Original Research

Geochemical Behaviours and Formation Mechanisms for Elevated Fluoride in the Drinking Groundwater in Sulin Coal-Mining District, Northern Anhui Province, China

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Abstract

There has been substantial research on the sources and geochemical processes associated with fluoride (F⁻) in agricultural groundwater. However, the spatial distribution, geochemical behaviours, and enrichment mechanisms of fluoride in the groundwater from a coal-mining district used for drinking water supply have not been fully understood. In this study, 42 drinking water samples of the groundwater were collected in May 2019 and March 2020 from the Sulin coal-mining district, Anhui, China. Samples were analysed to investigate the distribution, geochemical behaviour, and formation mechanisms of fluoride. The F⁻ concentrations in the groundwater samples ranged from 0.55 to 2.06 mg/L, with a mean value of 1.16 mg/L. The F⁻ concentrations in 54.76% of the water samples exceeded China’s national standards (1.00 mg/L). The results show that the F⁻ in the water was enriched in an environment with high pH and HCO₃⁻ content. The weathering of F⁻ bearing minerals was the main source of F⁻ in the drinking water supply. Evaporation, cation exchange, competitive effect, and anthropogenic activities were considered to have promoted elevated F⁻ concentrations in the groundwater resource. This research will aid policy development for properly managing drinking water to eliminate health problems in coal-mining districts due to excessive fluoride intake.

Keywords: high fluoride, geochemical behaviour, fluoride enrichment mechanism, groundwater resource

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Introduction

Fluorine (F) is a nonmetal element that is rarely present in its elemental form in nature as a result of its high chemical activity. As such, fluorine mostly occurs in the form of chemical compounds that are widely distributed throughout surface water, groundwater, and oceans [1, 2]. Groundwater is the principal source of fluoride (F) for human ingestion; it is controlled by low groundwater infiltration and flow rates, leading to prolonged water-rock interactions [2-4]. Excess F intake can lead to dental and skeletal diseases; as such, the ingestion of fluoride through drinking water has gained widespread attention [3, 4]. As excess fluoride is a public health concern, World Health Organisation (WHO) limits maximum F content in drinking water to 1.50 mg/L [4-7]. Water bodies with an F content above this maximum are considered unsuitable drinking water sources. The occurrence of groundwater with high F concentrations has been reported around the world; this is particularly problematic in China, India, Kenya, Iran, Pakistan, and Jordan [1-2, 4, 8-10]. The levels of F exceed 18.50 mg/L in India [2], whilst in Pakistan, the F concentration is up to 44.40 mg/L [9]. More than 41 million people in China have ingested high-fluoride groundwater. This groundwater is widely distributed throughout Inner Mongolia, Shanxi, Jilin, Anhui, and Gansu [11-4]. As such, the maximum permissible F concentration in drinking water in China is 1.00 mg/L [11].

Fluorite (CaF$_2$), fluorapatite [Ca$_5$(PO$_4$)$_3$F], biotite [K(Mg,Fe)$_2$Si$_3$O$_{10}$(OH,F)$_2$], phlogopite [KMg$_2$(AlSi$_3$O$_{10}$)], and hornblende [CaNa(Mg, Fe, Al)$_{10}$(OH, F)$_{2}$] are common F-bearing minerals [13-17]. Higher levels of fluoride are generally associated with high pH [17-20] and Na-HCO$_3$ type waters [1, 6, 21], although the evaporation and ion exchange factors [4, 10, 22, 23] may also play an important role in promoting elevated F concentrations in groundwater. In addition to natural processes, F concentration in groundwater can also increase owing to anthropogenic activities such as intensive agricultural activities, poorly planned urbanisation, and industrial and mining activities [9, 24, 25].

In the northern Anhui Province of China, deep confined aquifers in the thick loose-bed seam are the primary sources of drinking water. Numerous studies have been conducted on geochemistry [26-28], water-rock interactions [29, 30], and heavy metal pollution [31] of these deep confined aquifers in the Sulin coal-mining district. These studies aim to prevent the entry of deep confined water into the mining wells as this is a hazard in coal mining. Little attention has been directed at drinking water supply aquifers as the impact of coal mining on these resources is considered to be slight. Studies have found that the F content in drinking water aquifers in this area has reached 3.10 mg/L [12]; this is typical of high-fluoride content drinking water. Based on a rough estimation, approximately 5.6 million people in the area have been drinking high-fluoride groundwater for a long time. Moreover, almost half of the population lives in rural areas without the proper protection measures; approximately 60% suffer from dental fluorosis, of which 10% show symptoms of skeletal fluorosis [14, 32]. Despite this, few studies have been conducted on the spatial distribution and geochemical behaviour of F in drinking water aquifers in this area; the sources and formation mechanisms of high-fluoride content groundwater remain unclear.

