mountains, and used methods such as Piper three-line diagram and Durov diagram to determine the main hydrochemical phases. In 2019, Ren [3] used Shukarev classification, Gibbs diagram method and ion proportional coefficient method to systematically study groundwater samples in Jiuquan East Basin.

[1] Corresponding Author, Xiaohui LU, College of Earth Science and Engineering, Hohai University, Nanjing, Jiangsu, China; Email: luxiaohui945@hhu.edu.cn.

2. Overview of the Study Area

The study area is located in the transition zone between the top of the Yellow River alluvial fan in western Henan and the Loess Plateau. The valley-level area of the Yiluo River has a flat terrain, a gentle ground slope, and the buried depth of the groundwater level is less than 5 m, in the alluvial fan area at the trailing edge of the valley terrace, the ground slope is slightly larger, the burial depth of the phreatic level is greater than 10 m [4].

3. Groundwater Chemical Types

3.1. Distribution of Groundwater Sampling Points and Content of Main Components

According to the groundwater quality data in the study area, the milliequivalent percentage map of each component in the Yiluo Basin (Figure 1). From the water quality data and Figure 2, it can be seen that the milliequivalent percentages of cations Mg^{2+}, Ca^{2+}, and K^{+}+Na^{+} in the shallow groundwater aquifer in the study area are 23.02%, 57.81%, and 19.17%, respectively. The milliequivalent percentages of SO_4^{2-}, HCO_3^-, Cl^-, NO_3^- in the anions are 24.85%, 51.63%, 15.99%, 7.39%, and the content of Mg^{2+}, Na^{+}, NO_3^-, Cl^-, SO_4^{2-} varies widely [5].

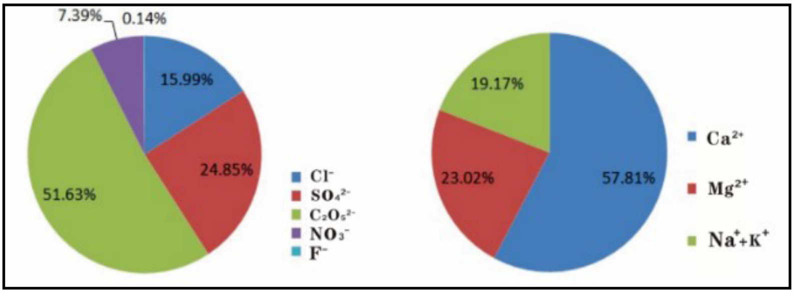

Figure 1. Anion and cation milliequivalent percentages in shallow water aquifers in Yiluo Basin.

Table 1. Shukarev classification table.

More than 25% milligram equivalent of ions	**HCO_3**	**HCO_3+ SO_4**	**HCO_3+ SO_4+ Cl**	**HCO_3+ Cl**	**SO_4**	**SO_4+ Cl**	**Cl**
Ca	1	8	15	22	29	36	43
Ca+Mg	2	9	16	23	30	37	44
Mg	3	10	17	24	31	38	45
Na+Ca	4	11	18	25	32	39	46
Na+Ca+Mg	5	12	19	26	33	40	47
Na+Mg	6	13	20	27	34	41	48
Na	7	14	21	28	35	42	49

- Shukarev classification

According to the combination of Table 1 and water quality data, the Shukarev classification table of Yiluo Basin is obtained, and the classification results are projected to the topographic map of Yiluo Basin through Kriging interpolation, and Figure 2 is obtained [6]. According to the analysis of the map, the types of groundwater in the basin north of Luo River and south of Cijian Town and Xin'an County, south of the Yellow River and west of Mengjin County, and south of Yihe River are HCO_3-Ca and HCO_3^- Ca·Mg; Luoyang The middle area between the two rivers to the south, the area to the north of Yima City and Xin'an County, the area to the west of Gongyi City, and the types of groundwater in the urban area of Yanshi City are HCO_3·SO_4-Ca and HCO_3·SO_4·-Ca·Mg; groundwater in other areas The types are HCO_3-Ca·Na and HCO_3-Ca·Na·Mg.

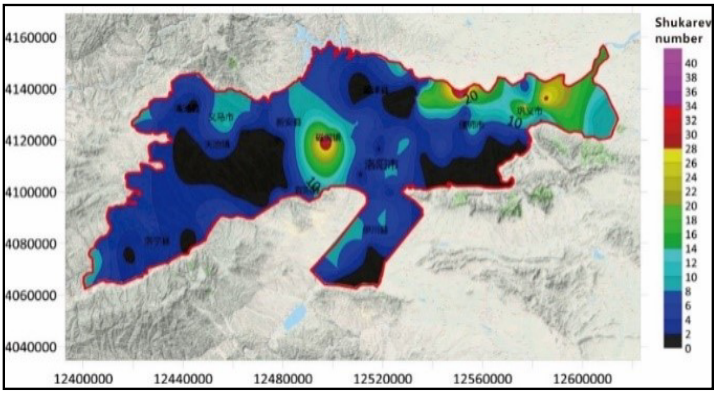

Figure 2. Shukarev classification map of groundwater.

