

Research Article

Hydrochemical Characteristics and Genetic Analysis of Shallow High-Fluorine Groundwater in Fuyang River Basin

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In order to understand the sustainable and effective utilization of groundwater resources in Fuyang River Basin, the chemical characteristics and genetic evolution process of characteristic shallow fluoride groundwater in the region were carried out. The results show that the chemical characteristics of groundwater are zonal in horizontal direction. From the piedmont plain to the central plain, the hydrochemical types of the first and second aquifers are mainly HCO₃-Ca-Mg-type water, HCO₃-Cl-Ca-Mg-type water, Cl-SO₄-Na-Ca-type water, and Cl-SO₄-Na-Mg-type water. The main mineral sources of hydrochemical ions are salt rock, carbonate rock, sulfate rock, and silicate rock. F⁻ has a significant positive correlation with HCO₃⁻ while it is negatively correlated with K⁺. In the strong evaporation and alkaline environment created by climatic conditions in the study area, F⁻ mainly comes from the dissolution of minerals. Gypsum and fluorite are in a relatively stable dissolved state continuously providing F⁻ and Ca²⁺ for groundwater; the adsorption of cation was gradually strengthened from the piedmont plain to the central plain. The high HCO₃⁻ content is also conducive to F⁻ desorption in alkaline environments. The samples with F⁻ concentration greater than 1 mg·L⁻¹ accounted for 35.7% and mainly distributed in the south of the study area. In summary, the chemical characteristics of shallow groundwater in Fuyang River Basin are affected by the combined effects including leaching effect, evaporation concentration, ion exchange-desorption, and human factors.

1. Introduction

As one of the essential trace elements in human bodies, fluoride can affect bone metabolism. Fluorine exists mostly in mineral form in nature, such as fluorite (CaF₂), cryolite (Na₃[AlF₆]), and fluorapatite (Ca₁₀(PO₄)₆F₂). If excessive fluoride is ingested through the digestive tract or respiratory tract for an extended period, it will be toxic to human bodies and endanger bone health, which is reflected in dental fluorosis and skeletal fluorosis. Endemic fluorosis is widely distributed and harmful. It has been found in all parts of China, involving a population of 100 million, seriously endangering the life and safety of people [1]. Due to the complex and changeable natural environment, meteorological climate, and hydrogeological conditions in northern China, the diversity of fluorine ion enrichment in regional groundwater is

caused, and the coexistence of high-fluorine water of various causes is often formed in some areas. North China Plain is the lowest level of terrain ladder in China. It has experienced complex geological environment changes in its geological history, forming quite a complex stratigraphic structure and water flow field [2]. The main water resource problems in Fuyang River Basin include the increasingly serious water shortage and water pollution, the intensification of competition among water users, and the incompatibility of regional economic structure and water resource conditions. With the rapid decline of groundwater level and increasing of environmental problems, the basin has changed from open to closed [3, 4]. There are nearly 2,500,000 permanent residents in the study area, where endemic fluorosis has occurred [5]. However, the hydrogeological conditions in the study area are complex, the types and quantities of surface water

systems are various, and the corresponding chemical causes and influencing factors of groundwater are diverse, specific analysis of regional. In this study, the hydrochemical characteristics and genetic analysis of shallow high-fluorine risk groundwater in the study area are expounded through field geological survey and water sample analysis. The concentration of fluoride in groundwater is affected by many components like pH, precipitated ions and colloids, temperature, the anion exchange capacity of aquifer materials, solubility of fluorine-containing minerals, and the size besides sorts of the geological establishment that the water passes through, as well as the contact time for the water towards maintaining contact with the specific creation. Analyzing the characteristics of fluorine content in groundwater in this area, finding out the distribution regularity of high-fluorine groundwater, and revealing the hydrochemical factors affecting high-fluorine groundwater are helpful for controlling endemic diseases and understanding the hydrogeochemical origin and influencing factors of high-fluorine groundwater in the research area.

2. General Situation of Research Area

The Fuyang River is 413 km long and has a catchment area of 21737 km² (Figure 1). It originates in Hecun town and converges with the Hutuo River in Xian County. Fuyang River meanders with more than 20 tributaries joining on the left bank, which mostly are seasonal rivers. The Fuyang River Basin, located in dry subhumid areas, has a temperate monsoon climate [6].

On hydrogeological conditions, Fuyang River Basin belongs to the hydrogeological area of Hebei Plain, covering the Hutuo River alluvial-pluvial hydrogeological sub-area and Fuyang River alluvial-lake hydrogeological subarea [7]. According to the formation age of strata, the Quaternary sedimentary strata are vertically divided into four water-bearing groups. The first water-bearing group of Holocene strata formed by fluvial alluvial deposits and marsh depressions. The second water-bearing group of Upper Pleistocene strata was dominated by fluvial alluvial deposits. The third water-bearing group of Middle Pleistocene strata was dominated by coarse sand in fluvial alluvial deposits. The fourth water-bearing group of Lower Pleistocene strata was dominated by fine sand in fluvial-lake facies [8].

According to the evolution of regional hydrogeological conditions and the current situation of local mining, we take 110~140 m as the boundary. The Quaternary aquifer rock group is divided into shallow aquifer rock group and deep aquifer rock group. The samples of this study were taken from the shallow aquifer rock group, equivalent to the first aquifer group and upper half of the second aquifer group.

