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Research Article

Hydrogeochemistry of Fluorine in Groundwater in Humid Mountainous Areas: A Case Study at Xingguo County, Southern China

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The understanding of F^- concentration in groundwater in humid areas is limited although there are lots of research on high-fluoride groundwater in arid areas. In this paper, with controlling factors of F^- concentrations in humid areas as the focus, 130 groundwater samples, obtained from four subsystems in Northwest Xingguo County, Jiangxi Province, China, were investigated to demonstrate the controlling factors of F^- concentrations in humid areas. According to analytical results, the following hydrogeochemical characteristics of the fluorine in humid mountainous areas were determined: (1) F^- concentration is positively correlated with total dissolved solids (TDS), Ca^{2+}, HCO_3^-, and pH; (2) the groundwater features a high flow rate and low TDS; (3) the equilibrium constant of CaF_2 is less than its solubility product constant, and the fluorine-bearing minerals in rocks are in a dissolved state; and (4) the dissolved fluoride-bearing minerals constitute the main sources of F^- in the groundwater. Fluorine mainly comes from groundwater fluorine-bearing minerals in metamorphic rocks. Moreover, the low F^- concentration in the groundwater mainly results from the fast flow rate of groundwater. Fluoride in groundwater has great potential hazards in humid areas.

1. Introduction

Fluorine is an indispensable trace element in the human body. It is an essential component to maintain the normal development of human bones. However, excessive fluoride in the human body can lead to endemic fluorosis [1]. It is stipulated in Standards for Drinking Water Quality (GB 5749-2006) and Quality Standard for Groundwater (GB/T 14848-2017) that F^- concentration in drinking water should be less than 1.0 mg/L. Water with F^- concentration greater than 1.0 mg/L is defined as high-fluoride water [2].

In recent years, fluorine hydrogeochemical study indicates that dissolved fluorine in groundwater mainly originates from fluorine-bearing minerals [3–8]. Climate, topography, hydrogeological conditions, and hydrochemical environment take the major control of the migration and enrichment of fluorine [9–15]. At the same mineralization level, the higher the hardness of water is, the higher the Ca^{2+} concentration is and the lower the F^- content is in arid areas [10]. In semiarid areas of China (e.g., North China Plain), F^- concentration in groundwater is positively correlated with Na^+ concentration and pH, while negatively correlating with Ca^{2+} contents [16–22]. Meanwhile, Ca^{2+} is the main hydrochemical factor that controls the formation of high-fluoride water in deep groundwater [11]. In shallow groundwater in the North China Plain, Ca^{2+} concentration exerts the greatest influence on the F^- content, which is significantly positively correlated with pH [23]. Fluorine is more liable to be enriched in the weakly alkaline groundwater environment (pH = 7–9) [6, 20–29]. There is a remarkable positive correlation between Na^+ and F^-, and the enrichment of Ca^{2+} and Mg^{2+} will inhibit the enrichment of F^- [30]. With respect to groundwater chemistry, the fluoride concentration is usually high in Na-HCO_3 type groundwater and low in Ca-HCO_3 type groundwater [6, 20, 31–35]. The deficiency of calcium ion concentration in the groundwater from calcite precipitation favors fluorite dissolution leading to excess fluoride concentration. The groundwater is oversaturated with respect to calcite and undersaturated with respect to fluorite [36–41]. Evapotranspiration leads to precipitation of calcite, lowering of Ca activity, and increase in Na/Ca ratios, and this allows an increase in F^- levels in the arid area [39, 42–44].

In a previous study on fluorine dissolved in groundwater, most scholars focused on the source, migration, and enrichment of fluorine in arid and semiarid areas and alkaline and weak alkaline environment, and they achieved many good results. The research results of this paper have important theoretical and practical significance for people to understand the migration and enrichment characteristics of fluorine in weak acidic and acidic groundwater in humid areas. The groundwater is widely distributed and the flow rate is fast; the F^- in groundwater will migrate to any areas where the groundwater flows. Therefore, fluorine in groundwater has great potential harm in humid areas. The hydrogeochemistry of fluorine in humid mountainous areas is still important. In this paper, the hydrogeochemistry of groundwater and factors controlling the distribution of fluoride in groundwater of Northwest Xingguo County, southern China, have been evaluated. The main objectives of this paper are as follows: hydrogeochemical characteristics of fluorine in groundwater in humid areas, including the source of fluorine and its influencing factors.

2. Geology and Hydrogeology

2.1. Geographical Setting. The study area, Northwest Xingguo County, Jiangxi Province (also referred to as the area) lies in E115°00′–E115°15′ and N26°20′–N26°30′, with an area of about 460 km^2. It features a humid subtropical monsoon climate, with an average annual temperature of 18.8°C and an average annual rainfall of 1560 mm. The surface water is composed of Suishui River, Jianshui River, Shuicha River, and Wushu River. In the low-middle mountains, it mainly develops metamorphic rocks and granite. Hilly terrain of granite is distributed in the southeastern. It is a low mountainous area in general with an altitude less than 1000 m. The terrain is steep, V-shaped valleys are commonly developed, and the elevation of the highest peak is 1176 m in the area.

2.2. Geology. The area is mainly comprised of strata of Sinian, Cambrian, Devonian, Carboniferous, and Quaternary with an outcrop area of 402 km^2, accounting for 87.3% of the total survey area. The strata of Sinian and Cambrian are well developed and fully exposed. Magmatic rocks, mainly including plutonic intrusion and vein rocks, are generally distributed in the southeastern part of the area. Granite is common in the area, with an outcrop area of 58.67 km^2. The vein rocks are mainly composed of quartz veins, granite veins, lamprophyre veins, and diabase veins (Figure 1).

