



Characteristics and effects of fluorine release from shallow high-fluoride soils

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Abstract

Areas with high fluoride content in shallow groundwater are usually also the areas where drinking-water endemic fluorosis was found, for example, in Gaomi, China. In recent decades, with the development of industry and agriculture and the improvement in living environments, the groundwater level has slowly declined, and the former high-fluoride conditions of shallow water-soil systems has changed. Shallow high-fluoride soils will release a large amount of fluorine downward under the leaching of rainfall, which poses a potential risk to the deep water-soil system. To evaluate the characteristics and effects of fluorine release from shallow high-fluoride soils, five soil samples were collected to conduct a static fluorine release experiment and a soil column leaching experiment. The results indicated that the release of fluorine from soils conforms to the Elovich model, and in the soil profile, the fluorine release gradually moves from up to down along the runoff direction. Components, such as Ca^{2+} , Mg^{2+} , K^+ , Cl^- and HCO_3^- , together with F^- , leached from the soil and migrated downward. With increasing leaching time, the concentrations of soluble salt components gradually decreased, the pH values increased, and the dissolution equilibrium of fluorite shifted toward the dissolution direction.

Keywords Characteristics of fluorine release · Groundwater · Hydrochemical · Shallow high-fluoride soil

Introduction

Fluorine is widely distributed in nature and is an essential trace element for the human body. Drinking water containing too much or too little fluorine is not conducive to human health. Shallow groundwater, as the main source of drinking water for humans, often causes regional fluorosis when its fluorine content is too high, which has been reported all over the world (Annadurai et al. 2014; Pillai and Stanley 2002; Singh et al. 2018; WHO 2006; Yadav et al. 2016). In Gaomi city, Shandong Province, China, due to the paleogeological environment and paleoclimatic conditions, there is a typical endemic fluorosis area caused by shallow groundwater with high fluoride content used as drinking water in northern

China (Feng et al. 2015; Gao et al. 2013, 2014a, b; Han et al. 2014; Li et al. 2008; Wang et al. 2011). In the past 2 decades, drinking water improvement measures implemented by local government, drilling deep wells to extract deep groundwater with lower fluorine content as drinking water and as part of the irrigation water for residents have greatly improved regional fluorosis (Chen et al. 2012a; Ge et al. 2002, 2004; Yun et al. 2011, 2014). With the development of local industry and agriculture and the improvement in the living environment, groundwater exploitation has gradually increased, the groundwater level has slowly declined and the original conditions of shallow water-soil systems with high fluoride have changed. After the decline in groundwater level, soils in the unsaturated zone still contain a large amount of fluorine. Under long-term leaching by rainfall and deep groundwater with low fluoride content, a large amount of fluorine will be released from shallow soils and migrate downward with the potential to damage deeper aquifers.

In a water-soil system, fluorine is in the two geochemical equilibrium processes of enrichment and release, specifically the adsorption and desorption of fluorine between the soil and groundwater. These two processes are influenced by many factors, such as geochemical characteristics

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and clay minerals in the soil, pH and salinity of the soil solution, climate, particle size and agricultural activities (Vijaya et al. 2016; Wang et al. 2017; Wei et al. 2016). Studies have shown that soluble salt components and the mineral composition of soils have certain influences on desorption and migration of fluorine. The content of soluble fluorine in soils most likely increases with the increasing clay content (Fung et al. 1999; Kafri et al. 1989; Pickering 1985; Ren and Jiao 1988). In addition, the pH value and concentrations of Ca^{2+} , HCO_3^- and H_2PO_4^- in the soil solution are closely related to the adsorption–desorption of fluorine on the soil surface (Zhu et al. 2015). Temperature and the value of Ca/Na are also important factors affecting fluorine release from soil (Du and Liu 2010). In addition, rainfall (Dissanayake 1979), agricultural use intensity, natural vegetation and even grazing (Reid and Horvath 1980) will affect the adsorption and desorption of fluorine by clay minerals. There have been many studies on the influencing factors of adsorption–desorption equilibrium of fluorine in water–soil systems. From another point of view, it can be found that these factors that affect fluorine adsorption–desorption equilibrium also change in the adsorption or desorption processes. In the soil fluorine release experiment, higher pH conditions are beneficial to fluorine release because of the substitution of F^- and OH^- . Therefore, increases in F^- can decrease OH^- so that the pH value will decrease with the fluorine release (Liu 2011). In addition, the conductivity of the soil solution will also decrease with fluorine release in a soil column leaching experiment, which indicates a decrease in the soluble salt content during the process of fluorine release (Zong et al. 2008).

In this paper, the characteristics of fluorine release from shallow high-fluoride soils were studied by soil fluorine release experiments and soil column leaching experiments. We discuss the characteristics and effects of fluorine release and associated hydrochemical changes under long-term leaching with a low fluorine solution.

