Spatial distribution characteristics and enrichment factors of high-fluorine groundwater in the Kuitun River basin of Xinjiang Uygur Autonomous Region in China

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ABSTRACT

The Kuitun River Basin of Xinjiang Uygur Autonomous Region in China is the area experiencing the first large-scale endemic arsenic and fluorine poisoning incident in mainland China. However, existing studies mostly focused on the enrichment factors of high-arsenic groundwater in this area. In this study, the distribution characteristics and formation factors of high-fluorine groundwater in the Kuitun River Basin were investigated with the aim of clarifying the migration and enrichment mechanism of high-fluorine groundwater in the study area. The source, distribution, and geochemical characteristics of the fluorine in groundwater in this area were studied in detail by water sample collection, hydrogeological survey, and mathematical statistics. The results show that the F^- concentration in groundwater in the Kuitun River Basin varied within the range of 0.48–6.41 mg L^{-1}, with a mean value of 1.13 mg L^{-1}; the distribution level of fluorine in groundwater was low in the south and high in the north; the majority of fluorine originated from the rock minerals in the aquifers of southern mountainous areas and plain areas. The formation of high-fluorine groundwater is related to the hydrochemical environment, where Ca^{2+} inhibits the enrichment of fluorine, while the weak alkaline environment, HCO_3^-, and Na^+ facilitate the enrichment of F^-. Dissolution and sedimentation of fluorine-containing minerals, cation exchange, and evaporation–concentration process are the major factors contributing to the formation of high-fluorine groundwater.

Keywords: Fluorine; Groundwater; Distribution; Cause analysis

1. Introduction

More than 300 million people around the world are exposed to health risks related to high-fluorine groundwater [1]. While a moderate intake of fluorine promotes the bone growth of the human body, excessive consumption causes harm to human health, resulting in dental fluorosis, osteoporosis, etc. [2]. The number of people affected by fluorine toxicity has increased significantly over the years worldwide, especially in Algeria, Argentina, Bangladesh, Brazil, Chile, China, Ethiopia, Ghana, India, Iran, Jordan, Kenya, Malawi, Mexico, Mongolia, Nepal, Norway, Pakistan, Sri Lanka, Thailand, Turkey, Vietnam, and other developing countries [3]. Most people in these countries use groundwater extracted from shallow and deep wells for daily use, including drinking [4]. According to China's Standards for Drinking Water Quality (GB5749-2006) [5] and Standard for Groundwater Quality (GB/T14848-2017)

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[6], the appropriate range of fluorine concentration for drinking water is 0.5–0.1 mg L^{-1}, and groundwater with fluorine concentration higher than 1 mg L^{-1} is considered as high-fluorine groundwater.

Many researchers studied the possible causes of the existence of fluoride in groundwater; they found that the hydrochemical and geological conditions of groundwater significantly affect the existence of fluoride [7]. It is reported that the main reason for the release of fluoride is evapotranspiration, as the iron oxides or hydroxides of fluorine are desorbed under alkaline pH conditions [8]. Fluorite dissolves under weak alkaline conditions [9]. In addition, the factors contributing to high levels of fluoride in groundwater also include human activities (such as coal mining), severe erosion of the surface of extremely huge and thick Holocene sediments, and huge extraction of groundwater from fluorine-rich aquifers that experienced early magmatism [10]. Therefore, the most important geological factor for the release of fluoride is the desorption of iron oxides.

This study was carried out in the Kuitun River Basin in Xinjiang Uygur Autonomous Region, China. The study area is located in the interior of the Eurasian continent, where rainfall is slight and evaporation is strong due to the control of temperate continental air masses, resulting in the shortage of surface water and heavy dependence on groundwater [11]. The total amount of water consumed by industry, agriculture, and residents increases with the increase of the economy, leading to the gradually increasing demand for groundwater [12]. It was reported in 1983 that the Kuitun River Basin area experienced the first large-scale endemic arsenic and fluorine poisoning in mainland China, and that arsenic poisoning was caused by drinking high-arsenic and high-fluorine groundwater for a long time had caused great harm to local residents [13]. After 40 y of improvement of water quality for the prevention and control of endemic diseases, the safety of residents' drinking water has been greatly improved [14]. Tap water has become the main source of drinking water for local residents, and high-arsenic and high-fluorine groundwater is mainly used for agricultural irrigation [15]. According to a survey by Yuan and Su [16], the residents in Kuitun still have high levels of arsenic and fluorine in their bodies, and irrigation of crops with high-arsenic and high-fluorine groundwater indirectly leads to the accumulation of arsenic in the human body, jeopardizing human health.

Considering that existing studies mainly concentrated on the distribution characteristics and enrichment factors of high-arsenic groundwater in the Kuitun River Basin, this study aims to explore the spatial distribution characteristics and enrichment factors of high-fluorine groundwater in the Kuitun River Basin, as this is of positive significance for rationally developing and utilizing water resources and limiting the harm of high-fluorine groundwater to human health.

2. Materials and methods

2.1. Overview of the study area

The Kuitun River Basin is located in the Xinjiang Uygur Autonomous Region of China, with Tianshan Mountain to the south and Junggar Mountain to the north [17]. A vast plain area lies between the mountains [18]. Located at 84.0°–85.0°E and 44.2°–45.2°N, the basin has a typical continental temperate arid climate, and it is hot in the summer and cold in the winter, with large temperature differences between day and night in springs and autumns [19]. The average annual rainfall in the basin is 187.4 mm, and the evaporation capacity is 1,693.6 mm [14].