2.3. Hydrogeology

2.3.1. Characteristics of Water-Bearing Formations. According to the geological and hydrogeological characteristics, the water-bearing formations in the area can be divided into three types: (1) porous water-bearing formation of loose rocks, (2) porous-fissured water-bearing formation of clastic rocks, and (3) fissured water-bearing formation of magmatic rocks and metamorphic rocks. The distribution areas of these three types are 20.78 km^2, 86.56 km^2, and 352.66 km^2, accounting for 4.52%, 18.82%, and 76.66% of the total area, respectively.

The porous water-bearing formations of loose rocks are mainly distributed along river banks, and the lithology of the aquifer is mainly characterized by sand, gravel, and pebble. The burial depth of the water table is 0.5–2.5 m, the TDS of groundwater samples is 0.029–0.145 g/L, and the hydrochemical type is HCO_3^- Ca.

The porous-fissured water-bearing formations of clastic rocks are distributed in the northeast, northwest, and southwest of the area, with a spring flow of 0.014–9.328 L/s and a single well water yield greater than 100 m^3/d. Hydrochemical types are mainly HCO_3^- Ca or HCO_3^- Ca·Mg, and TDS is 0.090–0.284 g/L for this type.

As for the granite bearing weathering-fissure water, the single well water yield is 4.73–12.66 m^3/d and the hydrochemical type is HCO_3^- Na. However, regarding the fissured water-bearing formations of metamorphic rocks of Cambrian and Sinian, single well water yields are 0.92–60.93 m^3/d and 2.65–3.82 m^3/d and share a common hydrochemical type of HCO_3^- Ca.

2.3.2. Groundwater System. The area is located in the upper reaches of the Ganjiang River, the third-scale (III) groundwater subsystem in the Yangtze River basin. There are fourth-scale groundwater subsystems in the area, precisely including Pingjiang River ($III_{2\text{-}1}$), Liangkou River ($III_{3\text{-}1}$), Yuntingshui River ($III_{4\text{-}1}$), and Wushu River ($III_{5\text{-}1}$). According to the Groundwater System Division Guideline (GWI-A5) issued by the China Geological Survey, the area is divided into four fifth-scale groundwater subsystems (Table 1).

2.3.3. Recharge, Runoff, and Discharge. According to the distribution characteristics of the topography, geomorphology, and surface water in the area, the groundwater is replenished through atmospheric precipitation. The groundwater flows from west to east in the Suishui groundwater system and from north to south in the Jianshui River and Wushu river groundwater systems. The groundwater discharges into rivers, springs, and wells.