Materials and methods

Materials

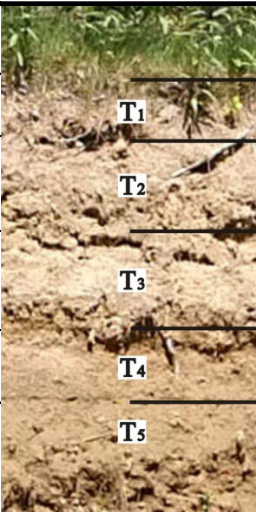
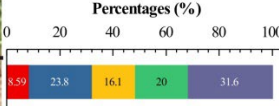

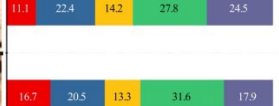
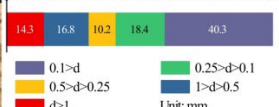

Five soils (in the same soil profile) used in this study were collected from the typical fluorosis area in Gaomi city, Shandong Province, China. Because of the special geographical conditions and historical reasons, this area was once one of the serious fluorosis areas in China (Gao et al. 2014a). The groundwater fluorine concentrations are generally approximately 5 mg/L and the highest value has reached 18 mg/L. The soil profile and descriptions of the five soil samples are shown in Table 1.

Methods

Soil fluorine release experiment

The soil fluorine release experiment belongs to the category of chemical kinetic experiments. Chemical kinetic experiments mainly study the influence of various external factors on the reaction rate and the relationship between the structure and properties of substances and the reaction rate, explore the possible mechanism that can explain the reaction

Table 1 Soil profile and particle composition of soil samples

No.	Description	Thickness (cm)	Soil profile	Particle composition
0	Vegetation: grassland	10–20		
T ₁	Humus layer : loam, root system rich	10	T ₁	
T ₂	Leaching layer A: sandy soil has roots	22	T ₂	
T ₃	Leaching layer B: silty soil has roots	23	T ₃	
T ₄	Sedimentary layer A: sandy soil	15	T ₄	
T ₅	Sedimentary layer B: silty soil has small granular calcareous concretions	>10	T ₅	

rate law, reveal the chemical reaction process, identify the key factors that determine the reaction rate, and propose the optimal control of the reaction (Lin 2003). A soil fluorine release experiment is also a common method for studying the hydrogeochemical behavior of fluorine in groundwater. In this paper, the soil fluorine release experiment was carried out as follows: (1) soil samples of T₁–T₅ were air dried and sifted through a 1 mm sieve. (2) Twelve small samples, each 10 g, were taken from each soil sample, and placed into plastic bottles with a capacity of 130 ml. (3) 100 ml of distilled water was added to each bottle according to a solid–liquid ratio of 1:10 and the bottles were put on a horizontal shaker with a frequency of 200 rpm. (4) Timing was started and the F[−] concentrations of the supernatant in the bottles were detected at 0.5, 1, 2, 3, 5, 8, 12, 17, 24, 36, 48 and 72 h.

Soil column leaching experiment

The soil column test device can be divided into undisturbed soil column, seepage sampling soil column, backfill soil column and groundwater exchange soil column test devices according to different structures and functions (Zhao et al. 2011). The backfill soil column was used in this study and filled with soils collected from the soil profile in the field according to the order and occurrence (Table 1). In the experiment, the water stop valves of the K₁–K₈ outlets were opened only when sampling. No water stop valve was installed in the K₉ outlet, and the outflow of leachate was collected separately without sampling (Fig. 1). The experiment began after the soil column was saturated with distilled water. The leachates were collected from each outlet according to a certain time interval and the pH values and F[−] and Cl[−] concentrations of the leachates were detected. In parts of

the leachates, the concentrations of HCO₃[−], Ca²⁺ and Mg²⁺ were also detected. The soil samples T₁–T₅ were collected before and after the experiment for the soil fluorine release experiment, and the changes in soluble fluorine contents in the soils following completion of the soil column fluorine release experiment were compared. In the experiment, a total of 391 water samples were collected from the leachate 44 times over 1046 h, and a total of approximately 300 L distilled water was used.

In both the above experiments, F[−] concentrations in the leachate were detected by the fluoride ion selective electrode method, the pH value by a pH meter, the HCO₃[−] by the titration method, and Ca²⁺ and Mg²⁺ were detected using an atomic absorption spectrophotometer. The F[−] concentrations of the distilled water used in the experiments were detected as 0.01 mg/L, pH 7.14.

Results

Soil fluorine release experiment

The results of the soil fluorine release experiment are shown in Fig. 2. The F[−] concentration of supernatants from the five soil samples changed similarly. At the beginning of the experiment, the F[−] concentration increased rapidly and then slowed down gradually. Among the five soil samples, the F[−] concentration of T₃ increased fastest in the rising stage. With the continuation of the experiment, desorption and adsorption of fluorine alternated between the soil and distilled water, but the overall trend of the fluorine was to remain desorbed and release from soil into the distilled water. The F[−] concentration of the supernatants ranged from 1.50 mg/L to 5.06 mg/L, and the amount of fluorine desorbed from the T₁–T₅ soil samples reached 24.49 mg/kg, 32.20 mg/kg, 33.49 mg/kg, 34.83 mg/kg and 49.53 mg/kg, respectively. The amount of fluorine released from soil samples T₁–T₅ increased gradually with depth from shallow to deep. The shallow high-fluorine soils are leached by low-fluorine rainwater under natural conditions for a long term, so the water-soluble fluorine in shallow soils is continuously leached. Whereas the deep soils are less leached by this effect or else have adsorbed the fluorine that leached from the shallow soils, which may be a major cause of the increase in water-soluble fluorine content in soils from shallow to deep. In the soil profile of this study, with the increase in depth, the content of calcareous minerals in the soil increased, and calcareous concretions appeared in soil samples T₄ and T₅, which was commonly called “Jiangshi”. The content of fluorine increases with the increase in soil calcium minerals, which leads to more desorption of water-soluble fluorine in deep soil than in shallow soil. The increase or changes in soil fluoride content with depth may