This study addresses three key objectives: (1) to evaluate the abundance and spatial distribution of F in groundwater that is used as a primary drinking water resource; (2) to evaluate differences in geochemical behaviours between high-fluoride and low-fluoride groundwaters; and (3) to understand the mechanism behind high-fluoride content groundwater in the study area.

Material and Methods

Regional Geology and Hydrogeology

Sulin coal-mining district has an area of approximately 100 km$^2$. It is located in the alluvial plain of the Yellow and Huaihe rivers in the northern part of Anhui Province, China. Its geographical coordinates are 116°15-117°12E and 33°20-33°42N. The area experiences a sub-humid monsoon climate, where the mean annual precipitation and evaporation is 860 and 1060 mm, respectively. In addition, the annual mean temperature is approximately 14-15°C. The wind in the area is predominantly by the southeasterlies. The Huaihe River system is the main water system, including Tuo, Hui, Xie, and Guo rivers. These rivers flow from the northwest to the southeast before entering the sea. The mean annual flow of these rivers ranges from 3.52 to 72.10 m$^3$/s.

Sulin coal-mining district is surrounded by the Ban Qiao Fault to the south, the Su Bei Fault to the north, and the Feng Wo Fault to the west (Fig. 1). As a concealed type colliery, coal deposits in the Sulin coal-mining district are covered by loose sediments. The thickness of the coal exceeds 1300 m, including three to 12 minable and locally minable coal seams. The area contained 19 coal mines with a total production capacity of 30.00 million t/y [33, 34]. After 69 years of mining, a large number of collapsed ponds and coal gangue piles have accumulated on the land surface [35]. Aside from the mining area, most of the land in this area is dedicated to agriculture where wheat and corn are the primary crops. The study area is lacking in surface water, and groundwater is the main source of water for domestic and industrial purposes [33].

Sulin coal-mining district is covered by a Quaternary loose layer that has a thickness of 100.50-771.70 m. The Cenozoic group in the study area
contains four aquifers; these are, from top to bottom, the first, second, third, and fourth aquifers. The second and third aquifers (80-130 m in depth, and a mean depth of 110 m) are widely used as the drinking water supply due to their abundant and high-quality groundwater [33]. The main components of the water-bearing medium are gravel and sand. As a confined aquifer, drinking water aquifers have poor hydraulic connections with lateral precipitation recharge, slow surface runoff, and excretion [33].

Sample Collection and Analysis

Fig. 1a) shows that a total of 42 groundwater samples from the drinking water supply were collected in May 2019 and March 2020. Prior to sample collection, the groundwater at every sampling site was drained for 10 to 15 min to access fresh groundwater. Sampling plastic bottles were first washed with distilled water two to three times and then washed with sample water another two to three times. Collected water samples
were all filtered using filter membranes with a pore size of 0.45 μm before being stored in the washed sampling plastic bottles. For each sampling site, three bottles (500 mL each) of the water samples were collected. To improve the analytical accuracy of the F− concentration, 5 mL of F standard solution (1.00 mg/L) was added as the recovery indicator in each water sample. The pH and concentration of total dissolved solids (TDS) were measured in the field using a portable pH metre (OHAUS ST20) and a portable TDS metre (OHAUS ST20T-B), respectively.

Concentrations of anions (Cl−, SO4−2, NO3−, and F−) and cations (Ca2+, Mg2+, Na+, and K+) were determined by ion chromatography (Dionex Integric GC, Thermo Fisher, USA). Prior to chemical analysis, instruments were calibrated against existing standards, and method detection limits were calculated by replacing with the proper citations. The concentrations of carbonates and bicarbonate anions were measured through acid-base titrations in the laboratory. Analytical grade reagents were used.

Analytical Quality Control

Each water sample had three duplicates, and each analysis was carried out in triplicate to ensure that the standard deviation was below 10%. Nine data points were averaged into one final data point to obtain the mean and the standard deviation. This means the final 42 test data points for the groundwater samples reported in this study analysing TDS, pH, Cl−, SO4−2, NO3−, HCO3−, F−, Ca2+, Mg2+, Na+, and K+ are the mean values of 378 test results. The recovery rate of the samples was randomly selected for re-analysis. The errors between the first and second analysis results of the samples were below ±10.00%.