3. Materials and Methods

The samples collected in this study are shallow groundwater samples with a total of 31 groups, which are collected in September 2019 and December 2020. The source is national, local, and factory monitoring wells. The depth of the wells

ranges from 4.5 to 100 meters, and that of the filter pipe is from 1.85 to 90 meters. The samples were collected at a depth of 2.05-17.57 m. According to the requirements of the specification, the water sampling place of the centralized water supply source is selected for water sample collection, and then, the preservation agent is added and stored in cold storage at 4°C. Groundwater collection and preservation are carried out according to the requirements of "Standard Test Method for Drinking Water" (GB/T 5750-2006). Shallow geological profile of Fuyang River Basin is shown in Figure 2.

The pH value was measured according to the Hash water quality multiparameter tester HQ40, and the TDS was measured by dry weighing method. The most accurate way to estimate the mass of a solid sample quantitatively is done through weighing by difference. The specified technique entails weighing a weighing container holding an amount of solid reagent on a regular basis. The mass of the weighing bottle contents reduces as the solid is removed towards another vessel. Cl⁻, SO₄²⁻, NO₃⁻, and F⁻ were determined by ICS-600 ion chromatograph; K⁺, Na⁺, Ca²⁺, and Mg²⁺ were determined by ICP-OES; and HCO₃⁻ and CO₃²⁻ were determined by titration. After the test, the reliability analysis was carried out according to the "Standard Test Methods for Drinking Water Quality Analysis Quality Control (GBT 5750.3-2006)" standard issued by the Ministry of Health. The pretreatment of each batch of samples shall include travel blank, laboratory blank, quality control sample, parallel sample, and actual sample, which shall be carried out in the same batch according to the pretreatment method of samples. According to the requirements of laboratory quality control, the travel blank value shall be deducted from the analysis results, the laboratory blank value shall be lower than the detection limit of the instrument, the recovery rate of quality control samples shall meet the requirements of method recovery rate, and the difference between parallel samples shall be less than 30%.

MapGIS software was used to analyze spatial distribution characteristics. Excel 2007 and SPSS 25.0 were used for data collection and statistical analysis. SPSS statistics is the world's most widely utilized statistical programme for ad-hoc analysis and hypothesis testing, in addition to predictive analytics in business as well as research. Along with the trial, a person can download the traditional user interface after enrolling. A geographic information framework (GIS) is a computer-based framework that assists in the storage, dissemination of data, collection, production, and information as well as analysis by MapGIS software. Spatial distribution patterns might have an outwardly balanced, central place distribution mode; an outwardly unbalanced distribution mode; a multicore central place distribution mode; and otherwise, a corridor balanced else imbalanced distribution mode, depending on the natural circumstances of various regions. Mineral saturation index was calculated using PHREEQC software lnl.dat database to analyze the water-rock interaction of related minerals in groundwater and to determine the direction and intensity of dissolution-precipitation of gypsum, fluorite, and other minerals [9, 10]. Through the

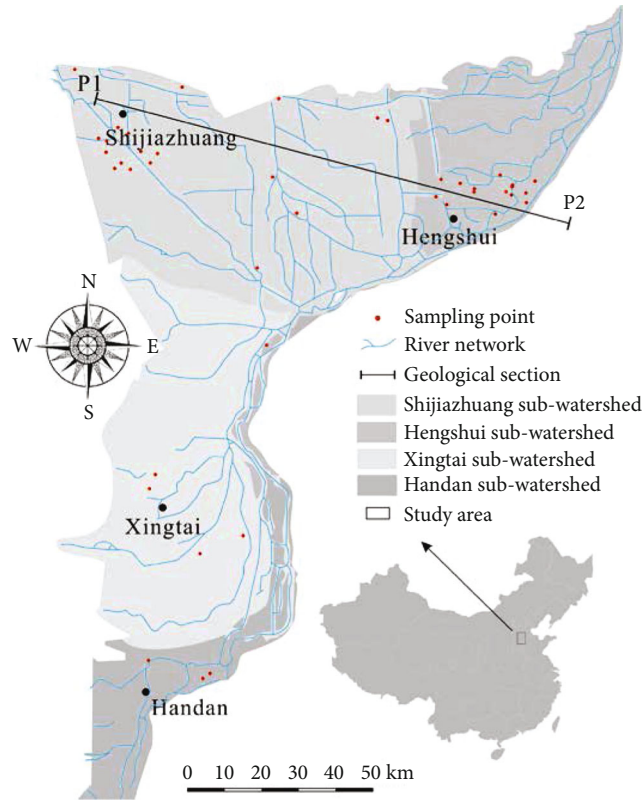


FIGURE 1: Distribution map of groundwater sampling points in Fuyang River Basin.