Hydrogeological cross-section from mountain area to fine soil plain of the study area is shown in Fig. 1. The main mountains in the north and south of the Kuitun River Basin are all composed of Paleozoic systems, Mesozoic, and Cenozoic tertiary systems are developed intermittently in the piedmont belt [14]. A vast plain area with a great change of terrain lies between the northern and southern mountains [17]. The elevation drops from 900–1,200 m to 250 m, showing the overall characteristics of high in the east and low in the west, high in the north and south, and low in the north and central. Quaternary sediments are widely distributed in the plain area. From south to north, the quaternary unconsolidated sediments change from scree to multilayer structures mixed by gravel, clay, and sand [20]. The type of groundwater also shifted from a single-layer structure to a multilayer underground water-confined water (artesian water) structure. At the lower part of the alluvial fan in front of the mountain, the buried depth of the unconfined water near the overflow zone is less than 10 m. The confined water is buried 20~30 m, and the artesian aquifer is below 40~70 m. 2–4 layers of confined aquifer within 150 m thickness can be exposed. At the fine soil plain, aquifer thickness is generally 20~50 m. In addition, the plain area mainly receives alluvial sediments from the Nanshan district; therefore, the alluvial sediments in the aquifers are mainly rocks from the Nanshan district [21]. The upper part of the piedmont alluvial-diluvial plain in the Nanshan district is a strongly inclined gravelly plain with high and steep terrain, where the formation particles are coarse and the groundwater alternates strongly. The middle part is a gently sloping gravelly plain, the main recharge runoff area of plain groundwater. It mainly receives lateral replenishment by the undercurrent in the valley of Nanshan district. The lower part is a flat plain of fine soil. The alluvial plain in the middle and lower parts is the discharge area of groundwater runoff [22]. It receives transverse recharge of alluvial plain in the horizontal direction, and longitudinal supply of agricultural irrigation water and rainfall infiltration in the vertical direction. The alluvial plain is the discharge area of plain groundwater, characterized by flat and low-lying terrain, poor groundwater runoff conditions, shallow phreatic water, and intense evaporation [23].

2.2. Collection method and test data

The survey area is mainly the plain area of the Kuitun River Basin, and the sampling content is mainly shown in Fig. 2. In this study, a total of 49 groups of groundwater samples were collected with a well-depth of 60~240 m. Sampling was conducted 20 min after the pump starts to obtain fresh groundwater. Groundwater samples were taken from the existing local wells, and the type, depth, and water table of the well, field temperature, pH, conductivity,
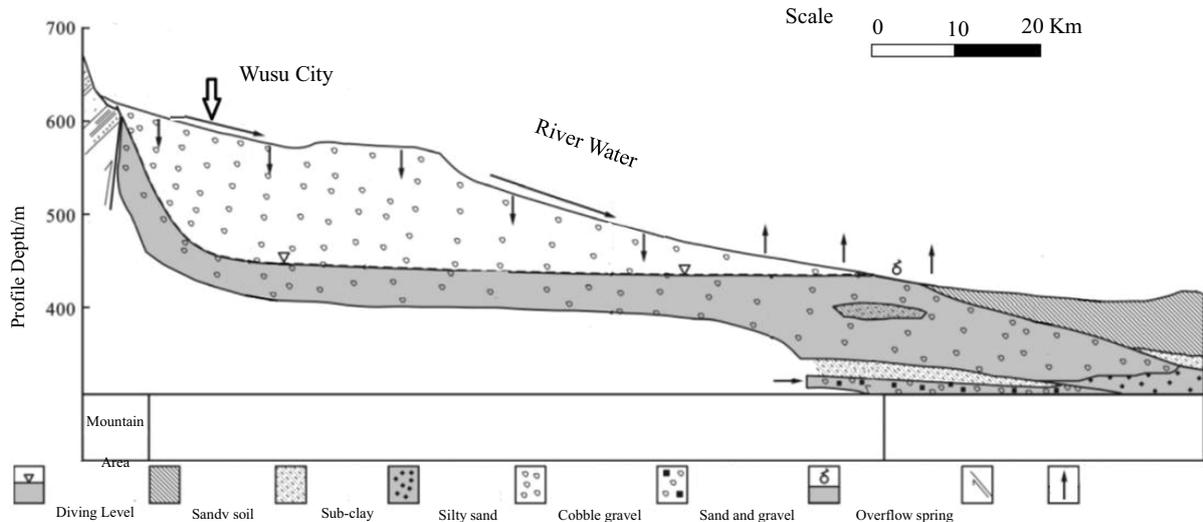
Fig. 1. Hydrogeological cross section for the study area.

dissolved oxygen, Eh (REDOX potential), and alkalinity were recorded. Water samples were collected in a 500 mL polyethylene bottle, which was moistened and washed three times with collected well water. All the samples were filtered through a 0.45 m filter membrane and then sealed and stored at low temperatures. Then, they were sent to the Laboratory of Xinjiang Uygur Autonomous Region No. 2 Hydrogeology Group for testing. The collection, preservation, and delivery of water samples were strictly in accordance with the requirements of technical specifications for groundwater environmental monitoring (HL/T164-2004) [24]. There were 16 test items, including K^+, Na, Ca^+, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, F^-, HPO_3^-, TDS, total hardness, permanganate index, total Fe, Mn, and pH.