Analytical Quality Control

Geological Characterisation

The geochemical characterisation of the groundwater samples is presented in Table 1. The pH of the water samples ranged from 7.20 to 8.28, with a mean value of 7.89. This indicates that the water body presented a weakly alkaline environment and that the samples are within China’s national standards – 6.50 to 8.50 – for drinking water [36]. Na+ + K+ were the dominant cations present and their cumulative content ranged from 20.32 to 311.24 mg/L, with a mean value of 141.23 mg/L. Mg2+ was the second most abundant cation ranging between 17.62 and 150.19 mg/L, with a mean value of 52.96 mg/L. The content of Ca2+ ranged from 15.16 to 76.01 mg/L, with a mean content of 39.80 mg/L; this is the lowest among the four cations. Mg2+ had a higher concentration than Ca2+. This may be due to the evapotranspiration precipitation of Ca2+. The anion concentrations in these water samples included (from highest to lowest) a HCO3− concentration between 300.61 and 853.02 mg/L (mean of 498.61 mg/L), a SO4−2 concentration between 12.03 and 462.39 mg/L (mean of 151.23 mg/L), and a Cl− concentration between 4.33 and 216.6 mg/L (mean of 72.30 mg/L). The SO4−2 content in 19.05% of the samples exceeded China’s national standards (250.0 mg/L) for drinking water. The TDS concentrations were between 319 and 1564 mg/L, with a mean of 958 mg/L. The TDS in 35.71% of the samples exceeded China’s national standards (1000 mg/L) for drinking water.

The piper diagram illustrates distinguishable geochemical features in the drinking groundwater samples [37]. Fig. 2 shows that the geochemical facies of the drinking groundwater samples were Na-Mg-HCO3 (46.62%), Na-Mg-HCO3-SO4 (38.10%), and Na-HCO3 (9.520%).

The F− concentrations in the groundwater samples ranged from 0.16 to 2.06 mg/L, with a mean of 1.11 mg/L. Among these samples, 54.76% had elevated F− concentrations that exceeded China’s national

| Types                  | K+    | Na+   | Ca2+  | Mg2+  | SO4−2 | Cl−   | F−    | HCO3− | NO3− | TDS | pH |
|------------------------|-------|-------|-------|-------|-------|-------|-------|-------|------|-----|----|
| Max                    | 4.110 | 218.5 | 69.20 | 94.49 | 459.5 | 184.1 | 0.9800| 488.9 | 5.790 | 1385| 8.060|
| Min                    | 0.230 | 20.32 | 35.53 | 17.62 | 12.03 | 4.33  | 0.1600| 300.6 | 0.000 | 319.0| 7.200|
| Mean                   | 1.120 | 106.8 | 52.29 | 52.25 | 164.2 | 75.79 | 0.7100| 421.8 | 0.670 | 838.0| 7.710|
| SD                     | 1.190 | 60.24 | 19.62 | 19.62 | 121.2 | 44.40 | 0.2400| 104.9 | 1.670 | 308.6| 0.310|
| Max                    | 1.85  | 311.2 | 76.01 | 150.2 | 462.4 | 216.6 | 2.0600| 853.0 | 8.510 | 1564 | 8.280|
| Min                    | 0.16  | 86.53 | 15.16 | 25.51 | 24.22 | 11.71 | 1.0400| 321.6 | 0.000 | 721.0| 7.790|
| Mean                   | 0.55  | 169.6 | 34.26 | 53.98 | 140.5 | 69.41 | 1.4400| 566.3 | 1.290 | 1057 | 8.050|
| SD                     | 0.35  | 68.19 | 15.04 | 29.33 | 117.9 | 53.28 | 0.3000| 145.4 | 2.210 | 241.4| 0.120|

Values less than LOD (limit of detection) were set to zero for statistical purposes.
standards (1.00 mg/L) for drinking water. The groundwater samples were divided into two groups based on China’s drinking water guidelines (1.00 mg/L); the low-fluoride drinking groundwater group (<1.00 mg/L), and the high-fluoride drinking groundwater group (>1.00 mg/L).

**High-Fluoride Geochemical Behaviours**

In the high-fluoride drinking groundwater group, the pH was between 7.79 and 8.28, and the Ca\(^{2+}\) concentration ranged from 15.16 to 76.01 mg/L, with a mean of 34.26 mg/L. The Na\(^+\) concentration ranged from 86.53 to 311.24 mg/L, with a mean of 169.62 mg/L. The HCO\(_3^-\) concentration ranged from 321.58 to 853.02 mg/L, with a mean of 566.28 mg/L, whilst the TDS concentration ranged from 721 to 1564 mg/L, with a mean of 1057 mg/L (Table 1).