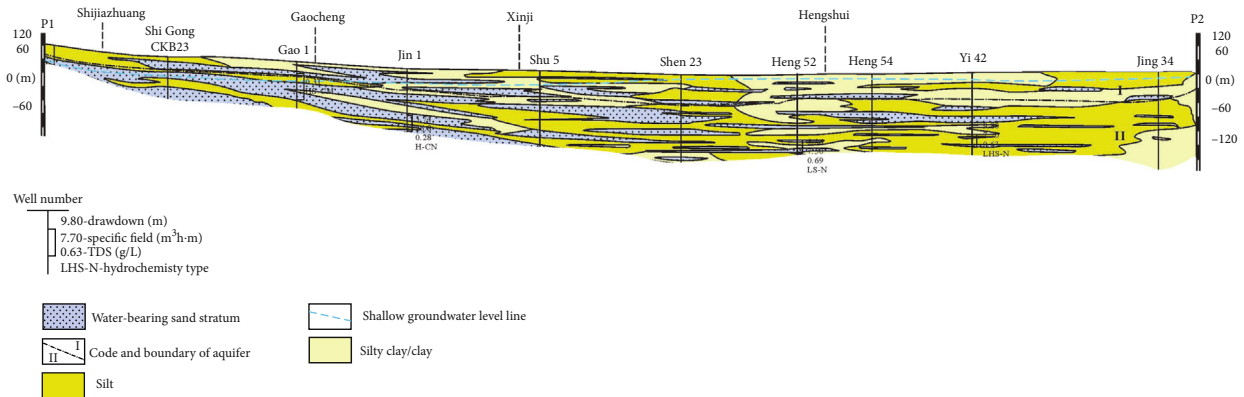


FIGURE 2: Shallow geological profile of Fuyang River Basin.

comparison of chemical activity (ionic activity product, IAP) of a dissolved mineral ion with its solubility product (K_{sp}), the saturation index (SI) is computed; then, the formula is $SI = \log(IAP/K_{sp})$. The hydrochemical characteristics and related causes were analyzed and studied by Piper trilinear diagram, Gibbs diagram, and chlor-alkali index. A form of graph that is utilized to chart the chemistry of water samples is termed as Piper trilinear diagram. Origin generates a Piper diagram from spreadsheet information with the XYZXY column plot designations. The percentage value of every ion group is listed in every column. Piper plots are extremely useful in the disciplines of

hydrogeology besides groundwater studies for displaying the relative concentration of common ions in water samples.

A popular tool for determining the connection betwixt water composition in addition to lithological features of aquifers is termed as Gibb's diagram. Evaporation dominance, rock-water interaction, and then precipitation dominance are 3 dissimilar disciplines. It is a useful tool for identifying the key natural geochemical processes that affect the hydrogeochemical properties of groundwater in an aquifer like the specified disciplines above. The word chlor-alkali refers to the 2 chemicals generated concurrently as an

TABLE 1: Main ion contents of shallow groundwater in Fuyang River Basin.

	Parameters	pH	TDS	SO ₄ ²⁻	Cl ⁻	HCO ₃ ⁻	CO ₃ ²⁻	NO ₃ ⁻	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	F ⁻
All samples (N = 42)	Mean value	7.77	4908.92	1345.10	1700.79	429.13	3.32	2.00	9.84	1134.36	228.40	339.56	0.81
	Maximum value	9.59	17800.00	5532.84	6480.00	1167.78	43.31	19.67	54.14	4332.90	843.32	1570.99	3.14
	Minimum value	7.13	179.95	24.56	19.78	85.10	0.07	0.01	0.94	32.00	3.77	3.27	0.01
Samples $m(\text{F}^-) \geq 1 \text{ mg}\cdot\text{L}^{-1}$ (N = 12)	Mean value	7.54	4036.12	1033.04	1413.45	638.09	0.42	0.12	5.45	1094.69	146.34	259.55	1.93
	Maximum value	7.98	6700.00	2148.67	2720.00	1167.78	0.76	0.43	12.65	1844.26	287.38	450.99	3.14
	Minimum value	7.13	1838.64	324.91	358.90	272.69	0.07	0.01	1.10	475.00	10.43	102.00	1.10

Note: unit $\text{mg}\cdot\text{L}^{-1}$.

TABLE 2: Relationship between main ions in shallow groundwater in Fuyang River Basin.

	TDS	SO ₄ ²⁻	Cl ⁻	HCO ₃ ⁻	CO ₃ ²⁻	NO ₃ ²⁻	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	F ⁻
TDS	1										
SO ₄ ²⁻	0.975**	1									
Cl ⁻	0.984**	0.937**	1								
HCO ₃ ⁻	0.096	0.061	0.026	1							
CO ₃ ²⁻	0.273	0.221	0.334*	0.048	1						
NO ₃ ⁻	-0.302	-0.284	-0.296	-0.281	-0.109	1					
K ⁺	0.096	0.094	0.108	-0.300	-0.017	-0.191	1				
Na ⁺	0.983**	0.954**	0.961**	0.143	0.181	-0.323*	0.045	1			
Ca ²⁺	0.929**	0.952**	0.894**	-0.019	0.166	-0.251	0.225	0.881**	1		
Mg ²⁺	0.992**	0.969**	0.975**	0.077	0.257	-0.264	0.082	0.979**	0.926**	1	
F ⁻	-0.274	-0.279	-0.271	0.52**	-0.16	-0.224	-0.357*	-0.199	-0.335*	-0.264	1

Note: **significant correlation in 0.01 level (double tail); *significant correlation at 0.05 level (double tail).

outcome of saltwater electrolysis (chlorine and an alkali). Chlorine besides sodium hydroxide (caustic soda) is the most frequent chlor-alkali compound, but potassium hydroxide besides muriatic acid is also possible.

4. Chemical Characteristics of Groundwater

The pH value of shallow groundwater in Fuyang River Basin was 7.17-9.59, with an average of 7.77, which was generally alkaline. The main cations in groundwater are Na⁺, Mg²⁺, and Ca²⁺, and the main anions are Cl⁻, SO₄²⁻, and HCO₃⁻. The content of soluble solids ranged from 179.95 to 17800 $\text{mg}\cdot\text{L}^{-1}$, with an average of 4908.92 $\text{mg}\cdot\text{L}^{-1}$. The F⁻ concentration was 0.01-3.14 $\text{mg}\cdot\text{L}^{-1}$, and the average was 0.81 $\text{mg}\cdot\text{L}^{-1}$ (Table 1). The concentration of F⁻ has a certain influence on the content of anions and cations in groundwater, reflecting a certain regularity. According to the toxicological requirements of groundwater quality standard (GB/T 14848-2017), fluoride content higher than 1 $\text{mg}\cdot\text{L}^{-1}$ is regarded as exceeding the standard and classified as Class IV and Class V water [1, 11, 12].