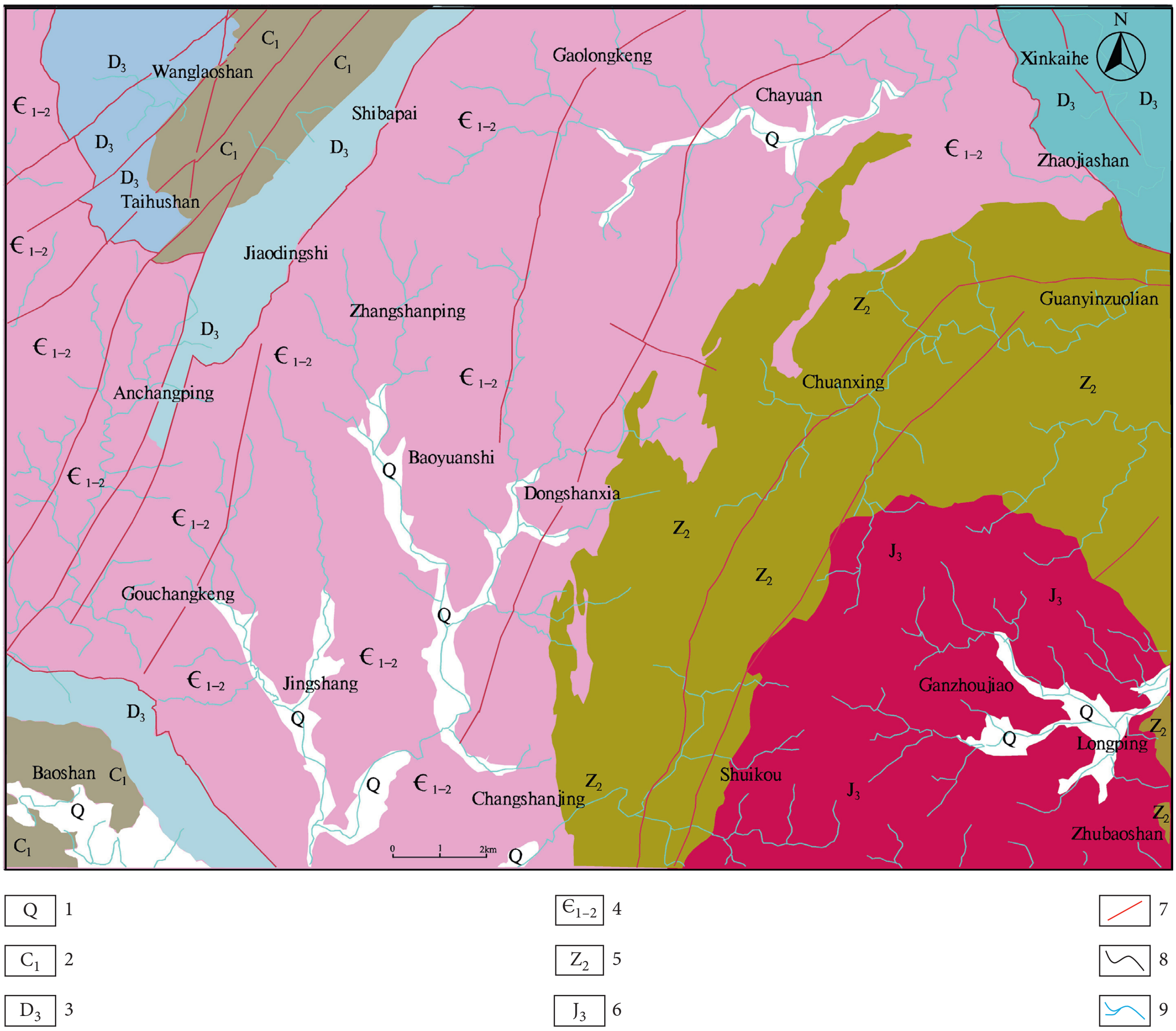


Figure 1: Geological map of Northwest Xingguo County. 1: quaternary; 2: early carboniferous; 3: late Devonian; 4: early and middle-late Cambrian; 5: middle Sinian; 6: granite in late Jurassic; 7: fault; 8: stratigraphic boundary; 9: river.

Table 1: Groundwater system division in Northwest Xingguo County.

Name and code of third-scale subsystem	Name and code of fourth-scale subsystem	Name and code of fifth-scale subsystem	Area (km^2)
Upper reaches of Ganjiang III_1			
Gongshui III_2	Pingjiang River $\mathrm{III}_{2\text{-}1}$	Suishui River $\mathrm{III}_{2\text{-}1\text{-}2}$	213
Gan III_3	Liangkou River $\mathrm{III}_{3\text{-}1}$	Jianshui River $\mathrm{III}_{3\text{-}1\text{-}1}$	152
Gan III_4	Yuntingshui River $\mathrm{III}_{4\text{-}1}$	Shuicha River $\mathrm{III}_{4\text{-}1\text{-}1}$	33
Gan III_5	Wushu River $\mathrm{III}_{5\text{-}1}$	Wushu River $\mathrm{III}_{5\text{-}1\text{-}1}$	62

3. Methods and Materials

A total of 130 groundwater samples were collected from the outcrops of the four groundwater subsystems: Suishui River $\mathrm{III}_{2\text{-}1\text{-}2}$, Jianshui River $\mathrm{III}_{3\text{-}1\text{-}1}$, Shuicha River $\mathrm{III}_{4\text{-}1\text{-}1}$, and Wushu River $\mathrm{III}_{5\text{-}1\text{-}1}$, from June 23 to August 23, 2017 (Figure 2). Major hydrochemical parameters (e.g., F^-, Ca^{2+}, HCO_3^-, pH, and TDS) in these water samples were analyzed in the field. Hash DR2800 spectrophotometer was employed for F^- testing, reagent titration method was adopted for Ca^{2+} and HCO_3^- testing, and acidimeter and test pen were used for pH and TDS testing, respectively. The results are shown in Table 2.

4. Results and Discussion

4.1. Hydrogeochemistry of Groundwater. The chemical composition of 15 representative groundwater outcrops (springs, wells) was tested in order to further determine the hydrogeochemical characteristics of groundwater in the