3. Results and discussion

3.1. Hydrochemical characteristics of groundwater in the study area

The dominant cation of high fluoride groundwater is Na^+. Hydrochemical types of groundwater in the study area are mainly $SO_4·HCO_3$-Na type and $Cl·HCO_3$-Na (Fig. 3).

The hydrochemical parameters of groundwater in the study area (Table 1) show that the pH of groundwater varied from 7.4 to 9, belonging to the category of alkaline water. To be specific, the pH values of phreatic water and confined water are 8.05 and 8.19, respectively. Besides, the orders of concentration of cations and anions in phreatic water and confined water are relatively consistent. Cations can be ranked as follows in the descending order of mass concentration: $Na^+ > Ca^{2+} > Mg^{2+} > K^+$, and anions can be ranked below: $SO_4^{2-} > HCO_3^- > Cl^-$. Compared with phreatic water, confined water has relatively high contents of Na^+, K^+, and Cl^-, while Ca^{2+}, Mg^{2+}, SO_4^{2-}, and HCO_3^- contents are relatively low. The TDS values of phreatic water in the study area were within the range of 140.74–3,535.89 mg L^{-1}, with an average value of 962.45 mg L^{-1}. The TDS values of artesian water were within the range of 114.48–5,211 mg L^{-1}, with an average value of 867.89 mg L^{-1}.

3.2. Distribution characteristics of high-fluorine groundwater

In horizontal direction (Fig. 2), the distribution characteristics of F^- in groundwater in the plain area of Kuitun River Basin are significant, and the mass concentration of F^- increases gradually from south to north. The high-fluorine groundwater is mainly distributed in the fine soil plain area north of the Wuyi Highway. Specifically, the high-fluorine water in the phreatic water layer is mainly distributed in Toutai Town in the central plains and the 123# Corp. in the north-central plain, while that in the confined water layer is mainly distributed in the north of the plain. The concentration of fluorine in groundwater ranges from 0.48 to 6.41 mg L^{-1} in the study area, with an average of 1.13 mg L^{-1}. The highest mass concentrations of F^- in phreatic water and confined water are both located in the lower part of alluvial–diluvial plain, while both the lowest values occur in the front gravelly inclined plain south of the Wuyi Highway.

In the vertical direction (Fig. 4), the high-fluorine groundwater is mainly distributed in confined water under 100 m, which is closely related to the depth of the water intake layer. At the depth of 100–200 m, the mass concentration of high-fluorine groundwater shows an increasing trend with the increase in well-depth. As shown in Table 1, the mass concentration of fluorine in phreatic water ranges from 0.55 to 1.32 mg L^{-1}, with an average of 0.89 mg L^{-1}, and the over-standard rate of F^- is 29%. The mass concentration of fluorine in confined water ranges from 0.48 to 6.41 mg L^{-1}, with an average of 1.36 mg L^{-1}, and the over-standard rate of F^- is 40%. Overall, the concentration of F^- in confined water is higher.