The chemical characteristics of groundwater in the Shijiazhuang-Hengshui section are zonal in the horizontal

direction, and the distribution of high-fluorine samples from the piedmont plain to the central plain in the southeast of the basin. The content of Ca²⁺ and Mg²⁺ decreased obviously in this part of the samples, and the content of Ca²⁺ was 10.43-287.38 $\text{mg}\cdot\text{L}^{-1}$, the content of Mg²⁺ was 102-450.99 $\text{mg}\cdot\text{L}^{-1}$, the concentration of HCO₃⁻ increased to 272.69-1167.78 $\text{mg}\cdot\text{L}^{-1}$, and the values of TDS, Cl⁻, and SO₄²⁻ decreased in varying degrees. The relationship between the source and content of groundwater ions in Fuyang River Basin is shown in Table 2; one must extract samples from said district and use SPSS 25.0 to establish the correlation matrix between water chemical components. There was a significant positive correlation between TDS and Na⁺, Mg²⁺, Ca²⁺, Cl⁻, and SO₄²⁻. The correlation coefficient showed a consistent trend, and the values were between 0.929 and 0.992, indicating that the above ions were the main sources of TDS in the study area, and the sources were highly consistent. There is a negative correlation between F⁻ and the above main ions. In a large number of ions, the correlation coefficient with K⁺ content is the largest, reaching -0.357 with a significant negative correlation. The difference shows there is a significant positive correlation between F⁻ and HCO₃⁻; the correlation is 0.52. The

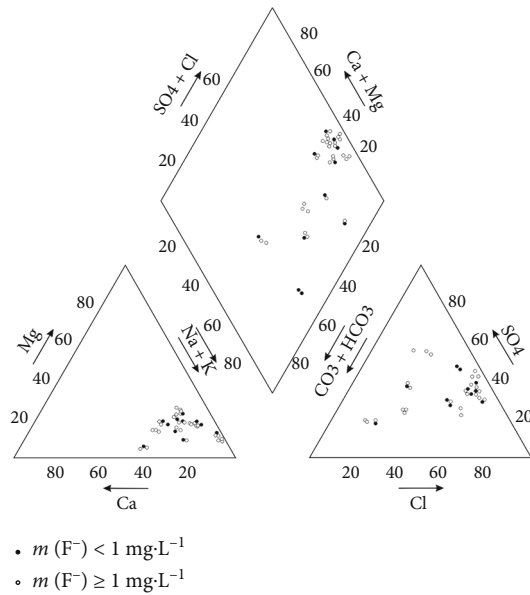


FIGURE 3: Piper diagram of shallow groundwater in Fuyang River Basin.

results showed that the high-fluorine water in Fuyang River Basin had the characteristics of high HCO_3^- and low K^+ in water chemistry.

Hydrochemical types of shallow groundwater in the study area are relatively complex. According to the Shukalev classification, the chemical characteristics of groundwater in the Shijiazhuang-Hengshui section are zonal in horizontal direction; from the piedmont plain to the central plain, the hydrochemical types of the first and second aquifers are mainly HCO_3^- -Cl-Ca-Mg-type water, Cl- SO_4^- -Na-Ca-type water, and Cl- SO_4^- -Na-Mg-type water (Figure 3). It can be seen from the Piper trilinear diagram that the anion distribution of the samples in the study area is relatively dispersed, and the cations are relatively concentrated. In addition, with the increase of F^- content, part of Ca^{2+} and Mg^{2+} in cations changes to Na^+ , while anions gradually change from the combination of SO_4^{2-} and Cl^- to Cl^- and HCO_3^- , and the trend is obvious. The ion composition of groundwater mainly comes from carbonate rock such as salt rock, calcite and dolomite, gypsum, and silicate rock. A widely used mineral is termed as gypsum. It can be discovered in strata that developed millions of years ago beneath salt water. Calcium sulphate (CaSO_4) besides water (H_2O) makes up gypsum. Calcium sulphate dihydrate is its chemical name ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$); because the capillary suction of the mentioned porous substance is responsible for slip dewatering, the gypsum mold is essential in slip casting. This phenomenon to some extent reflects the evolution characteristics of shallow high-fluoride water in the study area.