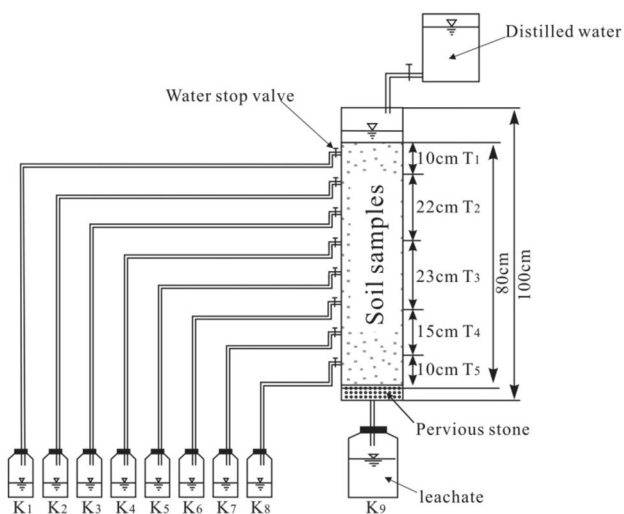
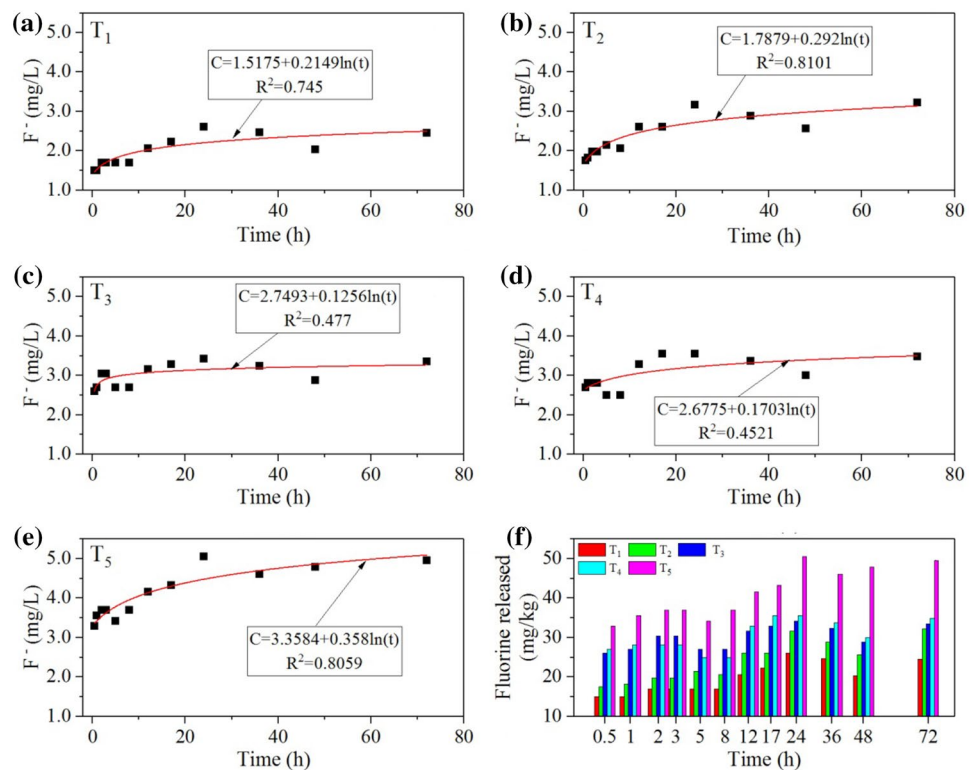


Fig. 1 Schematic diagram of the soil column leaching experiment apparatus

Fig. 2 Plots of the fluorine release of soils T₁–T₅



be another reason for the increase in the water-soluble fluorine content of soils with depth.

Soil column leaching experiment

The soil column leaching experiment simulated the long-term leaching process of the soil profile by rainfall with low fluorine content in the field. In the experiment, with the leaching process the F⁻ concentrations of the leachates from each outlet had different changes but also reflected a certain regularity. Figure 3 shows the change in fluorine content in leachate collected from the soil column during the experiment.