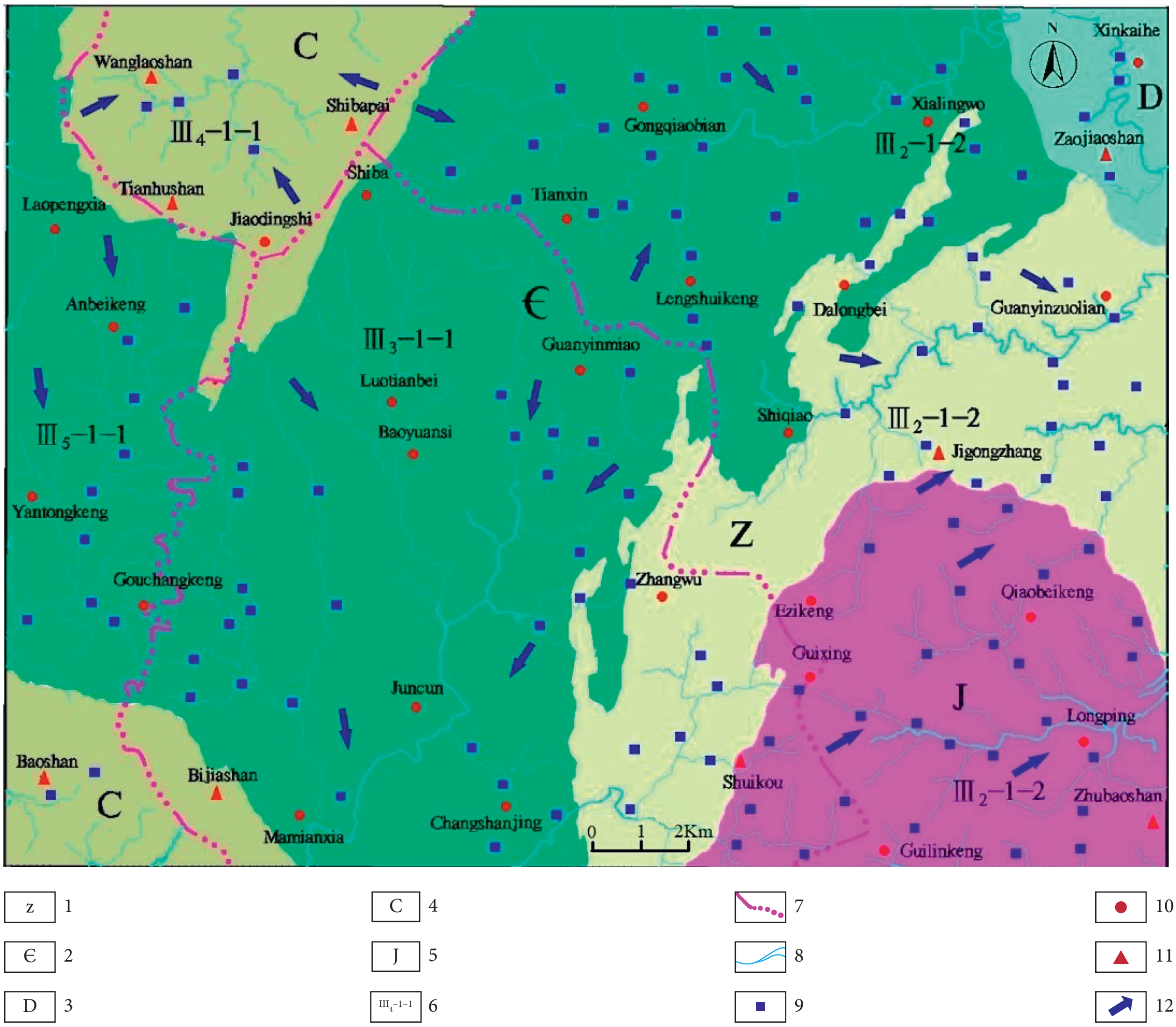


Figure 2: Sampling locations of groundwater in Northwest Xingguo County. 1: Sinian fissured water-bearing formation of metamorphic rock; 2: Cambrian fissured water-bearing formation of metamorphic rock; 3: Devonian porous-fissured water-bearing formation of clastic rock; 4: carboniferous porous-fissured water-bearing formation of clastic rock; 5: Jurassic fissured water-bearing formation of granite; 6: code of groundwater system; 7: boundary of fifth-scale groundwater subsystem; 8: surface water system; 9: sampling location; 10: village; 11: peak; and 12: groundwater flow direction.

Table 2: Summary of Ca^{2+}, HCO_3^-, pH, TDS, and F^- in groundwater of different groundwater subsystems.

Groundwater subsystem	Number of samples	Ca^{2+} (mg/L)		HCO_3^- (mg/L)		pH		TDS (mg/L)		F^- (mg/L)	
		Range	Average	Range	Average	Range	Average	Range	Average	Range	Average
Suishui River $III_{2\text{-}1\text{-}2}$	79	1–32	9.2	3.05–73.22	24.6	5.19–8.48	6.3	5–125	41.7	0.02–1.32	0.19
Jianshui River $III_{3\text{-}1\text{-}1}$	36	3–46	15.4	6.10–67.12	26.1	5.60–7.32	6.5	15–155	59.5	0.02–0.51	0.15
Shuicha River $III_{4\text{-}1\text{-}1}$	4	1–5	2.5	6.10–12.20	8.4	5.37–6.83	6.2	8–19	14.3	0.02–0.09	0.06
Wushu River $III_{5\text{-}1\text{-}1}$	11	2–54	15.2	6.10–140.35	34.4	5.85–7.42	6.7	16–194	64.7	0.01–0.28	0.08

study area. The groundwater chemical components were tested in various groundwater systems in this survey, and the test results show that the main ion components in groundwater under natural conditions are Ca^{2+}, Na^+, and HCO_3^-. The chemical type of groundwater is mainly HCO_3^- Ca·Na, and the second is HCO_3^- Ca·Mg (Table 3). According to the Piper triple-variation diagram, all groundwater in the study area is located in the bicarbonate type water area and is mainly located in the Ca type water area with low TDS hydrogeochemical characteristics (Figure 3).

4.2. Factors Affecting the Distribution of Fluoride in Groundwater

4.2.1. pH Condition. The fluoride contents are in positive correlation with pH [18, 19, 26, 45]. Previous studies show that pH value varies from 7.3 to 9.0 in high-fluoride water [46, 47]. Fluorine-bearing minerals in carbonate areas of weakly alkali environments are more liable to dissolve, resulting in high fluorine concentration in water [48]. The pH in groundwater is generally 6.3–6.7. The F^- concentration is positively correlated with pH in the groundwater of the three subsystems (Suishui River $\text{III}_{2\text{-}1\text{-}2}$, Jianshui River $\text{III}_{3\text{-}1\text{-}1}$, and Wushu River $\text{III}_{5\text{-}1\text{-}1}$) (Figure 4). It is not conductive to the dissolution of fluorine-bearing minerals owing to its low pH, and thus the F^- concentration in it is low.

4.2.2. The Impact of TDS. High fluoride groundwater generally has high TDS and high HCO_3^- in the weak alkaline environment [29]. The relationship between F^- and TDS in the groundwater samples collected from different groundwater subsystems in the studied area is shown in Figure 5. It is indicated that the F^- concentration is positively correlated with TDS in each groundwater subsystem. The reason is that ions in groundwater cannot be saturated owing to the fast water cycle rate in bedrock mountainous areas.