3.3. Factors influencing fluorine enrichment in groundwater

3.3.1. Source of fluorine in groundwater

The main formation condition of high-fluorine groundwater is the dissolution of fluorine-rich minerals in rock and soil. The groundwater in Kuitun River Basin mainly
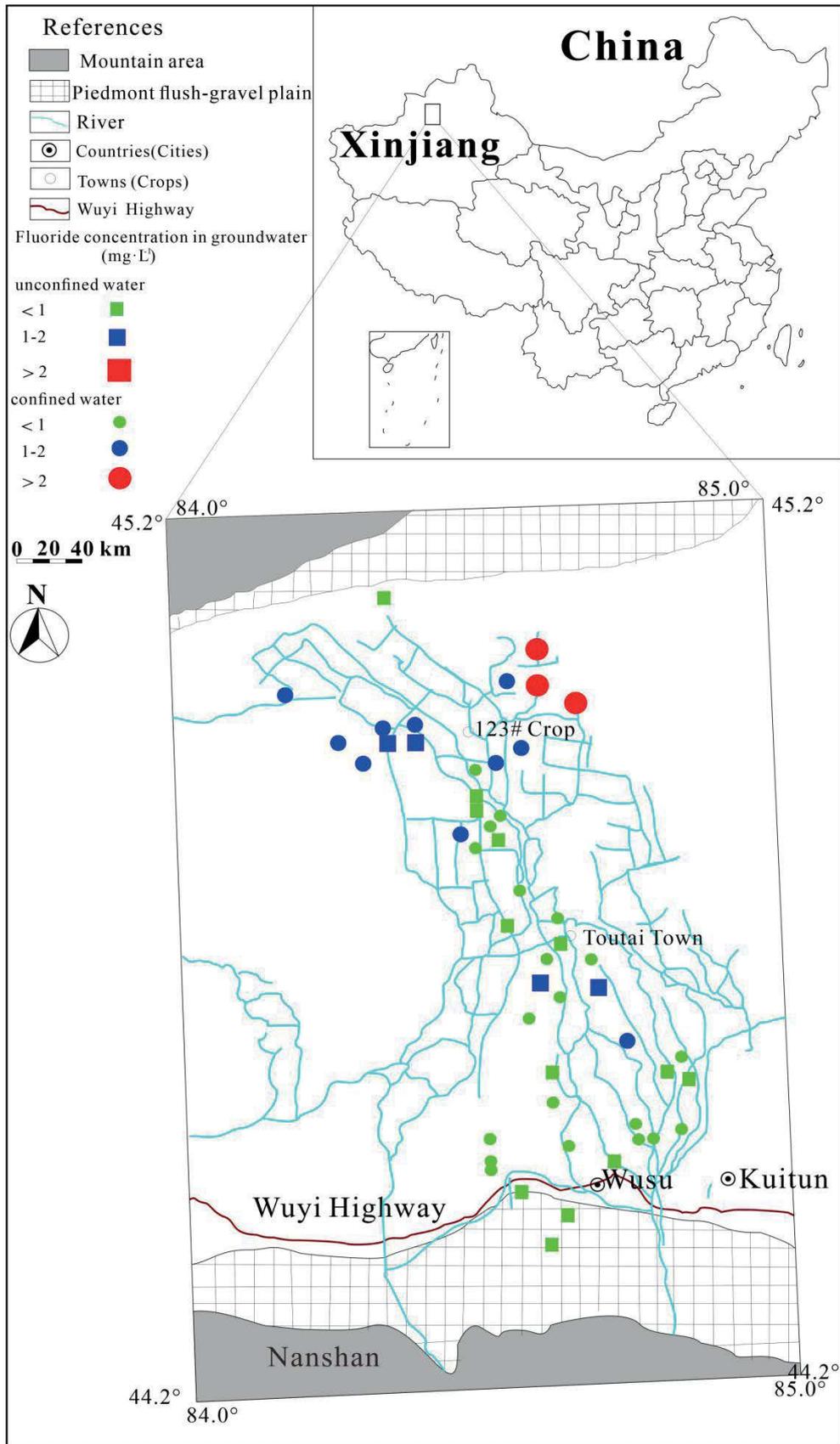
Fig. 2. Locations of study area and sampling sites.

originates from the southern mountains, and the nearby structural mountains are mainly composed of metamorphic rocks, magmatic rocks, and sedimentary rocks. Among them, magmatic rocks have the highest fluorine content, accounting for more than 45% of the total mineral amount [25]. Fluorine-bearing minerals such as fluorite are distributed in some areas. Fluorine-rich substances are also abundant in the sediments of the northern plain. Clay minerals are rich in kaolinite, montmorillonite, and hydromica, and the sand layer contains minerals such as mica, apatite, tourmaline, and amphibole [26,27]. Under the combined action of weathering and hydrochemical environment, these fluorine-containing minerals enter the groundwater, serving as an important source of fluorine in the groundwater of the study area.

3.3.2. Hydrochemical factor

The correlation analysis (Table 2) shows that F^- has a slight relationship with Cl^-, Mg^{2+}, SO_4^{2-}, or TDS, but a significant negative correlation with Ca^{2+}. Fluorite dissolution may be the main source of fluorine in groundwater in the study area, and an excessively high concentration of Ca^{2+} in groundwater can inhibit the enrichment of fluorine in

o The concentrations of F⁻ in groundwater≤1 mg·L⁻¹

• The concentrations of F⁻ in groundwater>1 mg·L⁻¹

Fig. 3. Piper diagram of groundwater in the study area.

groundwater. F^- shows significant positive correlations with pH and HCO_3^-, and the alkaline environment and HCO_3^- and Na^+ can benefit the enrichment of F^- in groundwater. OH^-, HCO_3^-, and F^- have similar ionic radii and charges, and high contents of OH^- and HCO_3^- in alkaline environment can easily undergo displacement reaction with the F^- adsorbed on the mineral lattice surface, inhibiting the adsorption capacity of fluorine ions on the mineral surface [28]. HCO_3^- and OH^- can also reduce the concentration of Ca^{2+} and promote the dissolution of fluorite in groundwater [29]. The reaction equilibrium can be expressed as follows:

$$Ca^{2+} + 2F^- \leftrightarrow CaF_2 \tag{1}$$

$$Ca^{2+} + 2OH^- \leftrightarrow Ca(OH)_2 \tag{2}$$

$$Ca^{2+} + 2HCO_3^- \leftrightarrow CaCO_3 \downarrow + H_2O + CO_2 \uparrow \tag{3}$$

As shown in this formula, when the contents of OH^- and HCO_3^- in the local subaqueous water increase, the reaction equilibrium of Eqs. (2) and (3) will move to the right; the decrease in Ca^{2+} content in groundwater causes Eq. (1) to move to the left, thus promoting the increase of F^- content in groundwater.