In the low-fluoride drinking water group, the pH was between 7.20 and 8.06, and the Ca\(^{2+}\) concentration ranged from 35.53 to 69.20 mg/L, with a mean of 52.29 mg/L. The Na\(^+\) concentration ranged from 20.32 to 218.47 mg/L, with a mean of 106.84 mg/L. The HCO\(_3^-\) concentration ranged from 300.61 to 488.94 mg/L, with a mean of 421.75 mg/L, and the TDS concentration ranged from 319 to 1386 mg/L, with a mean of 838 mg/L.

The high-fluoride drinking water group had a higher HCO\(_3^-\) concentration and pH compared with low-fluoride drinking water. This suggests that an alkaline environment may promote the dissolution of F\(^-\) [15, 38]. The F\(^-\) concentration was found to clearly increase with decreasing Ca\(^{2+}\) content, showing a good negative correlation (Fig. 3b). The high-fluoride drinking water samples also had a slightly higher Na\(^+\) content and TDS, indicating that TDS and Na\(^+\) content are not dominant factors of the F\(^-\) content.

The majority of the groundwater samples with high F\(^-\) content were of the Na·Mg-HCO\(_3^-\)SO\(_4\) type (53.81%) and Na·Mg-HCO\(_3^-\) type (25.76%), as shown in Fig. 2. In comparison, most of the groundwater samples with low F\(^-\) content were of the Na·Mg-HCO\(_3^-\) type (85.71%). This indicates that the hydro-chemical facies of the high-fluoride drinking groundwater are more complex and diverse. Generally, the high-fluoride groundwater belonged to the Na-HCO\(_3^-\) type, as dissolved Na\(^+\) and Mg\(^+\) promote elevated F\(^-\) concentrations in water [15, 16, 39, 40].

**Discussion**

**Dissolution and Precipitation Process**

Due to the poor solubility of CaF\(_2\), if CaF\(_2\) gets dissolved in a water body, when the content of Ca\(^{2+}\) increases, the F\(^-\) content will decrease. The more rapid the rise in the Ca\(^{2+}\) content, the more accelerated the reduction in the F\(^-\) content. Fig. 3b) shows that the Ca\(^{2+}\) content in the high-fluoride groundwater samples was lower than that in the low-fluoride groundwater samples. Moreover, the high HCO\(_3^-\) content promotes the dissolution of F\(^-\), as shown in Fig. 3d). The main source of HCO\(_3^-\) is the dissolution of calcite (CaCO\(_3\)) and dolomite (CaMg(CO\(_3\))\(_2\)) [21]. Based on this evidence, the main factors that control the weathering process of CaF\(_2\) may be expressed as:
\[
\begin{align*}
\text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 & \leftrightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- \quad (1) \\
\text{CaMg(CO}_3\text{)}_2\text{V} + 2\text{H}_2\text{O} + 2\text{CO}_2 & \leftrightarrow \text{Ca}^{2+} + \text{Mg}^{2+} + 4\text{HCO}_3^- \quad (2) \\
\text{CaF}_2 + 2\text{HCO}_3^- & \leftrightarrow \text{CaCO}_3 + 2\text{F}^- + \text{CO}_2 + \text{H}_2\text{O} \quad (3)
\end{align*}
\]

Based on Equations (1) and (2), the dissolution of CaCO₃ and CaMg(CO₃)₂ in the presence of CO₂ generates a large amount of Ca²⁺, Mg²⁺, and HCO₃⁻.

Fig. 3. Plots of a) pH versus F, b) Ca²⁺ versus F, c) Na⁺ versus F, d) HCO₃⁻ versus F, and e) TDS versus F of the drinking groundwater samples.
The high HCO$_3^-$ concentration may cause a left shift in the equilibrium (i.e., Equation (3)), leading to an increase in F$^-$ content [41, 42].

The saturation index (SI) may be obtained from Equation (4) [40, 42]:

$$SI = \log_{10}(K_{iap}/K_{sp})$$  \hspace{1cm} (4)

...where $K_{iap}$ is the ion activity product of a particular solid phase and $K_{sp}$ is the solubility product of the phase. The SI is a reliable means to determine whether a groundwater body is oversaturated (SI>0), undersaturated (SI=0), or saturated (SI < 0) [43]. Fig. 4 plots the SIs of minerals in the groundwater samples, including calcite, dolomite, and fluorite.

All samples were undersaturated with respect to fluorite, indicating that the F anions in the groundwater samples were mainly sourced from the dissolution of fluorite (CaF$_2$) [18]. Fig. 4a) shows that the SI values of most high-fluoride groundwater samples were higher than those of the low-fluoride groundwater samples, suggesting that the dissolution of fluorite ($K_{sp} = 10^{-10.5}$) has a higher influence on the high-fluoride groundwater group [38]. All high-fluoride groundwater samples were oversaturated with respect to dolomite and calcite.