4.2.3. F^- and Ca^{2+} Balance. The relationship between F^- and Ca^{2+} in the groundwater is shown in Figure 6. It is indicated that F^- concentrations are positively correlated with Ca^{2+} concentrations in the groundwater subsystems of Suishui River $\text{III}_{2\text{-}1\text{-}2}$, Jianshui River $\text{III}_{3\text{-}1\text{-}1}$, and Wushu River $\text{III}_{5\text{-}1\text{-}1}$. The groundwater features the temperature of 16–25°C, low TDS (14.3–64.7 mg/L), and low Ca^{2+} concentration (2.5–15.4 mg/L). Therefore, the Ca^{2+} and F^- concentrations can be considered as their activity values.

The equilibrium constant of CaF_2 ($K = [Ca^{2+}]\ [F^-]^2$) in the samples was calculated and compared to its solubility product constant (K_{sp}) (Table 4). The result indicates that, under natural conditions, the solubility product constants are higher than the equilibrium constants, whereas the saturation indexes (SI) of CaF_2 are negative. This further confirms that the fluorine-bearing minerals in rocks are in a dissolving state and the increase of Ca^{2+} will not lead to the precipitation of CaF_2. However, the F^- concentration tends to be negatively correlated with Ca^{2+} concentration in arid areas [2, 12, 14]. This is because Ca^{2+} and F^- are saturated in high-fluorine groundwater in arid areas and, therefore, the increase of Ca^{2+} concentration will lead to CaF_2 precipitation and the decrease of F^- concentration accordingly.

4.2.4. The Dissolution of Minerals. As mentioned above, high F^- groundwater mostly locates in Na-HCO_3 type. F^- concentrations in the groundwater are also positively correlated with HCO_3^- concentrations (Figure 7), indicating HCO_3^- concentration is another important factor affecting F^- concentration in the study area. The anions in the groundwater are mainly HCO_3^- (8.4–34.4 mg/L), and CaF_2 is in a dissolved state as mentioned above. The dissolution-precipitation equilibrium relationship between CaF_2 and $CaCO_3$ is expressed as follows:

$$\begin{aligned} CaF_2 = Ca^{2+} + 2F^- \quad K_{CaF2} = 1019.8 \\ CaCO_3 + H^+ = Ca^{2+} + HCO_3^- \quad K_{CaCO3} = 101.98 \end{aligned} \tag{1}$$

The number of F^- and HCO_3^- increases with the dissolution of $CaCO_3$ and CaF_2 in the groundwater subsystems. In other words, the dissolution will lead to a positive correlation between F^- and HCO_3^-. This is another hydrochemical characteristic of F^- in bedrock mountainous areas in a humid climate.

4.2.5. The Dissolution of Biotite. Fluorine concentration in granite ranges from 0.044% to 0.216%. The biotite [$K(Mg, Fe^{2+})_3(Al, Fe^{3+})Si_3O_{10}(OH, F)_2$], which accounts for 15%–30% in metamorphic rocks, constitutes the main fluorine-bearing minerals. Firstly, the fluorine-bearing minerals in these rocks dissolve and thus F^- is released into the groundwater. Secondly, a faster flow rate of groundwater occurs in the area since it is located in the low–middle mountainous area. This probably leads to low F^- concentration in the groundwater. Thirdly, the groundwater in the area shows weakly acidic characteristics, which may promote the dissolution of fluorine-bearing minerals. According to the results obtained from the hydrogeological survey in the area, it can be concluded that fluorine in the groundwater mainly comes from the interaction between the groundwater and the fluorine-bearing minerals in metamorphic rocks.

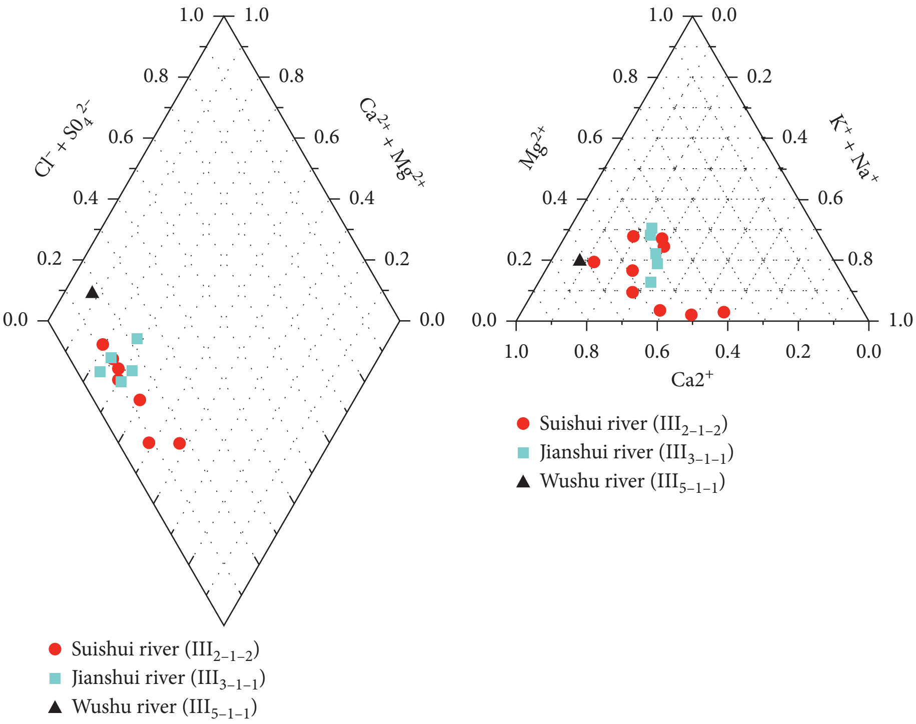
4.2.6. Gibbs Diagram. Gibbs diagram built a simple and effective diagram that can be used to compare TDS~($Na^+/(Na^+ + Ca^{2+})$) or TDS~($Cl^-/(Cl^- + HCO_3)$); this can be used to identify the influencing factors of the groundwater hydrochemistry. For example, the chemical composition is primarily affected by rock weathering, evaporation, and crystallization of soluble salts [50, 51].