5. Analysis of Hydrochemical Causes

5.1. Filtration Effect. The soil and groundwater in the study area are alkaline-weakly alkaline under the influence of long hydrological geochemistry and supergene. Plants accumulate nitrogen and organic matter through respiration, while

microorganisms transport carbon from organic matter such as animal, plant remains at the surface to deep groundwater systems, and large quantities of HCO_3^- and soluble mineral components are supplied to groundwater. The mineral saturation index can be used to judge the precipitation-dissolution dynamic process of the target minerals [9]. When the saturation index is negative, the mineral is in an unsaturated state in the water body, which is still in the phase of dissolution but not precipitation when the mineral saturation index is positive; the amount of substance in water solution has exceeded the solubility and is in the state of supersaturation. Fluorite is the main source mineral of F^- , which is usually formed in the vadose zone of pore water environment as secondary mineral [13]. This research uses the PHREEQC software `llnl.dat` database to calculate the saturation indices of calcite, dolomite, gypsum, and fluorite. A programme that simulates a wide range of reactions as well as processes in natural waters besides laboratory studies is termed as PHREEQC. It is a hydrogeochemistry simulation programme that can act out a wide range of geochemical situations. The results show that the saturation index of dolomite is positive, that of calcite is near 0 or slightly higher than 0, and that of fluorite and gypsum is negative, but the stone and the fluorite are still in dissolved state. The average saturation indices of dolomite and fluorite are 2.09 and -2.49, respectively, which indicates that the equilibrium of dissolution and precipitation is the main controlling factor of high-fluorine water chemical composition.

The saturation index of fluorite is negative in all groundwater samples, which indicates that the fluorite is in dissolved state. The dissolving process of fluorite is the reaction of Ca^{2+} with OH^- , and HCO_3^- in the environment forms $\text{Ca}(\text{OH})_2$ precipitation with CaCO_3 . It is also the main reason of enrichment of F^- in groundwater in the study area. From the correlation diagram of F^- content and mineral saturation index, it can be seen that with the increase of F^- content, the saturation indices of CaCO_3 (calcite), $\text{CaMg}(\text{CO}_3)_2$ (dolomite), and CaSO_4 (gypsum) all decrease slightly, because $\text{SI}_{\text{CaCO}_3}$ and $\text{SI}_{\text{CaMg}(\text{CO}_3)_2}$ are larger than 0; the effect of Ca^{2+} provided by the dissolution of fluorite on the saturation index is not obvious. In contrast, the dissolution of CaSO_4 provides a large amount of Ca^{2+} , which weakens the dissolution and rate of fluorite to a certain extent, thus inhibiting the enrichment of F^- in groundwater. It can be seen from the correlation diagram between Ca^{2+} content and saturation index of minerals that the saturation index of the four minerals as a whole tends to increase with the increase of Ca^{2+} content, which indicates that excess Ca^{2+} promotes the precipitation of dolomite and calcite; it also inhibited the dissolution of fluorite. In Table 3, it can be seen that the Ca^{2+} concentration is significantly or very significantly correlated with $\text{SI}_{\text{CaSO}_4}$, respectively, indicating that the Ca^{2+} in water mainly comes from the dissolution of gypsum and the formation of SO_4^{2-} changes the composition of anions in water chemistry. The dissolution of CaSO_4 inhibited the enrichment of F^- , so the concentration of SO_4^{2-} was lower in the groundwater with higher F^- concentration. In addition, HCO_3^- is positively correlated with F^- , and with the increase of F^- , the saturation index of

TABLE 3: Correlation between F^- and Ca^{2+} concentrations and SI.

	Calcite	Dolomite	Gypsum	Fluorite	Ca^{2+}	F^-
Calcite	1					
Dolomite	0.819**	1				
Gypsum	0.600**	0.35	1			
Fluorite	-0.12	-0.266	0.152	1		
Ca^{2+}	0.234	0.07	0.428*	0.166	1	
F^-	-0.232	-0.137	-0.039	0.687**	-0.067	1

Note: **significant correlation in 0.01 level (double tail); *significant correlation at 0.05 level (double tail).

dolomite and calcite decreases (Figures 4 and 5), especially calcite which becomes less and less saturated, indicating that calcite in higher F^- groundwater is still dissolving and producing HCO_3^- .

5.2. Evaporation Concentration. The study area belongs to the continental semiarid monsoon, with an average annual rainfall of 498.5 mm and evaporation of 1545.4 mm in the past 10 years [10]. The evaporation concentration is very strong. Considering the depth of the water table in the study area, the evaporation makes the shallow groundwater move up through the capillary pores of the soil layer, and all kinds of ions carried in the groundwater are trapped in the soil, and the soil alkalinity in the unsaturated zone increases accordingly. Since it shields other buffers from fast pH fluctuations, alkalinity is vital for fish as well as aquatic life. Acid rain besides other acid pollutants will be buffered through higher alkalinity levels in surface waters, preventing pH fluctuations that are detrimental towards aquatic life.

When it rained, the precipitation through the soil vadose zone vertical infiltration recharges to groundwater, water, and soil between the dissolution, hydration, hydrolysis, ion adsorption, and a series of physical and chemical reactions; the fluoride salts that had previously been deposited by evaporation in the soil, as well as the fluorine salts contained in the soil itself, are transferred to the groundwater through dissolution and leaching, resulting in an increase in the fluorine content of the groundwater; under the continuous action of "strong evaporation concentration-leaching-infiltration-strong evaporation concentration," the fluorine groundwater is finally enriched. Gibbs diagrams can be divided into three types: evaporative concentration type, rock-soil weathering type, and precipitation control type by the proportion of specific ions [4]. A phrase that refers to any circumstance in which salt-containing water evaporates off the surface, leaving the salts behind, causing the salts to build up towards a greater level than the concrete over time is said to be an evaporative conservation. The disintegration of rocks as well as minerals into soils is known as weathering. Sedimentary, igneous, and metamorphic rocks are the 3 primary types of rocks. The rock cycle depicts the formation of many types of rocks. Precipitation is any result of the buildup of air water fume that falls under gravitational draw from clouds in meteorology which is termed as precipitation control. Rain, ice particles, drizzle, sleet, slush, graupel, and hail are the primary types of precipitation. It

happens at the time when the climate becomes soaked with water fume (arriving at 100% relative stickiness), so the water gathers then accelerates else falls. In this way, haze and fog are not precipitation but rather colloids, on the grounds that the water fume does not consolidate adequately to encourage.