- Piper's three-line diagram of groundwater chemistry

Project the data of the water quality data into the Piper three-line diagram, as shown in Figure 3. The cations in the whole area are mainly alkaline earth metal ions, the anions are mainly weak acids and ions in most areas, and strong acid radicals are mainly in a small part, mainly including Gongyi, Huimeng Town, Cijian Town, Xin'an County, Yinghao Town, Zhuge Town. Carbonatite hardness is greater than 50% in most areas [7].

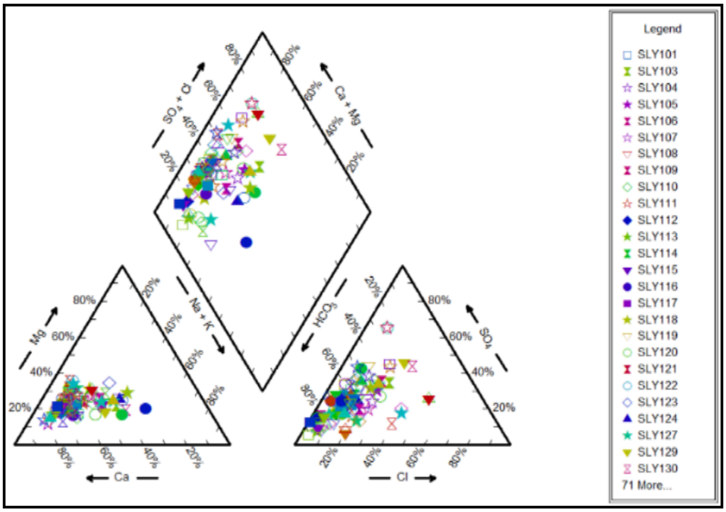

Figure 3. Piper three-line diagram of Yiluo Basin.

4. Formation Mechanism of the Main Components of Water Chemistry—Taking Fluoride Ion as an Example

4.1. Distribution Characteristics of Fluoride Ions

Fluorine in groundwater has a great impact on human production and life activities [8]. Second, the study area is large, the groundwater environment and the formation mechanism of each component are very complex, so it is difficult to study all components of groundwater. The source of Fluorine in groundwater is more concentrated than other ions, and fluorite (CaF_2) is the main source of fluorine in groundwater, and its dissolution and precipitation characteristics have a greater impact on the concentration of fluoride ions in groundwater [9]. Therefore, this paper takes fluoride ion as an example, and uses PHREEQC software to simulate the hydrogeochemical behavior of fluorine dissolution and precipitation in groundwater in the study area [10].

4.2. Fluoride Ion Migration Evolution Model

Simulation principle: Simulation calculation of aqueous solution balance and simulation calculation of water-lithofacies interaction are realized through PHREEQC.

- Existence form of fluorine in groundwater

Fluorine exists in complex and diverse forms in groundwater under natural conditions, and fluorine also exists in water in various derivative forms such as F^-, HF, CaF^+, MgF^+, etc. According to the law of conservation of mass, the derivation of available fluorine in natural groundwater is:

$$m(F) = m_{F^-} + m_{HF} + m_{NaF} + \cdots + m_{CaF} + m_{MgF^+} \tag{1}$$

where *m*=molarity; *m(F)*=The total concentration of fluorine in the solution, i.e., the analytical concentration.

The analytical concentration of fluorine was calculated as

$$m(F) = m(F^-) + \sum_{i=1}^{n} P_i \cdot C_i \tag{2}$$

where P_i=The stoichiometric number of fluorine in solution relative to the *i*th derivative component; C_i=Molar concentration of the *i*-th derivative component with fluorine in solution.

When the reaction reaches equilibrium, its equilibrium constant *K* be expressed as:

$$K = \frac{C_i}{\prod_{k=1}^{n} m(F^-)^{P_i}} \tag{3}$$

Substituting equation (3) into equation (2), we have:

$$m(F) = m(F^-) + \sum_{i=1}^{n} P_i \cdot K \cdot \prod_{k=1}^{n} m(F^-)^{P_i} \tag{4}$$

The solution is to assume a specific component concentration value that can satisfy all stoichiometric equations of chemical equilibrium in the system, and approach the target successively through an iterative method to obtain the quantitative relationship between all morphological components conforming to the corresponding equilibrium constant value [11].