As shown in Fig. 3a, there is a downward moving peak of the F⁻ concentration of leachate in the soil column in the longitudinal direction during the experiment. At 0 h, the peak is located at 60–70 cm in the soil column, and at 62 h, it has moved down to 50–60 cm. With the downward moving of the peak, the F⁻ concentration in leachate from the upper soils in the soil column decreased continuously, while that of the leachate from the lower soils increased relatively. After continuous leaching by low-fluorine distilled water, a low-fluoride area was generated and gradually extended downward, and a large amount of fluorine was released from the soils and discharged from the soil column with the runoff of distilled water. Figure 3c shows the changes in the F⁻ concentration from high to low in different positions in the soil column. The reduction rate of the F⁻ concentration

in the upper part of the soil column is higher than that in the lower part. However, the release rate of fluorine was relatively stable for the whole soil column, and the average rate of F⁻ concentration reduction was about 1.55×10^{-5} mg/L h. Figure 3b shows more intuitively the downward movement of the F⁻ concentration peak, and at the end of the experiment, the peak has basically disappeared from the bottom of the soil column.

In the soil column leaching experiment, there was a total of 983.4 mg of fluorine released from the soils to the distilled water in the soil column. After the experiment, the contents of water-soluble fluorine in soil samples T₁–T₅ were determined, and the results (Table 2) showed that a large amount of fluorine was released into the distilled water, and the release of water-soluble fluorine reached 50.36–75.46%.

Hydrochemical changes in the process of fluorine release

Figure 4 shows the changes in ions of Cl⁻, HCO₃⁻, Ca²⁺, Mg²⁺ and K⁺ and the pH of the leachates during the soil column leaching experiment. The concentrations of various ions decreased continuously during the experiment, which indicated that the release of fluorine and the dissolution of various minerals in the soil increased the dissolved salt content of the distilled water. However, with the extension of the leaching by distilled water the dissolution of minerals gradually decreased, and the loss of ions caused by distilled

Fig. 3 Characteristics of fluorine release in the soil column. **a** Time spectrum of F⁻ concentration in the soil column; **b** curves of the distribution of F⁻ concentration in the soil column at different times (50, 400 and 900 h); **c** changes in F⁻ concentration at different positions (K₂, K₅, K₈) in the soil column

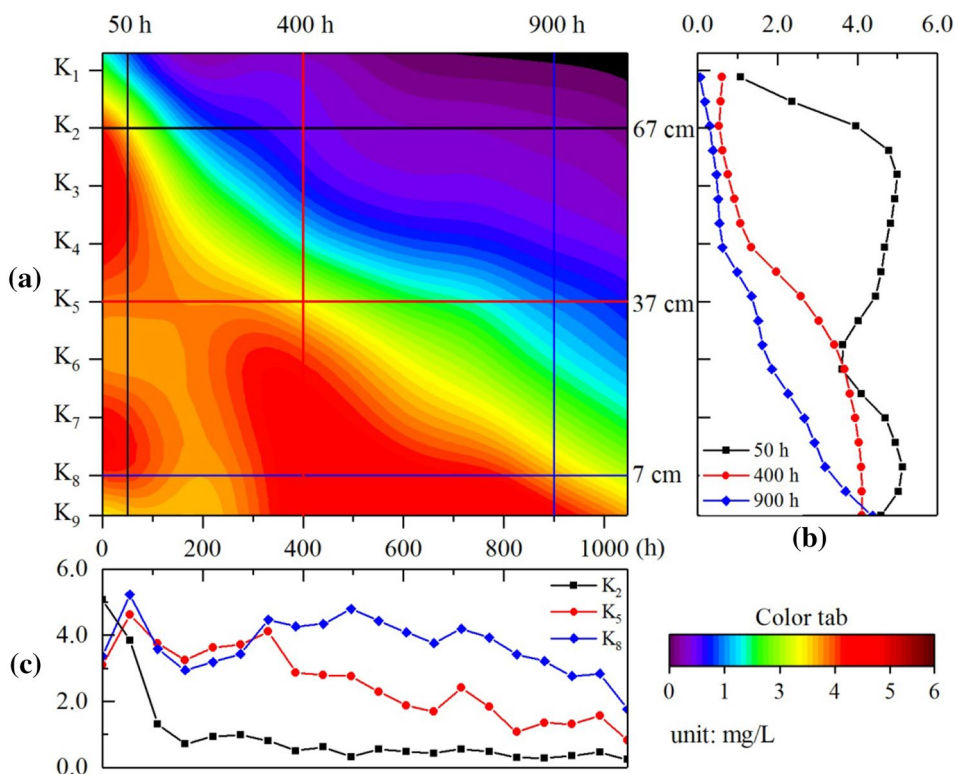


Table 2 Soil-soluble fluorine content before and after the test

No.	Before	After	Release	Release percentage (%)
T ₁	24.49	6.01	18.48	75.46
T ₂	32.20	8.55	23.65	73.45
T ₃	33.49	11.69	21.80	65.09
T ₄	34.83	17.29	17.54	50.36
T ₅	49.53	23.65	25.88	52.25