In Figure 6, the samples are mainly distributed in the upper right corner, indicating that the evaporation and concentration of groundwater in the study area are strong, and a few substances (such as HCO_3^-) come from rock and soil weathering. From Figure 6(a), it can be seen that the distribution of the high F^- sample is near the right, which means that the Mg^{2+} equivalent concentration of Ca^{2+} in the high F^- sample is relatively low in the cations.

The distribution of the samples in Figure 6(b) is relatively dispersed. Some of the samples, together with the two high F^- points on the far right, are moved to the left of the image. This shows that the matter in the groundwater of the study area is affected by evaporation concentration; there is also a fair percentage of F^- that comes from the weathering of rock and soil.

5.3. Ion Alternating Adsorption. Ion exchange and adsorption are surface chemistry else surface complexing processes that result in the conversation of chemical substances betwixt the aqueous solution and the surface of minerals that appeared in geologically porous formations. Influenced by the change of environment and medium, the underground water exchanges with the top and bottom soil and rock mass all the time [14]. In this process, the main cations K^+ , Na^+ , Ca^{2+} , and Mg^{2+} and anion F^- , HCO_3^- , and OH^- exchange at the same time in the selective adsorption; this role is the ion exchange adsorption. It has been found that F^- can be replaced by OH^- when alkalinity is low, because the ionic radius of F^- and OH^- is very close [15]. The high-fluorine water in the study area has a low pH value between 7.17 and 8.25, which provides the conditions for the adsorption-desorption of anions. The cation exchange is mainly between Na^+/Ca^{2+} ions. The chlorine-alkali index (I_{CAI-1} , I_{CAI-2}) can directly reflect the direction and intensity of cation exchange in groundwater:

$$I_{CAI-1} = (\gamma(Cl^-) - (\gamma(Na^+) - \gamma(K^+))) \cdot \gamma(Cl^-)^{-1},$$

$$I_{CAI-2} = (\gamma(Cl^-) - (\gamma(Na^+) - \gamma(K^+))) \cdot (\gamma(HCO_3^-) + \gamma(SO_4^{2-}) + \gamma(CO_3^{2-}) + \gamma(NO_3^-))^{-1}. \quad (1)$$

When the chlorine-alkali index (I_{CAI-1} , I_{CAI-2}) is negative, Ca^{2+} and Mg^{2+} exchange from groundwater to soil in the direction of K^+ and Na^+ ; when it is positive, Ca^{2+} and Mg^{2+} migrate from soil to groundwater, replacing K^+ and Na^+ ions in groundwater; the absolute value represents the strength of the ion exchange reaction [3].

As can be seen from Figure 7, when the content of F^- is low, the distribution of chlor-alkali index is relatively uniform near 0, and the direction of ion migration in groundwater and soil is not clear, but with the increase of the content of F^- , the chlor-alkali index decreases and the

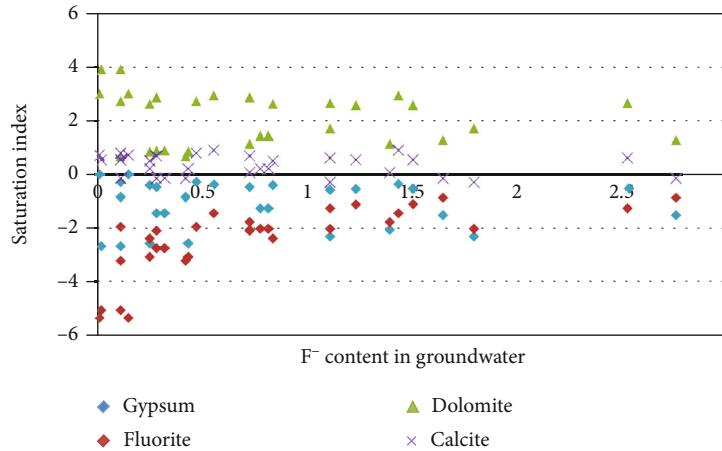


FIGURE 4: Relationship between SI and F⁻ content.

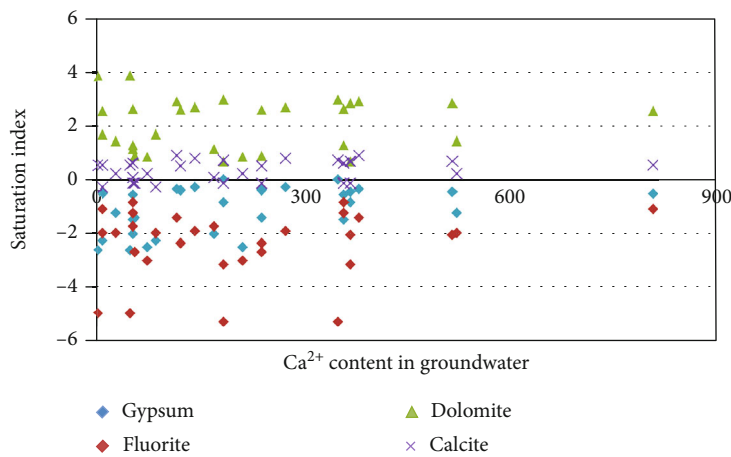


FIGURE 5: Relationship between SI and Ca²⁺ content.

absolute value increases; with the increase of ion exchange intensity, K⁺ and Na⁺ were gradually replaced from the soil into the solution, and Ca²⁺ and Mg²⁺ gradually left the water body in the form of precipitation [16].