- Fluorite saturation index

The saturation index SI reflects the state between the solution and the solid phase, whether it is an equilibrium state, or an unsaturated or supersaturated state. It is the base ten logarithm of the ratio of the ionic activity product (IAP) to its solubility product constant (K_{sp}) [12]. The expression is:

$$SI = \log \frac{IAP}{LP} \tag{5}$$

For the dissolution-precipitation equilibrium of fluorite:

$$CaF_2 \rightleftharpoons Ca^{2+} + 2F^- \qquad K_{CaF_2} = 10^{-9.8} \tag{6}$$

Its saturation index calculation formula is:

$$SI = \log \frac{\left[Ca^{2+}\right]\left[F^-\right]^2}{K_{CaF_2}} \tag{7}$$

In the formula, $[Ca^{2+}]$ and $[F^-]$ represent the activities of Ca^{2+} and F^-, respectively.

- Analysis of results

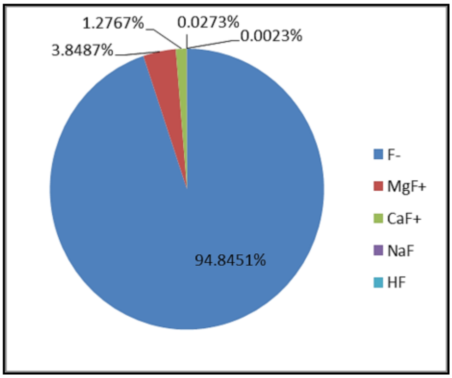

Figure 4. Existing form and distribution of negative ions in water samples.

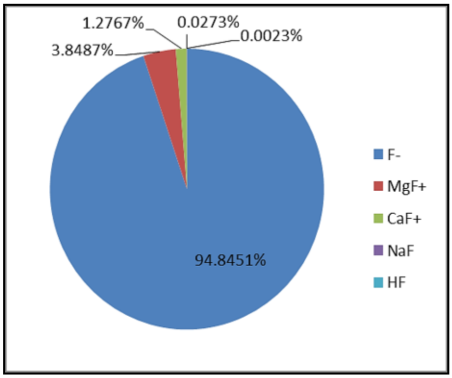

Figure 5. Comparison chart.

It can be seen from Figures 4 and 5 that fluorine mainly exists in the form of F- in groundwater, and its content accounts for 97.61%-89.24% of the total fluorine, with an average of 94.85%. The content of MgF^+ accounts for 1.48%-8.86% of the total fluorine, with an average of 3.85%. It exists less in the form of CaF^+, accounting for 0.64%-2.22% of the total fluorine, with an average content of 1.28%. A very small part exists in the form of NaF and HF, and the content is less than 0.1%. It shows that F^- is the main form of fluorine in groundwater. The fluorite saturation index in the sampled groundwater in the Yiluo Basin is all less than 0, reflecting that the dissolution of fluorine-containing minerals in the groundwater in the study area has not reached saturation [13, 14].

5. Conclusion

The shallow groundwater in the Yiluo Basin is dominated by HCO_3-Ca, HCO_3-Ca·Mg and HCO_3·SO_4-Ca, and other groundwater types are distributed in densely populated urban areas in the basin, while in Gongyi City, Yanshi City, relatively concentrated contiguous distribution, contiguous groundwater types of HCO_3·SO_4-Ca·Na, HCO_3·SO_4-Ca·Mg and SO_4-Ca·Mg appear in some areas of Gongyi City, and the shallow groundwater types in Yanshi City are more Cl·SO_4-Ca·Mg and HCO_3-Ca·Na dominated. The NO_3-content in many areas of the Yiluo exceeds 50.00%, and is concentrated in the Mianchi Yima-Cijian Town area, Luoyang North-Yanshi City area, and Gongyi area. Yiluo Basin have many places where the F- content exceeds 2.00%, which are distributed in densely populated urban areas, indicating that the distribution of F- is mainly affected by human activities.

Under the condition of groundwater balance, fluorine mainly exists in the form of F-, and its content accounts for 94.85% of the total fluorine. And MgF^+ is 3.85%. There is less in the form of CaF^+, which is 1.28%. The saturation index of fluorite in groundwater in each area of Yiluo Basin is less than 0, indicating that fluorite is in a dissolved state. When determining the boundary values of F- and Ca^{2+} concentration for CaF^2 dissolution and precipitation, it is considered that Ca^{2+} in water is not only produced by fluorite, and its destination is not only produced by fluorite precipitation, and the use of PHREEQC to solve the boundary concentration of Ca^{2+} found that it did not converge, so only fluorine is considered in the solution boundary value, and the actual F- concentration of groundwater is much smaller than its concentration boundary value. The fluorine-containing minerals in groundwater have a large space for dissolution.

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