According to the chemical composition data of groundwater, the Gibbs diagram of the study area is shown in Figure 8. The TDS of groundwater in the study area is located in 47.7–172.3 mg/L, and the ratio of $Na/(Na + Ca)$ and $Cl/(Cl + HCO_3)$ is between 0.056–0.554 and 0.010–0.114, respectively. It shows that the groundwater is characterized by high Na+ and Ca^{2+} and suggests a geochemical source of granite and metamorphic rocks. Therefore, it can be considered that fluorine in groundwater comes from the dissolution of fluorine-containing minerals in these rocks. The Gibbs analysis of groundwater also indicates that the formation of groundwater chemical

Table 3: Chemical composition of various groundwater systems in the study area.

Groundwater system	Sample number	Water chemical composition (mg/L)										Chemical type of groundwater
		K^+	Na^+	Ca^{2+}	Mg^{2+}	HCO_3^-	CO_3^{2-}	SO_4^{2-}	Cl^-	NO_3^-	TDS	
Suishui River ($\text{III}_{2\text{-}1\text{-}2}$)	SJ051	3.10	8.84	7.13	0.30	43.01	0.00	2.23	3.54	20.55	88.7	HCO_3^- Na·Ca
	SJ014	1.21	4.49	5.01	0.11	37.63	0.00	2.06	0.57	0.12	51.2	HCO_3^- Ca·Na
	GJ002	1.09	6.99	10.34	0.38	53.76	0.00	3.98	1.74	0.17	78.5	HCO_3^- Ca·Na
	SJ070	0.56	2.48	4.06	1.30	37.63	0.00	2.60	0.61	0.90	50.1	HCO_3^- Ca·Na
	GJ003	0.78	2.48	15.42	2.61	69.89	0.00	3.69	1.12	0.10	96.1	HCO_3^- Ca
	SJ104	0.77	2.03	6.58	2.08	37.63	0.00	2.50	1.03	0.11	52.7	HCO_3^- Ca·Mg·Na
	SJ058	1.27	1.37	5.03	0.45	26.88	0.00	1.80	3.47	7.45	47.7	HCO_3^- Ca·Na
	SJ036	6.43	3.77	21.01	3.54	83.33	2.64	6.62	1.80	1.52	130.7	HCO_3^- Ca·Na
	SJ154	1.69	3.54	7.35	2.66	48.38	5.29	3.77	1.11	0.11	73.9	HCO_3^- Ca·Na·Mg
Jianshui River ($\text{III}_{3\text{-}1\text{-}1}$)	GJ001	0.89	3.92	8.26	2.93	59.13	0.00	5.43	0.61	1.12	82.3	HCO_3^- Ca·Mg
	SJ113	7.64	4.59	18.45	4.96	86.01	0.00	8.23	8.19	7.91	146.0	HCO_3^- Ca·Na
	SJ184	1.38	11.52	18.32	4.07	94.08	2.64	7.24	1.35	0.10	140.7	HCO_3^- Ca·Na
	SQ049	0.56	2.40	5.04	2.01	43.01	0.00	1.61	0.55	0.10	55.3	HCO_3^- Ca·Mg
	SJ029	10.80	5.17	23.86	3.26	102.14	0.00	8.65	4.71	13.68	172.3	HCO_3^- Ca·Na
Wushu River ($\text{III}_{5\text{-}1\text{-}1}$)	SQ052	0.91	0.77	12.97	2.11	56.45	2.64	7.88	0.91	1.32	86	HCO_3^- Ca

Note: the data in the table is tested by the Nanchang Supervision Center of Mineral Resources, Ministry of Land and Resources, 2017.



(a) (b)

Figure 3: Continued.