3.4. Causes of high-fluorine groundwater

3.4.1. Rock weathering

Specific hydrogeochemical conditions play an important role in the enrichment of fluorine in groundwater [30]. The effect of natural conditions (evaporation concentration, rock weathering, and atmospheric sedimentation) on the hydrochemical characteristics of groundwater can be analyzed using the Gibbs chart. As shown in Fig. 5, high-fluorine water ($\rho(F^-) > 1$ mg L^{-1}) is mainly located in the middle of the Gibbs map and partially at the upper right, suggesting that the formation of high-fluorine groundwater in the study area is mainly influenced by a combination of evaporation concentration and rock weathering. During enrichment, fluorine-bearing minerals in the southern mountain area first migrate into groundwater with runoff under the action of weathering and then accumulate in plain runoff discharge areas with flat and low-lying terrain,
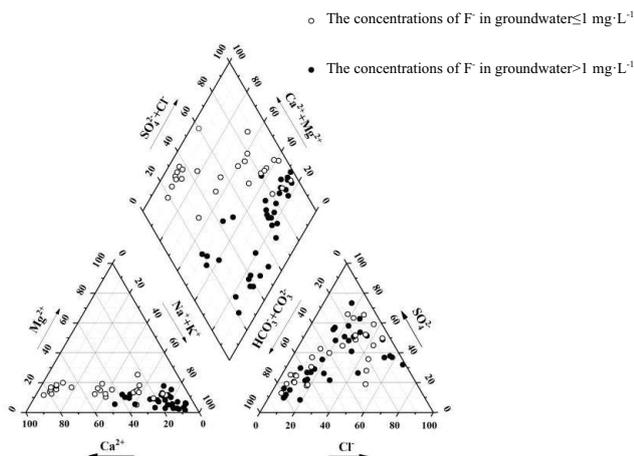
Table 1
Statistical eigenvalues of hydrochemical parameters in study area

Groundwater Type	Parameter	Na⁺	Ca²⁺	SO₄²⁻	K⁺	Mg²⁺	HCO₃⁻	Cl⁻	F⁻	TDS	pH
		mg L⁻¹									
Unconfined water (*n* = 17)	Minimum	1.01	5.24	27.79	1.03	4.15	83.07	8.53	0.55	140.74	7.4
	Maximum	685.61	374.53	1,574.08	3.73	300.45	486.2	853.35	1.32	3,535.89	8.9
	Mean	173.53	78.44	376.39	1.98	44.74	155.00	192.17	0.89	962.45	8.05
Confined water (*n* = 32)	Minimum	1.01	4.03	13.06	0.83	1.71	85.51	7.11	0.48	114.48	7.4
	Maximum	1,281.43	178.41	1,962.44	5.68	256.48	342.05	1,671.15	6.41	5,211	9
	Mean	184.46	58.75	305.98	2.25	31.56	139.03	198.63	1.26	867.89	8.19
Total	Minimum	1.01	4.03	13.06	0.83	1.71	83.07	7.11	0.48	114.48	7.4
	Maximum	1,281.43	374.53	1,962.44	5.68	300.45	486.2	1,671.15	6.41	5,211	9
	Mean	180.67	65.58	330.41	2.16	36.13	144.57	196.39	1.13	900.7	8.14

poor hydrodynamic conditions, and slow groundwater runoff. The evaporation reduction ratio in the study area has been above 9 for many years; thus, the intense evaporation has improved the concentration of F^- in the shallow groundwater. The formation of high-fluoride groundwater in deep groundwater is mainly affected by two factors: On one hand, the study area has formed deep sedimentary layers dominated by argillaceous and clay-argillaceous under continuous geological tectonic movement. The fluorine-rich minerals in these sedimentary layers transfer abundant fluorine to the deep groundwater under water-rock interactions, and the thick sedimentary layers ensure that the chemical elements in the groundwater are not easily lost. Under the influence of long-term geological processes and hydrochemical environment, the continuous accumulation of F^- in deep underground water leads to the formation of high-fluorine groundwater. On the other hand, the water quality of underground water in the middle and lower parts of the plain is poor; therefore, the exploitation of groundwater is dominated by deep confined water, resulting in the decline of the water table of deep groundwater; the replenishment of shallow high-fluorine groundwater increases the content of F^- in deep groundwater. Therefore, the F^- concentration eventually exceeds the standard in deep groundwater.

3.4.2. Dissolution–deposition

Dissolution–deposition plays a decisive role in the enrichment and migration of F^- in groundwater, and it directly affects the enrichment of F^- in groundwater [31]. Fig. 4 shows the activity divergence diagram of Ca^{2+} and F^- in the study area; all the points are located below the lower left part of the fluorite dissolution equilibrium line (lgK = 10.6). This indicates that the upper limits of mass
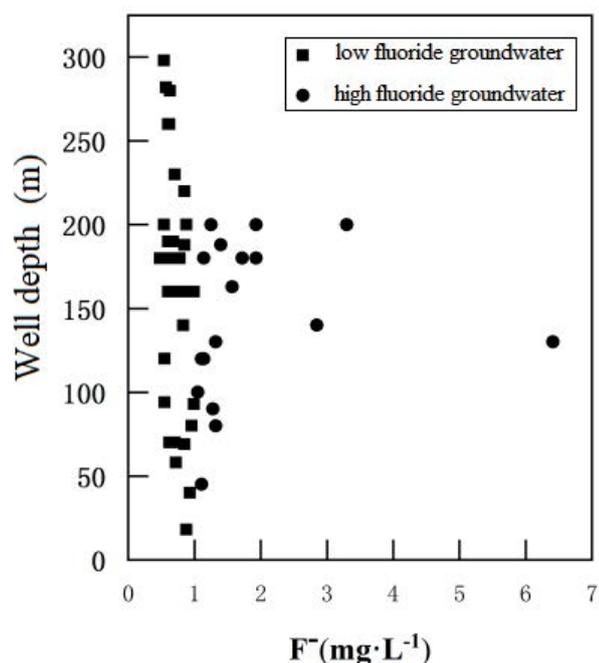
Fig. 4. Relationship between fluorine and well-depth.