Unit: mg/kg

water runoff could not be compensated. According to the experimental results, the average concentration of different ions in the leachates collected from each outlet at the same time was calculated, and a scatter plot of the relationship between the averages and test time is drawn in Fig. 5. Among the several ions, the Cl⁻ concentration declines most rapidly from 0 h to 86 h, dropping from 39.83 to 1.19 mg/L, a decrease of 97%, which is related to its own characteristics that are not easily absorbed as a conservative element. Compared with Cl⁻, the dissolution and release of other ions are relatively slow. Throughout the experiment, changes in the concentrations of Ca²⁺ and Mg²⁺ are similar. The rate of dissolution and release of Ca²⁺ and Mg²⁺ decreased continuously, and the average concentrations of Ca²⁺ and Mg²⁺ in

the leachates were 20.13 mg/L and 29.92 mg/L, respectively, at the end of the experiment. The decrease in K⁺ was slight in the experiment, which was obviously different from the other ions. The change in HCO₃⁻ is related to the change in the organic matter content of soils during the leaching process (Gray 2018). The pH increased gradually with the release of fluorine. At the end of the experiment, the average pH value of the leachate increased from the initial value of 7.99–8.81. This is the result of water-soil reactions under long-term leaching, which characterizes the changes in the conditions of fluorine release.

Discussions

Characteristics of fluorine release from shallow high-fluoride soils

The process of soil fluorine release from soil is a dynamic process in which desorption and adsorption of fluorine exist simultaneously in the water-soil system. When the rate of desorption is higher than that of adsorption, it is shown that fluorine is released from the soil to water. In contrast, fluorine is adsorbed from the water by the soil. The rates of desorption and adsorption were controlled by many factors, such as the content of fluorine in the soil and water and the hydrogeochemical conditions of the water-soil system. The