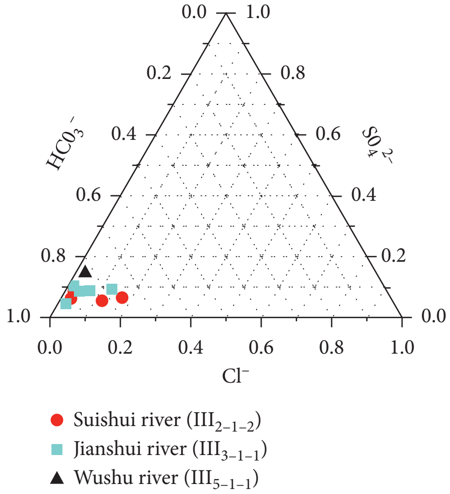


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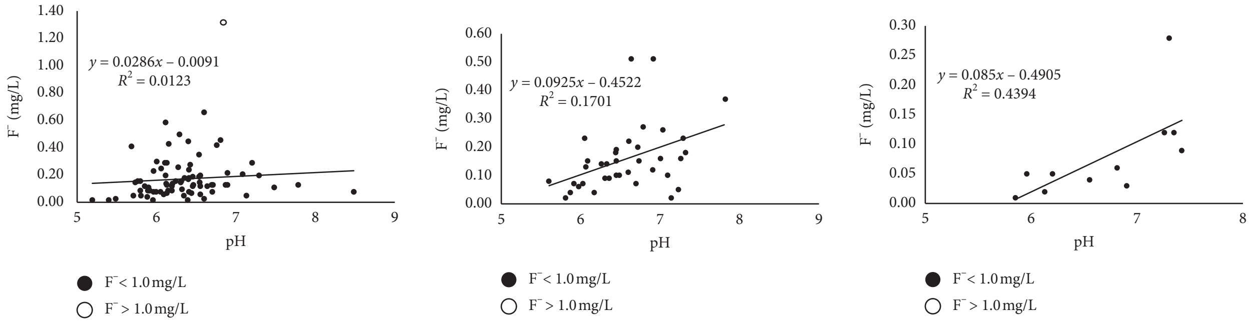
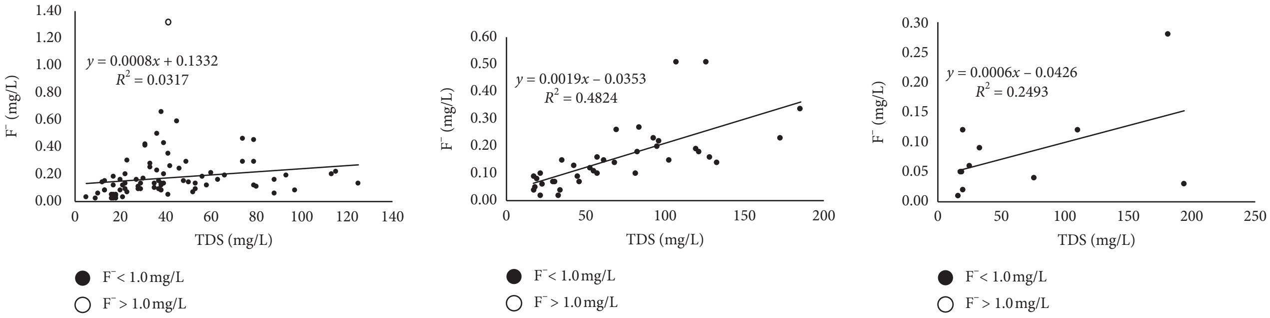
Figure 3: The water chemical pipe triple-variation figure of Northwest Xingguo County.



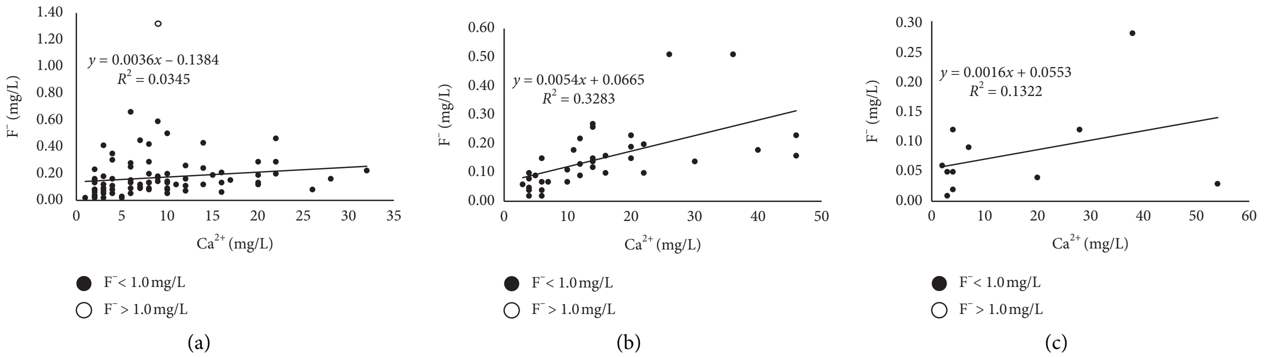
(a) (b) (c)

Figure 4: Relationship between F^- and pH in the groundwater of different subsystems. (a) Groundwater subsystem of Suishui River. (b) Groundwater subsystem of Jianshui River. (c) Groundwater subsystem of Wushu River.



(a) (b) (c)

Figure 5: Relationship between F^- and TDS in groundwater of different subsystems. (a) Groundwater subsystem of Suishui River. (b) Groundwater subsystem of Jianshui River. (c) Groundwater subsystem of Wushu River.

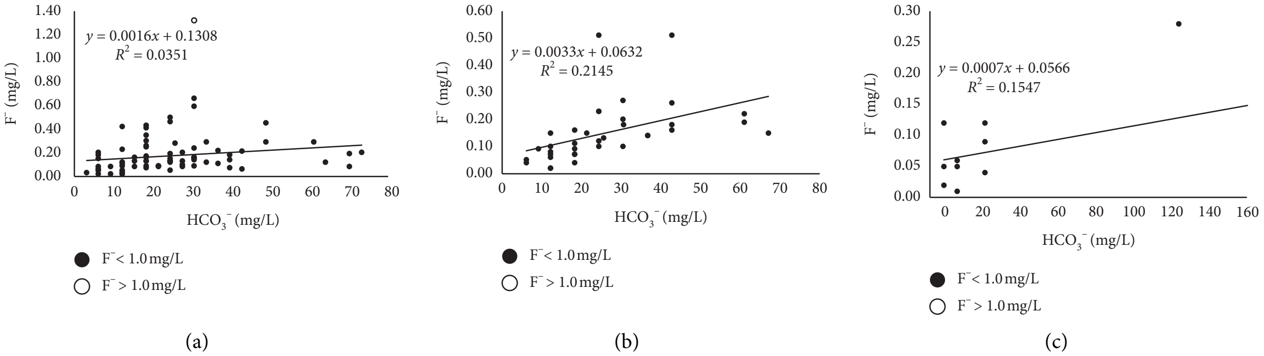


(a) (b) (c)

FIGURE 6: Relationship between F^- and Ca^{2+} in groundwater of different subsystems. (a) Groundwater subsystem of Suishui River. (b) Groundwater subsystem of Jianshui River. (c) Groundwater subsystem of Wushu River.