concentration of Ca^{2+} and F^- in groundwater are mainly controlled by the solubility of fluorite; therefore, the dissolution of fluorite is the main source of F^- in groundwater in the study area. In addition, when the activity relationship between F^- and Ca^{2+} in local groundwater is consistent with the direction of trend (1), it suggests that the concentrations of Ca^{2+} and F^- in groundwater at this point are only affected by fluorite dissolution. However, in Fig. 5, the majority of points are located on the right of trend (1), suggesting that the mass concentration of Ca^{2+} in groundwater in the study area is not affected by the dissolution of CaF_2 alone. When calcite and fluorite are dissolved in water at a mass ratio of 200:1, the concentration of Ca^{2+} increases along the trend line (2) as the concentration of F^- increases. Most of the points shown in Fig. 5 are between the trend lines (1) and (2), indicating that the concentration of F^- in groundwater in the study area is mainly affected by fluorite and calcite. Besides, a small number of points are located on the right of the trend line (2). In addition to calcite, the mass concentration of F^- in groundwater in the study area is also affected by other calcium-containing minerals. The correlation analysis (Table 2) shows that Ca^{2+} and SO_4^{2-} have a significant positive correlation, indicating that a considerable part of Ca^{2+} in groundwater also originates from the dissolution of gypsum.

The saturation indexes (SIs) of calcite, gypsum, and fluorite were calculated using PHREEQC software. When the SI of a mineral is >0, it indicates that the mineral is in a supersaturated state relative to the aqueous solution. When the SI of the mineral is <0, it means that the mineral is undersaturated relative to the aqueous solution. A SI of 0 suggests that the mineral is in equilibrium with an aqueous solution [32]. As shown in Fig. 6, the saturation indices of gypsum and fluorite in all water samples are less than 0, and the SI of calcite is greater than 0 in 79% of water samples. Fluorite and gypsum in this area are unsaturated, and calcite is oversaturated. As shown in Fig. 7a, the concentration of F^- in groundwater also increases with both the increase in the saturation indices of CaF_2 and $CaCO_3$ and the decrease in the SI of $CaSO_4$. As shown in Fig. 7b, calcite, fluorite, and gypsum all show a trend of gradual increase with the increase in Ca^{2+} concentration in groundwater. Considering the activity relationship between F^- and Ca^{2+}, it can be concluded that the concentration of fluorine in groundwater in the study area is mainly affected by the combined action of fluorite, gypsum stone dissolution, and calcite precipitation. In addition, some sampling points in Fig. 6 gradually decline along trend line (3), probably related to cation exchange. Cation exchange will reduce the content of Ca^{2+} in groundwater, thus affecting the concentration of F^- in groundwater.

3.4.3. Ion-exchange

As shown in Fig. 8, the concentration of F^- in groundwater in the study area increases with the increase in Na^+/Ca^{2+} and Na^+/Mg^{2+}; therefore, the formation of high-fluorine water may be related to cation exchange. Cation exchange can reduce the concentration of Ca^{2+} in groundwater and promote further dissolution of fluorite in groundwater, leading to the increase of F^- content.

Table 2
Correlation analysis of different elements in groundwater of kuitun river basin

	F^-	Cl^-	Ca^{2+}	Mg^{2+}	HCO_3^-	SO_4^{2-}	pH
F^-	1	0.237	−0.301*	−0.087	0.343*	0.186	0.541**
Cl		1	0.725**	0.817**	0.400**	0.938**	−0.296*
Ca^{2+}			1	0.874**	0.229	0.749**	−0.737**
Mg				1	0.434**	0.874**	−0.644**
HCO_3^-					1	0.499**	−0.280*
SO_4^{2-}						1	−0.394**
pH							1

*indicate significant correlation at 0.05; **indicate significant correlation at 0.01.

The terrain gradually becomes gentle, and the content of clay minerals in the aquifer gradually increases from the groundwater runoff area to the drainage area. The Na^+ attached to the surface is easily replaced by Ca^{2+} and Mg^{2+} dissolved in water, resulting in a decrease in the content of Ca^{2+} and Mg^{2+} in groundwater. To further illustrate the possibility of cation exchange in groundwater in the study area, the Chlor-alkali indices (CAI1 and CAI2) proposed by Schoeller [33] can be used to determine the exchange of Na^+ and K^+ with adsorbed Ca^{2+} and Mg^{2+} in groundwater. CAI1 and CAI2 can be expressed as follows:

$$CAI1 = \left[Cl^- - \frac{\left(Na^+ + K^+ \right)}{Cl^-} \right] \tag{4}$$

$$CAI2 = \frac{\left[Cl^- - \left(Na^+ + K^+ \right) \right]}{\left(SO_4^{2-} + HCO_3^- + NO_3^- + CO_3^{2-} \right)} \tag{5}$$