This is evidence demonstrating that the precipitation of dolomite and calcite reduces Ca$^{2+}$ content, promoting the dissolution of fluorite generating an elevated F$^-$ content [3, 40, 44].

Fig. 4c) shows the SI of fluorite (CaF$_2$) versus the F$^-$ content (mg/L); this relationship may assist in determining the connection between fluorite dissolution and the F$^-$ content in the groundwater samples [43, 45]. The positive correlation ($R = 0.78$) between the F$^-$ concentration and the SI of fluorite (CaF$_2$) in the high-fluoride drinking groundwater implies that fluorite dissolution plays a significant role in leaching F$^-$ into the groundwater [5, 43, 46].

The dissolution of other sources of fluoride, including biotite, phlogopite, and hornblende may also cause an increase in the Ca$^{2+}$ and Mg$^{2+}$ content [47, 48]. However, the high-fluoride groundwater samples...
collected in this study had low Ca\textsuperscript{2+} content. This may attributable to the ion exchange interaction between the Ca\textsuperscript{2+} in groundwater and other cations (such as Na\textsuperscript{+}) in clay minerals [49, 50].

The relationship between the Ca\textsuperscript{2+}+Mg\textsuperscript{2+} content and the HCO\textsubscript{3}\textsuperscript{-}+SO\textsubscript{4}\textsuperscript{2-} content is commonly used to analyse water-rock interactions in groundwater [49, 51]. Fig. 5a) shows that 92.86\% of groundwater samples used for drinking water supply sit below the 1:1 dissolution line. This indicates that the dissolution of Ca\textsuperscript{2+} and Mg\textsuperscript{2+} into groundwater is more gradual than that of HCO\textsubscript{3}\textsuperscript{-} and SO\textsubscript{4}\textsuperscript{2-}. This evidence suggests that the dissolution of biotite, phlogopite, and hornblende plays a significant role in the groundwater geochemistry for the study area. Additionally, the high-fluoride groundwater samples contain more HCO\textsubscript{3}\textsuperscript{-} and SO\textsubscript{4}\textsuperscript{2-} (Fig. 5a) than the low-fluoride groundwater samples. Fig. 5b) shows the high Na\textsuperscript{+}/Ca\textsuperscript{2+} ratio (>1), a favourable condition for fluoride dissolution, which suggests that the Ca\textsuperscript{2+} in the high-fluoride groundwater has been exchanged by the Na\textsuperscript{+} in clay minerals, leading to a low Ca\textsuperscript{2+} content [52].

**Evaporation Factor**

The Gibbs map was used to evaluate the contribution of the evaporation process, [5, 25, 53]. The TDS concentrations of the groundwater samples were plotted against the ratios of Na\textsuperscript{+}/(Na\textsuperscript{+}+Ca\textsuperscript{2+}) in Fig. 6a). It was found that 91.30\% of the high-fluoride groundwater samples had Na\textsuperscript{+}/(Na\textsuperscript{+}+Ca\textsuperscript{2+}) values ranging between 0.80 and 1.00. These samples were in the evaporation crystallisation dominance field although outside the rock weathering field and the atmosphere precipitation dominance field (Fig. 6a). As such, evaporation is a dominant factor in geochemistry for increased F\textsuperscript{-} content in drinking water [22, 25, 41].

**Fig. 5.** Plots of a) (Ca\textsuperscript{2+}+Mg\textsuperscript{2+}) versus (HCO\textsubscript{3}\textsuperscript{-}+SO\textsubscript{4}\textsuperscript{2-}) and b) F versus Na\textsuperscript{+}/Ca\textsuperscript{2+} of the drinking groundwater samples.

**Fig. 6.** Plots of a) Gibbs diagram and b) F\textsuperscript{-} versus F\textsuperscript{-}/Cl\textsuperscript{-} of the drinking groundwater samples.
The F/Cl ratio was plotted as a function of F content in Fig. 6b, to investigate the influence of evaporation on the geochemical behaviour of fluoride in drinking water. When rainwater was the source of the F cations, the groundwater samples were around the F/Cl = 0.02 line [5, 16]. Moreover, a high F content and a low F/Cl value in a water body indicates that the main source of F is F-bearing minerals formed during the evaporation process [4]. For 69.57% of the high-fluoride groundwater samples, the F/Cl values exceeded 0.02 mg/L. This indicates that evaporation also contributes to elevated F content in drinking water [16, 54]. Under the influence of evaporation, the concentrations of various ions in groundwater increase, and CO₂ escapes from the water body, resulting in an elevated TDS concentration (Table 1) and the precipitation of dolomite. This produces favourable conditions (low Ca²⁺ and high Na⁺ contents) for the dissolution of F [10].