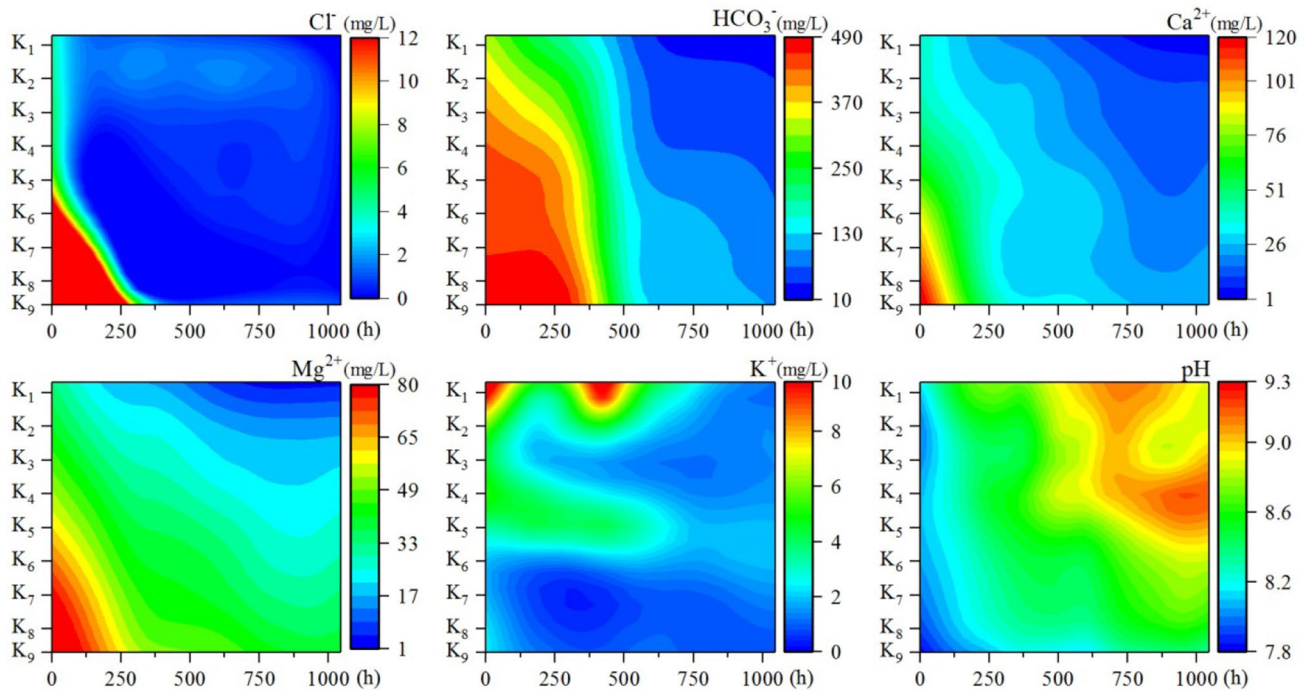


Fig. 4 Time spectrum of ion concentrations of leachate in the soil column

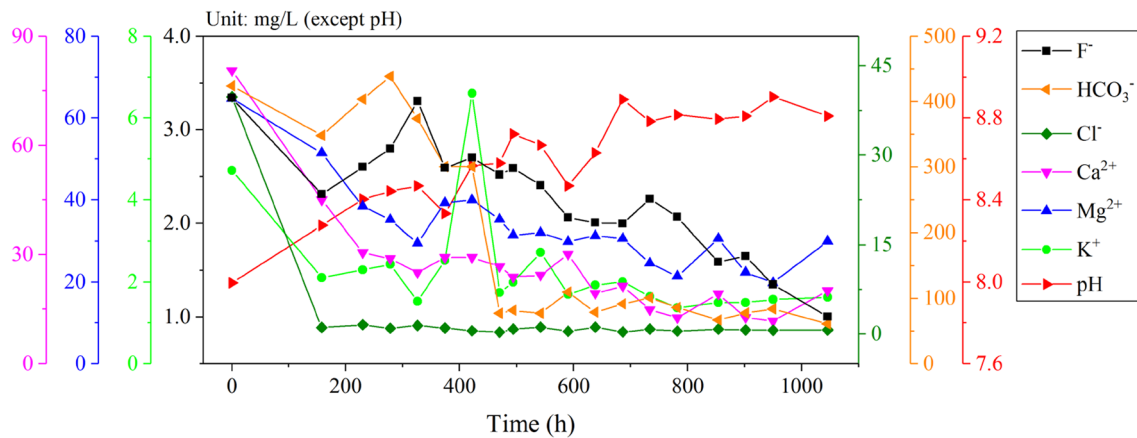


Fig. 5 Relationship between the averages of ion concentration and time

vertical distribution of fluorine in shallow soils has a certain regularity due to the influence of regional geology, climate and other environmental conditions. The total soil fluorine concentrations decreased from 0 to 50 cm, but increased significantly from 50 to 100 cm in the research of Gray (2018). In this paper, the vertical distribution of fluorine in shallow soil showed a gradual increase, from 0 to 80 cm, and the content of water-soluble fluorine increased from 24.49 to 49.53 mg/kg. The difference between Gray and this study lies in the source of the fluorine. In Gray’s research, chemical fertilizer is an important source of fluorine in the shallow

soil. However, in Gaomi city, the source of fluorine in shallow soil is mainly its own fluorine-bearing minerals (Gao et al. 2014a; Li et al. 2008). The vertical increase in fluorine content in shallow soil may be due to the long-term leaching of low-fluoride rainfall (Wang et al. 2018), and the results of the soil column leaching experiment in this paper can provide good evidence.

In the soil column leaching experiment, under the vertical one-dimensional leaching by distilled water, the upper soils in the soil column preferentially received the leaching by the lower F⁻ concentration of the distilled water, and the

water-soluble fluorine was released to the maximum extent. The release of fluorine from the lower soils was relatively delayed, and sometimes fluorine released from the upper soil was adsorbed from leachate with higher F⁻ concentration. This explains the results of the soil fluorine release experiment in which the water-soluble fluorine content of soil samples T₁–T₅ increases with depth. For the soil profile of this study, when distilled water forms long-term vertical runoff or seepage in the soil, a large amount of fluorine in the soil can be released to a maximum extent and reduced to a lower level. When fluorine content in a layer of soil in the vertical profile is higher than that in the underlying soil and when the fluorine content in the underlying soil is unsaturated, the underlying soil will first absorb and then release. This fluorine release process was completed in a top-down sequence (Zhang 2005).

In addition, the release of fluorine from soil is slow. In the soil fluorine release experiment, in the first 2 h, the F⁻ concentration of the supernatants of soil samples T₁–T₅ reached a range of 1.69–3.70 mg/L, but at the end of the experiment (72 h), the F⁻ concentrations were only in the range of 2.45–4.95 mg/L (Fig. 2). In the soil column leaching experiment, taking the K₂ outlet data as an example, from 0 to 86 h, the F⁻ concentration decreased from 5.08 mg/L to 1.2 mg/L, and at the end of the experiment (1046 h), it only decreased to 0.24 mg/L. The rate of fluorine release from the soil was faster in the initial stage. With a decrease in the fluorine content of the soil, the rate of fluorine release slows down (Liang et al. 2014; Ying et al. 2014).

The fitting results of the F⁻ concentration of the supernatant of soil samples T₁–T₅ show that the fitting curves of fluorine release from different soil samples conformed to the distribution characteristics of logarithmic curves (Fig. 2). Fitting equations of the five soil samples are basically consistent with the expansion form of the Elovich model. Therefore, we considered that the reaction rate model of fluorine release from soil samples conforms to Elovich’s form. The basic form of Elovich model is as follows (Liang 2008):

$$\frac{d(C - C_0)}{dt} = k_1 e^{-k_2 C}, \tag{1}$$

where *C* is the F concentration of supernatant, mg/L; *C*₀ is the F concentration of the distilled water, 0.01 mg/L; and *k*₁ and *k*₂ are the reaction rate constants.

For Eq. (1), integral changes are made as follows:

$$C - C_0 = \frac{1}{k_2} \ln(k_1 k_2) + \frac{1}{k_2} \ln t. \tag{2}$$

Hydrochemical changes in the fluorine release process

Fluorine has a more active chemical property. It can exchange and complex with different ions in groundwater