When Na^+ and K^+ are exchanged with adsorbed Ca^{2+} and Mg^{2+}, the values of CAI1 and CAI2 are both greater than 0. When Ca^{2+} and Mg^{2+} are exchanged with adsorbed Na^+ and K^+, the values of CAI1 and CAI2 are all less than 0. The greater the absolute value of the two, the stronger the exchange between ions [34]. As shown in Fig. 9, all CAI1

values in the study area are less than 0 except one point, and all CAI2 values are less than 0, indicating that Ca^{2+} and Mg^{2+} in groundwater undergo exchange with Na^+ and Ka^+ adsorbed in clay minerals. Moreover, the values of |CAI2|
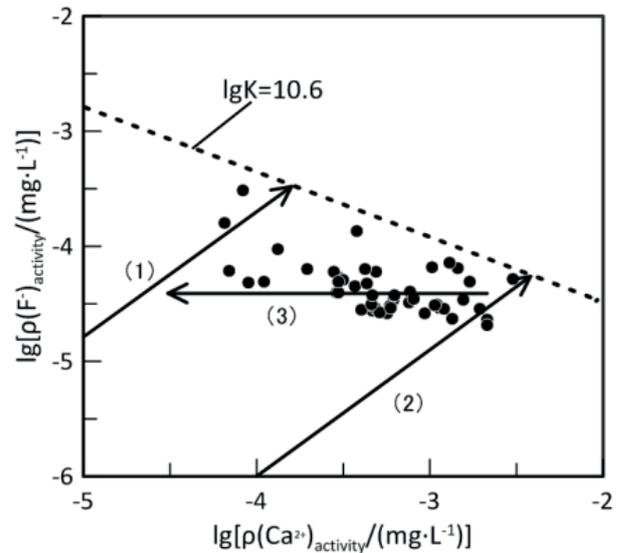
Fig. 6. Relationship between the activities of F^- and Ca^{2+}.
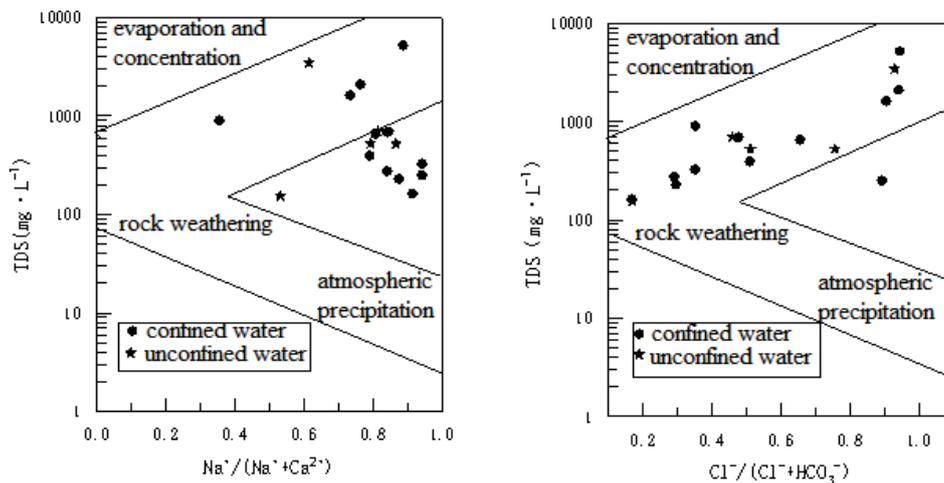
Fig. 5. Gibbs diagram of high-fluorine groundwater in study area.
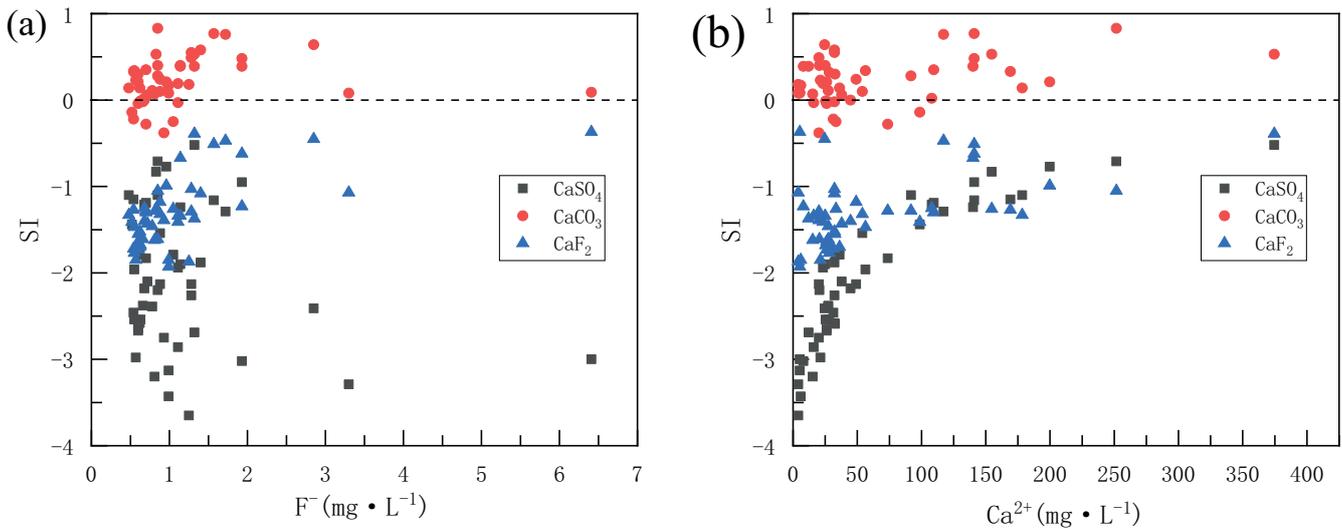
Fig. 7. Plot of (a) F^- and (b) Ca^{2+} vs. $SICaF_2$, $SICaCO_3$, and $SICaSO_4$ for groundwater.
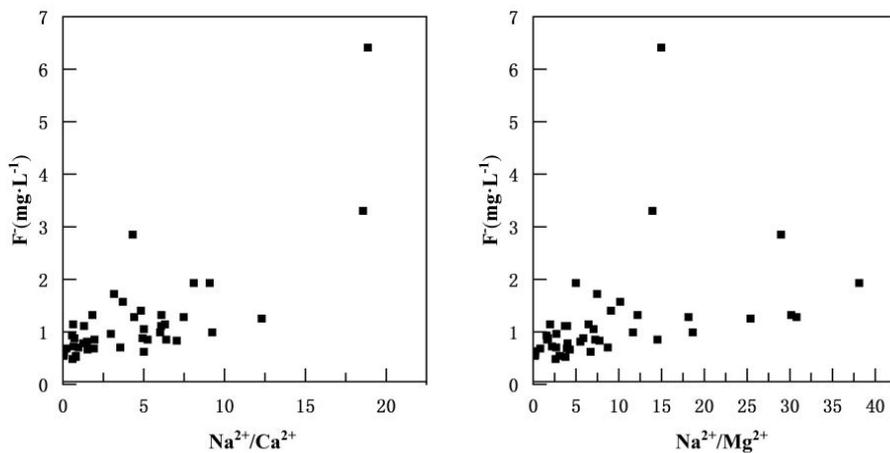
Fig. 8. Relationship between F^- and Na^+/Ca^{2+}, Na^+/Mg^{2+}.