In high-fluoride water, the average molar fraction of Na⁺ in cations (76.48%) was significantly higher than that in other samples (70.54%). The correlation diagram of $\gamma(\text{Na}^+) - \gamma(\text{Cl}^-)$ and $\gamma(\text{Ca}^{2+}) + \gamma(\text{Mg}^{2+}) - (\gamma(\text{HCO}_3^-) + \gamma(\text{SO}_4^{2-}))$ can also be used to show cation exchange [17]. It is generally believed that the fitting line with a slope of -1 represents the most ideal negative correlation of $\text{Na}^+ / (\text{Ca}^{2+} + \text{Mg}^{2+})$. As can be seen from Figure 8, the shallow groundwater samples in the study area are distributed near the fitting line with a slope of -0.446, and the $\gamma(\text{Na}^+) - \gamma(\text{Cl}^-)$ values of most samples are between -15 and 10, indicating that the cation alternation is not very strong on the whole; however, the distribution of high-fluorine water samples is relatively to the right of the image, and the slope of the fitting line is closer to -1, indicating that the enrichment of F⁻ is still dependent on the cation alternation. The results show that clay minerals are important sites and media for ion adsorp-

tion in groundwater due to their large negative charges and large specific surface area [18]. This characteristic is very suitable for the ionic adsorption of fluorine.

Because the ionic radius of F⁻ (0.133 nm) is very close to that of OH⁻ (0.137 nm) and the electric charge of OH⁻ (0.137 nm) is the same, the competition between F⁻ and OH⁻ is easily formed; as alkalinity increases, more F⁻ ions are released into groundwater [19, 20]. The adsorption capacity of HCO₃⁻ is the weakest among the three, and it cannot form direct alternating adsorption with F⁻. However, after HCO₃⁻ enters the water body, it can be hydrolyzed to increase the alkalinity of the water body and finally create the alkalinity environment which is beneficial to the enrichment of F⁻.

5.4. Human Factors. Through the hydrogeological investigation in the region, the surface Yellow River water is used for farmland irrigation in many places [21, 22]. In this process, because the water from the Yellow River has a high content of fluorine, the fluorine enters into the shallow groundwater through irrigation, which leads to the increase of the fluorine

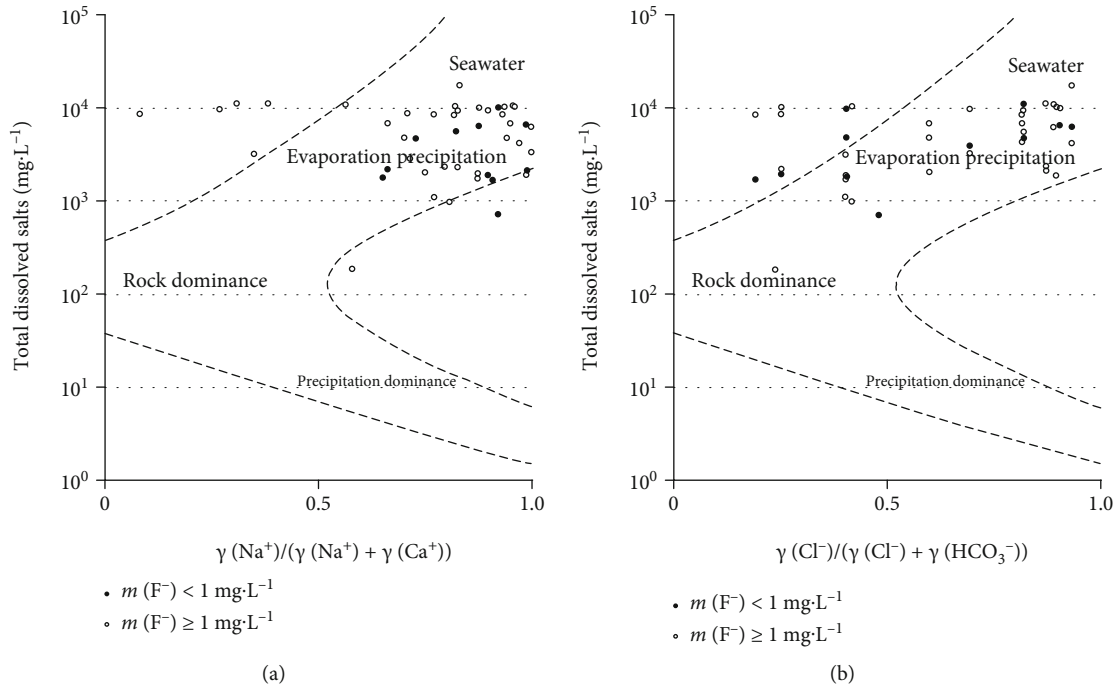


FIGURE 6: Gibbs diagram of shallow groundwater in Fuyang River Basin.