(Liu and Xu 2010). The release of fluorine from soil can not only change the concentration of fluorine in the groundwater, but also change the content of different ions through a series of reactions. Therefore, the content of F⁻ and other ions in groundwater affects each other in the process of fluorine release from soil. Figure 6 is a Pearson correlation heatmap of ions of leachates in the soil column leaching experiment. The hierarchical cluster analysis classifies the chemical indicators measured in the experiment into three clusters: the first is F⁻, TDS, HCO₃⁻, Ca²⁺, Mg²⁺ and Cl⁻; the second is K⁺; and the third is pH. The three clusters of chemical indicators have different changing characteristics as described above. In addition, the three clusters also indicated the degrees of interaction among ions and pH and TDS. The higher positive correlation between F⁻ and TDS indicates that the change in TDS affects F⁻ concentration, and F⁻ concentration can indicate the content of TDS (Zong et al. 2008). The correlation between HCO₃⁻, Ca²⁺, Mg²⁺, Cl⁻ and F⁻ decreases in turn, which indicates that the participation of ions in fluorine hydrochemical reactions decreases in turn. There is a good inverse correlation between pH and F⁻, which seems to be contrary to the conclusions of some studies (Liu et al. 2009, 2011a, b; Sun et al. 2013; Wang et al. 2018; Zhu 2009). The reasons are as follows: under the continuous leaching of distilled water, F-containing minerals in soils in the soil column are dissolved continuously, the content of F-containing minerals is reduced, and the dissolution is reduced, so the reduction in the F⁻ concentration of leachates will be inevitable. To promote the dissolution of more F-bearing minerals in soils in the water-soil system of the soil column, it is natural that the increase in pH will lead to a more favorable hydrochemical environment for the dissolution of F-bearing minerals (Mondal and Gupta 2014).

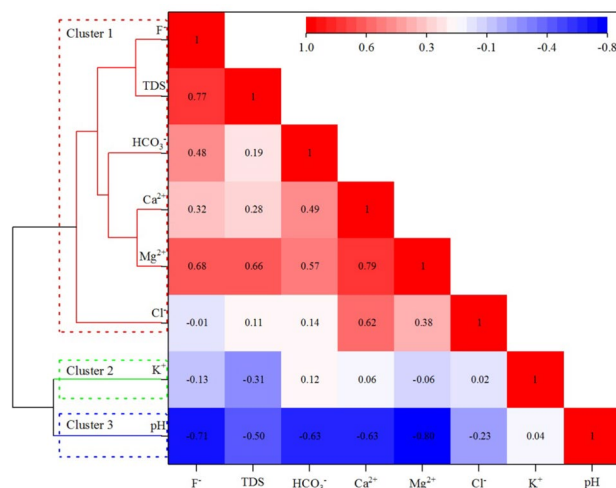


Fig. 6 Pearson correlation heatmap of ions of leachates in the soil column leaching experiment

For the same reason, on one hand, the decrease of Ca^{2+} and Mg^{2+} formed the conditions conducive to the dissolution of F-bearing minerals, but the more important reason is that the dissolution rate of related minerals slows down, which is similar to the reason for the decrease in F^- concentration. However, the decrease in HCO_3^- may be related to the decrease in organic matter content of the soils under long-term leaching by distilled water (Kumar and Anshumali 2016; Wang et al. 2018).

Many studies note that the inverse correlation between F^- and Ca^{2+} is often observed in the saturation state (Ozsath 2009), because the maximum concentration of fluorine is generally restricted by CaF_2 (Apambire et al. 1997; Cronin et al. 2000; Saxena and Ahmed 2003). In the soil column leaching experiment, the pH values of the leachates are weak alkaline, which may reduce the concentration of Ca^{2+} in the solution (Chen et al. 2012b; Kouzana et al. 2009), promote the dissolution of fluorine and cause the dissolution reaction of CaF_2 to proceed in the direction of dissolution.



In the dissolution of CaF_2 , at equilibrium, the aqueous concentrations obey the solubility product:

$$K_{\text{fluorite}} = [\text{Ca}^{2+}][\text{F}^-]^2 = 10^{-10.57} \text{ at } 25^\circ\text{C}. \tag{5}$$

On a logarithmic plot, the equilibrium condition (Eq. (5)) between CaF_2 and the solution is a straight line, as shown in Fig. 7. All combinations of Ca^{2+} and F^- that plot below the line are subsaturated with respect to CaF_2 , while those that plot above the line are supersaturated for CaF_2 (Appelo and Postma 2005). Figure 7 shows that the dissolution strength of CaF_2 in the soil column leaching experiment is constantly changing. With the gradual progress of the experiment and the decrease in concentrations of Ca^{2+} and F^- , combinations of Ca^{2+} and F^- are farther and farther away from the equilibrium line. This indicates that the long-term leaching by the distilled water takes away a large amount of fluorine from the soils and changes the high-fluorine state of the original water-soil system to the low-fluorine state. However, because of the gradual decrease in the content of F-bearing minerals in the soils, the dissolution of F^- and other ions decreases. It is no longer possible to compensate for the loss of ions