vary within a small range and fluctuate around 0, while the values of |CAI1| increase with the concentration of F^- as a whole. The high-fluorine groundwater is entirely located in the region where the absolute values of CAI1 and CAI2 are large. This indicates that the strong exchange between Ca^{2+} and Na^+ has promoted the enrichment of fluorine in groundwater and that the exchange between cations has indirectly affected the chemical evolution of regional groundwater.

3.5. Countermeasures of high fluoride groundwater in the research area

- To take measures to reduce fluorine of high-fluorine groundwater in the study area, the methods available include electrochemical method, ion exchange method, membrane treatment method, an adsorption method, etc.
- To search for low-fluorine groundwater sources, groundwater with good quality in the upstream of the study area can be considered.

- During well drilling, make sure differential water shut-off well to prevent high fluorine groundwater from entering the low fluorine aquifer.

4. Conclusions

- The concentration of F^- in groundwater in the study area varies greatly within the range of 0.48–6.41 mg L^{-1}, with an average of 1.13 mg L^{-1}. The over-limit ratio is 37%. The mass concentration of fluorine in groundwater increases gradually from south to north, and the concentration of F^- in deep groundwater is relatively high.
- The enrichment of fluorine in the study area is related to the hydrochemical environment in which it is located, and the alkaline environment and HCO_3^- and Na^+ promote the enrichment of fluorine in groundwater. However, Ca^{2+} inhibits the dissolution of calcium-fluorine minerals such as fluorite, which not conducive to the enrichment of F^- in groundwater.
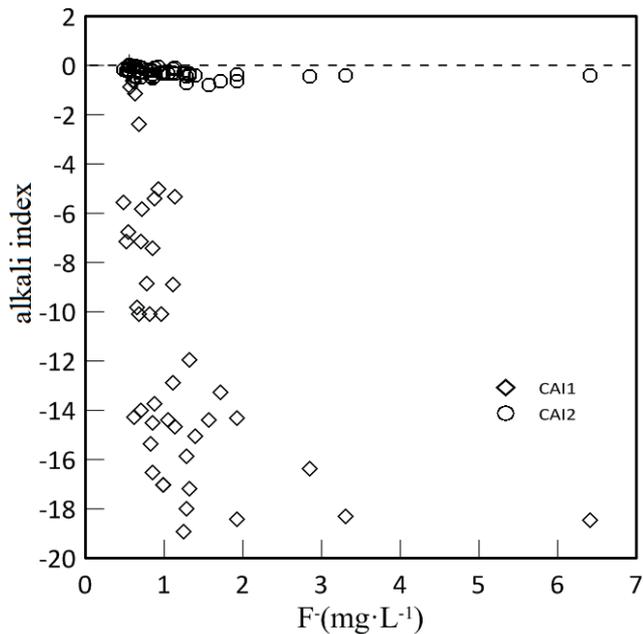
Fig. 9. Relationship between alkali index and F⁻ for groundwater.

- The formation of high-fluorine groundwater in the study area is mainly affected by the dissolution and precipitation of minerals, rock weathering, and cation exchange. The rock strata and the sediments in the plain area of the Nanshan district are the main sources of fluorine in groundwater. The dissolution of fluorite and gypsum and the precipitation of calcite are the main controlling factors of fluorine enrichment in groundwater. The exchange of Na^+ and Ca^{2+} promotes the dissolution of fluorite, increasing the F^- concentration in groundwater.

Acknowledgments

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