Cation Exchange

Schoeller [55] proposed two indices (CAI 1 and CAI 2) to determine the possible ion-exchange reactions in groundwater. CAI 1 and CAI 2 may be calculated using Equations (5) and (6) (meq/L):

\[
\text{CAI 1} = \frac{[\text{Cl}^- - (\text{Na}^+ + \text{K}^+)]}{\text{Cl}^-} \quad (5)
\]

\[
\text{CAI 2} = \frac{[\text{Cl}^- - (\text{Na}^+ + \text{K}^+)]}{(\text{SO}_4^{2-} + \text{HCO}_3^- + \text{CO}_3^{2-} + \text{NO}_3^-)} \quad (6)
\]

If CAI 1 and CAI 2 are all positive, the K⁺ and Na⁺ in groundwater have been exchanged for Ca²⁺ and Mg²⁺. In contrast, if CAI 1 and CAI 2 are negative, the Ca²⁺ and Mg²⁺ in groundwater have been exchanged by K⁺ and Na⁺. Finally, if CAI 1 and CAI 2 are 0.00, the ion exchange reaction has not occurred in groundwater [49, 50, 56, 57]. Moreover, the larger the CAI 1 and CAI 2 values, the stronger the ion exchange reaction.

Fig. 7a) shows that the CAI 1 and CAI 2 of high-fluoride groundwater samples were all negative, indicating that the Ca²⁺ and Mg²⁺ in groundwater were exchanged for K⁺ and Na⁺. As a result, the Ca²⁺ and Mg²⁺ contents were lower than the K⁺ and Na⁺ content in drinking water, and the excess K⁺ and Na⁺ balance the HCO₃⁻ and SO₄²⁻ content (Fig. 5a). Fig. 8 shows the X-ray diffraction (XRD) spectrum of a sediment sample obtained from the study area, revealing its mineral composition. Clay minerals, such as montmorillonite and illite, were found throughout the study area, providing the environment for cation exchange [12]. The indices of high-fluoride groundwater samples scatter within a narrow range from -17.34 to -0.31, and from -0.94 to -0.18 for CAI 1 and CAI 2, respectively (Fig. 7a). The CAI 1 and CAI 2 values of the high-fluoride groundwater samples were much higher than the low-fluoride groundwater samples, suggesting that the ion exchange reaction is more intense in the former. As cation exchange contributes to the increase of Na⁺ content in the high-fluoride groundwater, this high Na⁺ content promotes the leaching of F into the groundwater [8, 44]. The process may be described by Equation (7):

\[
\text{Na}_{2}\text{-Clay} + \text{Ca}^{2+} \leftrightarrow \text{Ca-Clay} + 2\text{Na}^+ \quad (7)
\]

The relationship between TDS and Na⁺/(Na⁺+Cl⁻) is another significant piece of evidence demonstrating cation exchange in groundwater. If the Na⁺ content in water is sourced from seawater, the Na⁺/(Na⁺+Cl⁻) value should theoretically be equal to or below 0.50, and the TDS value should be higher than 1000 mg/L. The Na⁺/(Na⁺+Cl⁻) of the collected samples was above 0.50, suggesting the occurrence of cation exchange during the formation of this groundwater resource (Fig. 7b). All samples were also within the ion exchange dominance field (Fig. 6a), indicating that excess Na⁺ in the high-fluoride groundwater originates from cation exchange.
(Dehbandi et al. 2018). The dissolution of calcite and dolomite did not promote Ca\textsuperscript{2+} concentrations due to cation exchange (Equations (1) and (2)).

**Competitive Effect**

In an alkaline environment, OH\textsuperscript{−} and HCO\textsubscript{3}\textsuperscript{−} in groundwater competes with clay minerals for fluoride anions [60]. The F\textsuperscript{−} content in high-fluoride groundwater had a weak positive correlation with the HCO\textsubscript{3}\textsuperscript{−}/(HCO\textsubscript{3}\textsuperscript{−}+Cl\textsuperscript{−}) ratio, as shown in Fig. 9. This suggests that the adsorbed F\textsuperscript{−} on the surface of minerals may be released under high HCO\textsubscript{3}\textsuperscript{−} conditions [10]. As such, the high HCO\textsubscript{3}\textsuperscript{−} environment promotes the enrichment of F\textsuperscript{−} in groundwater by reducing the adsorption capability of minerals [5].

Fig. 3a) shows that the F\textsuperscript{−} concentration in the groundwater had a slight increasing trend in terms of its pH, which may be due to the competitive effect. In an alkaline environment, the surface of minerals is neutral or negatively charged, inhibiting the adsorption of F\textsuperscript{−} and leading to the release of F\textsuperscript{−} into the groundwater [10, 61].