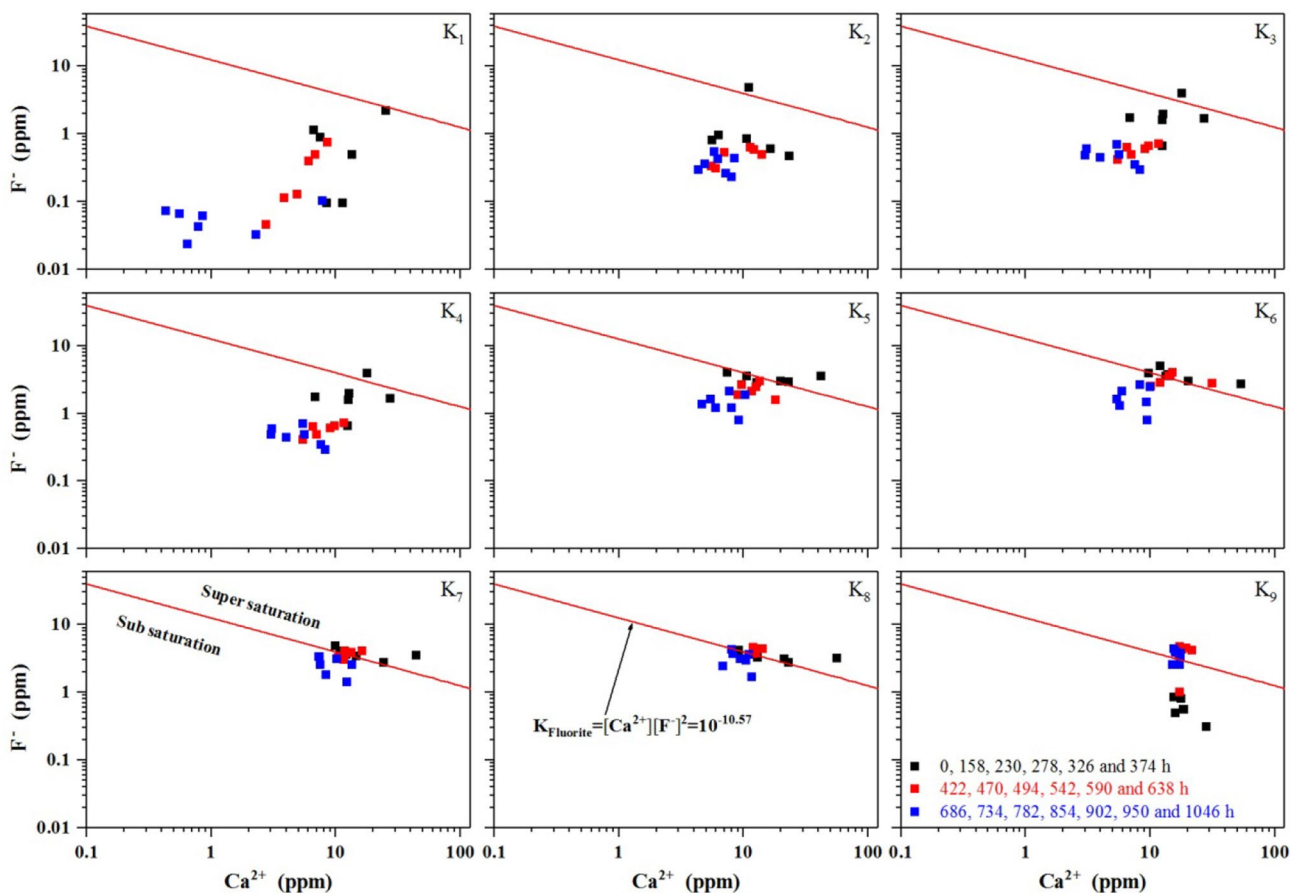


Fig. 7 Plots of combinations of Ca^{2+} and F^- in the dissolution equilibrium of CaF_2

carried by the distilled water runoff, and the demand for the dissolution of fluorite and other minerals is increasing. As a result, the concentration of F^- and other ions gradually decreased with the continuation of the experiment. In addition, the figures of different outlets of K_1 – K_9 in Fig. 7 show that the combinations of Ca^{2+} and F^- were close to the dissolution equilibrium of CaF_2 from K_1 to K_9 . This was synchronized with the gradual increase in F^- concentrations in the leachate from K_1 to K_9 in the soil column, which indicated that the F^- concentrations have a great influence on the dissolution of CaF_2 in the water-soil system.

Conclusions

Fluorine release from shallow high-fluoride soils is a potential threat to regional groundwater safety. After stratified sampling of the shallow high-fluoride soil profile in the field, the characteristics of fluorine release in the shallow high-fluoride soil profile were studied by soil fluorine release experiments and soil column leaching experiments, and the characteristics and effects of fluorine release in the shallow high-fluoride soil profile were discussed. The results indicated the following:

1. Fluorine release from high-fluoride soils is a slow process, and the rate equation of fluorine release conforms to the Elovich model. The release of fluorine in the shallow high-fluoride soil profile is gradually along the direction of runoff (vertical in this study), with preferential release from upstream soils. The content of fluorine in the lower soils may also increase during the process of fluorine release, which is due to the leaching of higher F^- concentration solutions from the upper soils. The vertical increase in the fluorine content of the shallow soil profile in the field (from top to bottom) is the result of long-term leaching by rainfall.
2. Fluorine in high-fluoride soils was fully released by long-term leaching by distilled water. At the same time, a large amount of other soluble salts were dissolved from the soils and migrated downward with the distilled water along with F^- . With increasing leaching time, the release of F^- and other ions and the concentration of F^- and other ions in the leachate gradually decreased, the pH value increased, and the dissolution equilibrium of CaF_2 increased in the direction of unsaturation.

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