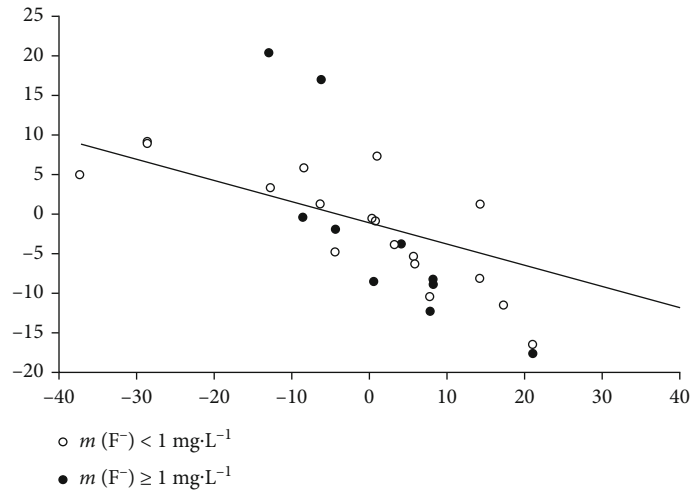


FIGURE 7: Relationship between chlor alkali index and F⁻ content.

ion content in the shallow groundwater [23]. At the same time, irrigation led to the accumulation of some fluoride ions in shallow soil; under the action of rainfall leaching, fluoride ions from the soil enter into shallow groundwater again, resulting in an increase in the content of fluoride in shallow groundwater; it can be said that the more frequent the exploitation of surface water for irrigation, the higher the content of fluoride in shallow groundwater will be. In addition, the study area belongs to the river alluvial plain [24]. Some studies show that the frequent human activities in this area result in a single plant community structure and often cannot form a perfect root group layer [25, 26]. At the same time, the reduction of vegetation coverage can weaken the

interception and purification function of nutrients and mud and sand lost by surface slope flow in most areas, resulting in the infiltration of fluoride in the aeration zone into the phreatic layer with the leaching of soil water, resulting in the enrichment of fluoride.

6. Conclusion

The geological background is the material basis for the formation of all kinds of high-fluorine water. The strong adsorption of fluoride by soil containing most clay is the main source of F⁻, and the alkalinity of circulating water is also the reason for the existence of F⁻. The fluoride content

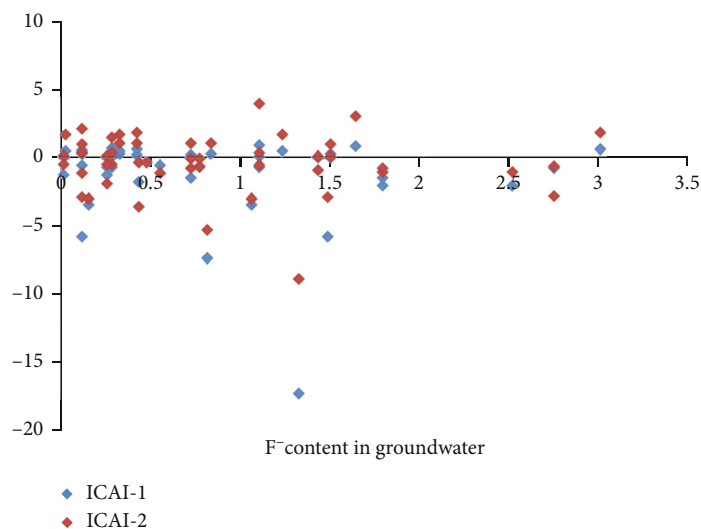


FIGURE 8: Relationship between $\gamma(\text{Na}^+) - \gamma(\text{Cl}^-)$ and $\gamma(\text{Ca}^{2+}) + \gamma(\text{Mg}^{2+}) - (\gamma(\text{HCO}_3^-) + \gamma(\text{SO}_4^{2-}))$.

in the distribution area of sodium water is high, but it is opposite in the distribution area of calcium water. The arid climate determines the wide distribution of high-fluorine water. The closed or semiclosed terrain, poor groundwater runoff conditions, high evapotranspiration rate, and low head conductivity of weathered area lead to the long retention time of water in the aquifer, which is also one of the reasons for the dissolution of fluorine-containing minerals and the increase of F^- content in groundwater. The main conclusions of this paper are as follows:

- (1) The F^- concentration of shallow groundwater in Fuyang River Basin is $0.11\text{--}2.75\text{ mg}\cdot\text{L}^{-1}$, and the average is $0.80\text{ mg}\cdot\text{L}^{-1}$. The main ions in groundwater are Cl^- , SO_4^{2-} , HCO_3^- , Na^+ , Ca^{2+} , and Mg^{2+} . The hydrochemical types are mainly $\text{Cl}\text{-SO}_4\text{-Na}$ and $\text{HCO}_3\text{-Cl-Na}$; the reason lies in the change process of anions and cations from Ca^{2+} , Mg^{2+} to Na^+ and Cl^- , SO_4^{2-} to HCO_3^- in water
- (2) The samples with F^- concentration greater than $1\text{ mg}\cdot\text{L}^{-1}$ accounted for 35.7% and mainly distributed in the south of the study area. The distribution regularity of high-fluorine water in the shallow underground is poor, which is caused by the control of hydrochemical environment, climate, and human influence. In the groundwater with different concentrations of F^- , the composition ratio and change law of anion and cation are also different
- (3) The soil and groundwater in the study area are alkaline; the regional climate and hydrochemical environment promote the dissolution of F^- from minerals or soil and enhance the concentration of F^- in water to a certain extent. An important condition for the formation of high-fluoride water is the coexistence of alkaline and high HCO_3^- with evaporation and condensation; the dissolution-precipitation equilibrium of fluorite, gypsum, cal-

cite, and dolomite and the alternating adsorption of anions and cations are the main controlling factors for the formation and distribution of high-fluoride water

Data Availability

The data used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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