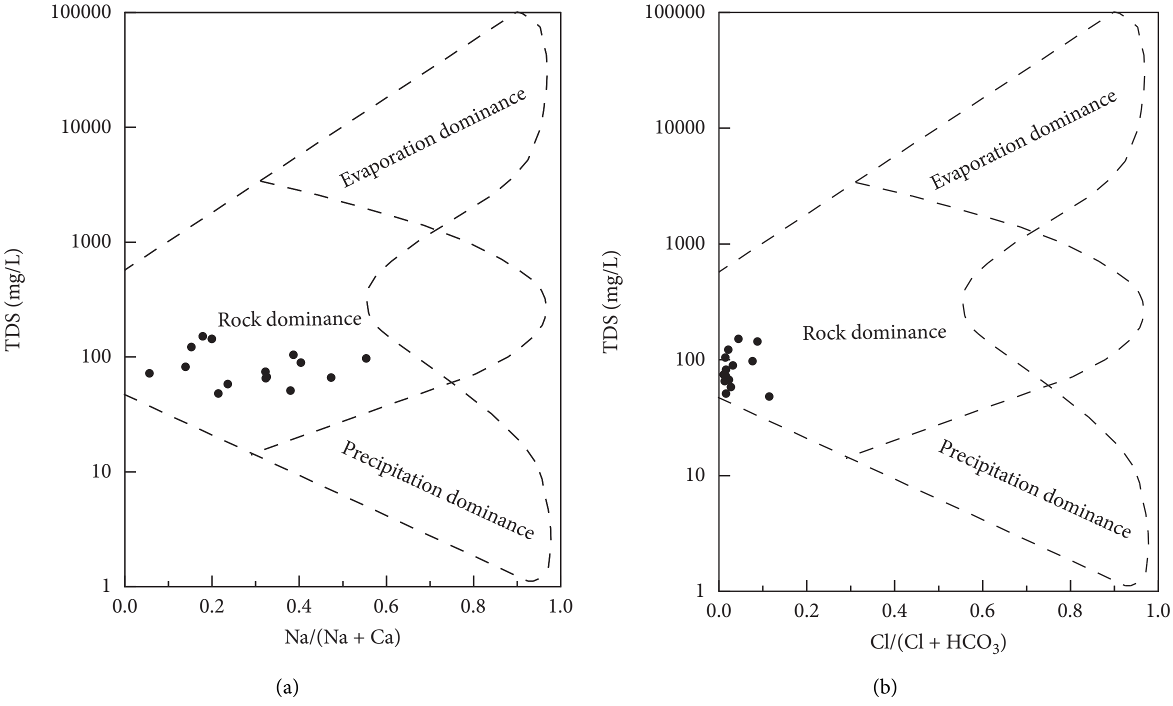
TABLE 4: Equilibrium constant (K), solubility product constant (K_{sp}), and SI of CaF_2 in groundwater.

Sample no.	F^- (mg/L)	Ca^{2+} (mg/L)	K	K_{SP} ($t = 18°C$)	K_{SP} ($t = 25°C$)	SI ($t = 18°C$)
SJ157	0.09	2	1.122×10^{-15}	3.40×10^{-11}	3.95×10^{-11}	−4.482
SQ066	0.02	5	1.385×10^{-16}			−5.390
SJ148	0.62	24	6.389×10^{-13}			−1.726
SJ156	0.03	54	3.366×10^{-15}			−4.004
SJ097	0.76	20	8.000×10^{-13}			−1.628
SJ138	0.2	60	1.662×10^{-13}			−2.311
SJ103	1.18	89	8.582×10^{-12}			−0.598
SJ184	0.32	130	9.219×10^{-13}			−1.567



(a) (b) (c)

FIGURE 7: Relationship between F^- and HCO_3^- in groundwater of different subsystems. (a) Groundwater subsystem of Suishui River. (b) Groundwater subsystem of Jianshui River. (c) Groundwater subsystem of Wushu River.



(a)

(b)

Figure 8: Gibbs diagram for groundwater samples.

components in Xingguo County is dominated by rock weathering reactions; that is, water-rock interaction plays an important role in the migration and enrichment of fluoride in groundwater.

5. Conclusion

In this paper, the migration, enrichment characteristics, and influencing factors of fluorine in weak acidic and acidic groundwater in humid mountainous areas are described. The F^- concentration is positively correlated with the contents of TDS, Ca^{2+}, and HCO_3^- and pH value in the groundwater subsystems in the area owing to the intensive exchange of groundwater with aquifer minerals. In the study area, TDS of groundwater is low and the fluorine-bearing minerals (mainly CaF_2) in the rocks are in a dissolved state, with solubility product constant less than its equilibrium constant. Fluoride mainly originates from the interaction between the groundwater and fluorine-bearing minerals. Moreover, the F^- concentration is low in the area due to the fast flow rate of groundwater. Fluoride in groundwater has great potential hazards in humid areas. This study has important theoretical and practical significance for understanding the hydrogeochemical characteristics of fluorine in humid areas.

Data Availability

The data have been published in the Geological Cloud.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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