**Anthropogenic Activities**

NO\textsubscript{3}\textsuperscript{−} originates from untreated irrigation water, the infiltration of organic matter, synthetic fertilisers, and runoff from the surrounding agricultural fields [58, 59]; the NO\textsubscript{3}\textsuperscript{−} content in the groundwater exceeds 5 mg/L [5, 59]. The relationship between the F\textsuperscript{−} and NO\textsubscript{3}\textsuperscript{−} concentrations may aid in determining the influence of anthropogenic activities on groundwater.

The drinking water aquifer in this study area is a confined aquifer that exists within an anaerobic reduction environment. The NO\textsubscript{3}\textsuperscript{−} content in the drinking water aquifer should be close to zero. However, 33.81% of the groundwater samples contained NO\textsubscript{3}\textsuperscript{−}, whilst the NO\textsubscript{3}\textsuperscript{−} content in 14.54% of the groundwater samples exceeded the pollution limit (5 mg/L). These results suggest that part of the drinking water aquifer is significantly impacted by anthropogenic activities. The percentage of high-fluoride groundwater samples that contained NO\textsubscript{3}\textsuperscript{−} was 33.33%; this is significantly higher than the low-fluoride groundwater samples (15.78%). The NO\textsubscript{3}\textsuperscript{−} concentrations in two high-fluoride groundwater samples were 8.51 and 5.43 mg/L, respectively. The corresponding F\textsuperscript{−} concentrations in these two samples were 1.42 and 1.96 mg/L, respectively; this was higher than the mean F\textsuperscript{−} concentration (1.42 mg/L). The positive correlation between the NO\textsubscript{3}\textsuperscript{−} and F\textsuperscript{−} content indicates that anthropogenic activities are important factors that contribute to the elevated F\textsuperscript{−} content in drinking water.

**Principal Component Analysis**

To elucidate potential sources of variations in the hydrochemistry of the water resources in the study area, the pH and ion contents were statistically analysed using principal component analysis (PCA) [52, 62]. Three factors were extracted sequentially representing four different F\textsuperscript{−} sources, accounting for 80.99% of the total variables (cumulative) (Table 2).

The first factor (PC1) accounted for 34.47% of the total variables, which respectively, showed positive loadings with the F\textsuperscript{−} (0.56), HCO\textsubscript{3}\textsuperscript{−} (0.62), and Na\textsuperscript{+} (0.40) content and a negative loading with the Ca\textsuperscript{2+} (-0.77) content, suggesting a potential natural source for the dissolution of F-bearing minerals in the study area [16, 52]. The second factor had a negative loading with the Ca\textsuperscript{2+} (-0.77) and Na\textsuperscript{+} (0.40) and K\textsuperscript{+} (0.34) content, indicating that cation exchange also governs the water chemistry [14]. The second component (PC2) accounted for 24.03% of the total variables, exhibiting a positive loading with the Na\textsuperscript{+}, K\textsuperscript{+}, Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, Cl\textsuperscript{−}, TDS, and SO\textsubscript{4}\textsuperscript{2−} content. However, all of these parameters were lower than 0.50, indicating a group effect. The positive loading of the cations (Na\textsuperscript{+}, Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, and K\textsuperscript{+}) explains their natural occurrence in water, potentially
due to weathering and the dissolution of minerals. The increased contribution of anions (SO$_4^{2-}$ and Cl$^-$) and decreased contribution of HCO$_3^-$ (-0.25) was also evidenced in the TDS, which may be attributed to the evaporation effect [52, 62, 63]. The third component accounts for 11.81% of the total variables showing positive loadings with the F$^-$ (0.33) and Mg$^{2+}$ (0.42) and NO$_3^-$ (0.43) content and pH (0.27), and negative loadings with the HCO$_3^-$ (-0.43) content; this may be a possible source for the competitive effect. The final component (PC4), was the lowest and accounted for 10.68% of the total variables. It showed only a strong correlation (0.68) with the NO$_3^-$ content, which was sourced from anthropogenic activities.

**Fluoride Formation Mechanisms Discussion**

Fig. 10 provides a schematic that elucidates the fluoride enrichment process for the groundwater in the study area.

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**Table 2. The PCA date for F- sources of the study area.**

| Variable | Component 1 | Component 2 | Component 3 | Component 4 |
|----------|-------------|-------------|-------------|-------------|
| pH       | 0.3942      | -0.0742     | 0.2720      | 0.1114      |
| Na$^+$   | 0.4047      | 0.2436      | -0.3459     | 0.0338      |
| K$^+$    | -0.3368     | 0.0017      | -0.3002     | -0.1449     |
| Ca$^{2+}$| -0.7689     | 0.4217      | -0.0529     | 0.4245      |
| Mg$^{2+}$| -0.0126     | 0.3826      | 0.4312      | -0.5276     |
| Cl$^-$   | 0.1819      | 0.4828      | 0.0090      | -0.0666     |
| SO$_4^{2-}$ | 0.2156   | 0.4843      | -0.0191     | 0.2145      |
| HCO$_3^-$ | 0.6237     | -0.2461     | -0.4331     | -0.1120     |
| F$^-$    | 0.5619      | -0.2097     | 0.3255      | -0.3185     |
| NO$_3^-$ | 0.1215      | -0.2382     | 0.4306      | 0.6849      |
| TDS      | 0.4538      | 0.4019      | -0.2197     | 0.0186      |
| % of variance | 34.47 | 24.03      | 11.81       | 10.68       |
| Cumulative % | 34.47 | 58.50      | 70.31       | 80.99       |

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Fig. 10. Mechanism of the formation of the high-fluoride drinking groundwater (left to right).
It is proposed that the initial F in groundwater is mainly sourced from the weathering of F-bearing minerals, cation exchange, the competitive effect, and agricultural activities. The initial hydro-chemical facies of the groundwater was the Na·Mg-HCO$_3$ type. With the gradual reduction in groundwater flow, an increasing amount of CO$_2$ dissolves, causing a rise in the pH of groundwater, whilst the TDS of groundwater gradually increases. With Ca$_2^+$ precipitation, the TDS and Na$^+$ content in groundwater had become the dominant factors, and the diversity of hydro-chemical facies of the groundwater had increased (Na·Mg-HCO$_3$ type and Na·Mg-HCO$_3$·SO$_4$ type).

The increases in pH, HCO$_3^-$, and TDS provided suitable conditions to form high-fluoride content water. The weathering of F-bearing minerals and cation exchange with clay minerals promoted the dissolution of F into the groundwater system. Additionally, agricultural activities and competitive effects were important factors that contributed to the elevated F content. All of these factors contributed to fluoride enrichment in the groundwater beyond the permissible limits as per China’s drinking water regulations, generating a drinking water supply that is considered to have a high content of fluoride.

**Conclusions**

Few studies exist on the spatial distribution and geochemical behaviour of F in drinking water aquifers in coal-mining areas. As such, the sources and mechanism behind high-fluoride groundwater have not yet been fully understood. The present study attempts to understand the spatial distribution of F in groundwater used as a drinking water source in the Sulin coal-mining district. It also identifies major geochemical processes and formation mechanisms controlling the fluoride content in this groundwater resource. The findings of this study include:

1. The F concentrations in the groundwater samples were between 0.16 and 2.06 mg/L, with a mean of 1.11 mg/L. In addition, 54.76% of the groundwater samples exceeded China’s national standards (1.00 mg/L);

2. The high-fluoride groundwater (>1.00 mg/L) had a higher pH and HCO$_3^-$ content compared to the low-fluoride groundwater (<1.00 mg/L). The hydro-chemical facies reflect that low-fluoride groundwater was confined to the Na·Mg-HCO$_3$ type. Hydrogeochemical investigations revealed that the fluoride content was associated with the Na·Mg-HCO$_3$·SO$_4$ and Na·Mg-HCO$_3$ types;

3. Several geochemical processes, such as evaporation, F-bearing mineral dissolution, cation exchange, competitive effects, and anthropogenic activities, were identified as the primary mechanisms for F enrichment in the groundwater. PCA also demonstrated that F also increased the contribution of the HCO$_3^-$ and Na$^+$ content and decreased the contribution of Ca$_2^+$ in PC1 (34.47%). This indicates that F-bearing minerals were the main source of F in the groundwater. Positive loadings of Na$^+$, K$^+$, Ca$_2^+$, Mg$_2^+$, Cl$^-$, TDS, and SO$_4^{2-}$ in PC2 (24.03%) suggested an evaporation effect. The positive loadings with F, pH, NO$_3^-$, and negative loadings with HCO$_3^-$ in PC3 (11.81%), indicate the potential for the competitive effect.

The increased in pH, HCO$_3^-$, and TDS provided suitable conditions to form high-fluoride content water. The weathering of F-bearing minerals and cation exchange with clay minerals promoted the dissolution of F into the groundwater system. Additionally, agricultural activities and competitive effects were important factors that contributed to the elevated F content. All of these factors contributed to fluoride enrichment in the groundwater beyond the permissible limits as per China’s drinking water regulations, generating a drinking water supply that is considered to have a high content of fluoride.

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**Conflict of Interest**

The authors declare no conflict of interest.

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