Fluorine Speciation in Loess in The Shaanxi Loess Plateau, Related Quality Assessment And Exposure Risks Implication

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Research Article

Keywords: Fluorine speciation, Loess, Exposure, Risk, High-fluoride groundwater

Posted Date: November 9th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-1032899/v1>

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Fluorine speciation in loess in the Shaanxi Loess Plateau, related quality assessment and exposure risks implication

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Abstract

In this study, distributing characteristics of five fluorine (F) species in loess in the Shaanxi Loess Plateau (SLP) were determined including unextractable residual F (F_{re}), extractable water-soluble F (F_{ws}), exchangeable F (F_{ex}), F bound to Fe-Mn oxides (F_{fm}), and F bound to organics (F_{or}). The results show that unextractable F_{re} represents most percentage of F_{tf} in loess. Of the four extractable F species, the content of F_{ws} is higher than the other three extractable F species in most loess samples. The loess in the southeast SLP has the highest F_{ws} content while the loess in the southwest has the highest F_{tf} content. And the loess in the north SLP contains the lowest overall concentrations of F_{tf} and F_{ws} . Similar to F_{ws} , the respective content of F_{ex} , F_{fm} , and F_{or} in the loess is also very low. However, the total of them and F_{ws} cannot be negligible for F mobility in loess. Overall, the loess in the SLP can be assessed as inferior quality in terms of F as a result of high F_{ws} content in most samples. Based on the F speciation in the loess, F exposure to grazing animals and humans, in fact to children, was assessed, indicating that F in the loess in the southwest SLP might pose a much greater risk to grazing animals than in other part of SLP as the loess contains more F_{tf} . However, there is no concern for the children's exposure to loess F via ingestion in the study area in the present condition. As for the loess F risk to groundwater, it can be concluded that not only F_{ws} but also the other extractable F including F_{ex} , F_{fm} and F_{or} in loess may be responsible for the F enrichment in local groundwater in the area with the aid of the characteristics of F speciation in loess and distribution of local high-fluoride groundwater.

Key words: Fluorine speciation; Loess; Exposure; Risk; High-fluoride groundwater

Introduction

Fluorine (F) is a critical element for animals and humans, particularly for the development of bones and dental enamel (Loganathan et al. 2006; Jha et al. 2011; WHO, 2017). It has a beneficial effect on health only if the F intake amount is not in excess of the limit dose. Otherwise, harmful effects

would have on animals and humans like dental and skeletal fluorosis (Fewtrell et al. 2006). Soils are a source of F for the biosphere (Davison and Weinstein 2006). Highly enriched F in soils may constitute potential risks for animals and humans. For animals, previous studies showed that grazing animals were faced with potential fluorosis due to large rates of ingestion of high-fluorine soil (Cronin et al. 2000; McLaughlin et al. 2001). In this case, total F (F_{tf}) content in soils was considered responsible for the fluorosis risk to grazing animals (Loganathan et al. 2006). On the other hand, for humans, soil intake may also cause potential exposure risks to environmental contaminants, particularly for young children sometimes with up to 10 times more soil ingested than adults, per kilogram body weight (Egeghy et al. 2007). To evaluate whether high-F soils would pose direct potential risk to humans, it is not enough just to determine F_{tf} content in soil. This is because exposure to contaminants via ingestion of soil also depends on combined ingestion rate of soil, and relative oral bioavailability in the human body for contaminants in soil besides their content (Bierkens et al. 2011). The relative oral bioavailability of F in the human body is governed by many factors and hard to assessed. In comparison, water-soluble fluorine (F_{ws}) in soils may be more easily determined and it is bioaccessible F in a labile form, which closely reflects the mobility of soil F (Xie et al. 1999; Cronin et al. 2000; Loganathan et al. 2006; Yi et al. 2013). Therefore, it is reasonable and feasible that F_{ws} is used in the assessment of human's exposure to soil F.

In addition, F enrichment in groundwaters was generally attributed to geogenic F (D'Alessandro et al. 2008; Borgnino et al. 2013; Li et al. 2014; Brindha et al. 2016; Fuge 2019). Fluorine-bearing minerals in rocks and soils are the most important geogenic source of fluoride enrichment in groundwater (Ayenew 2008; D'Alessandro et al. 2008; Arveti et al. 2011; Andrade 2012). Under some conditions, F in soils is prone to migrate to groundwater and available to plants and hence constitute risks of F-elevation to groundwater and F-toxicity risks to plants (Cronin et al. 2000; Loganathan et al. 2006; Yi et al. 2013). However, it was reported that F-contamination risk to groundwater depends on the soluble soil F concentrations instead of F_{tf} in soil. In other words, the presence of soluble and/or labile fluoride in soils is the major controlling factor for the fluoride levels in groundwater (Loganathan et al. 2006; Jayawardana et al. 2012). Since comprehensive studies on the geochemistry of F in soils are still generally lacking, there are only limited studies focused on soluble F concentrations or fluorine speciation in soils in spite of the large number of studies on F_{tf} concentrations (Berger et al. 2016). Therefore, research on F speciation may help

elucidate labile forms of soil F and aid in profound studies on geochemistry of F in soils. Moreover, the relationship between soil F speciation and groundwater F content will be helpful in better understanding genesis of groundwater F, which is important to formation mechanisms of local high-fluoride groundwater.

Loess is widely distributed in China with its typical and deep sediments in the Chinese Loess Plateau (CLP). People in the CLP heavily rely on groundwater for daily life, whereas groundwater quality there is usually not qualified enough due to excessive salinity and some toxic elements (Li et al. 2019). F is one of such toxic elements (Zhu et al. 2006; Currell et al. 2011). Particularly in the Shaanxi Loess Plateau (SLP), which is the core area of the CLP and within the scope of Shaanxi Province, high-F groundwater has long been a major hydrogeological issue. Geologic F was found to be the origin of fluoride in the groundwater in the area (Zhu et al. 2008; Deng et al. 2009b; Li et al. 2019). As loess is an important source of fluorine in the groundwater, F_{lf} in basic loess units has been evaluated in some regions in the SLP with limited F_{ws} records obtained (Liu, 1985; Zhu et al. 2008; Liu et al. 2009). Previous analyses show that F content in loess ranges from 74-653 mg kg⁻¹ while F_{ws} content is between 1.75 and 38 mg kg⁻¹ (Liu et al. 2009). Nevertheless, information on labile forms of F in loess is still far from enough as there are few studies on F speciation in loess. Much less is the exposure and risk implication related to labile forms of F in loess. Therefore, this study aims to: (1) determine characteristics of the F speciation in loess in the SLP; (2) assess the quality of the loess in the area in terms of F based on the F speciation; (3) disclose the exposure and risk implications of F in loess associated with the F speciation, including that to animals, humans and groundwater. This study may enhance the understanding of F geochemistry in loess, improve knowledge on animal and human health protection related to F in the area and afford further information on genesis of high-fluoride groundwater in the SLP.

Regional setting

The SLP is located in the central of the CLP with widely distributed thick loess accumulations. It is generally agreed that loess is an accumulation of wind-borne dust and silt derived from deflation of surface rocks in arid areas with severe winters to the north and west of the main loess belt. The mineralogy of loess is mainly composed of quartz, feldspar and muscovite and such clay minerals like illite, kaolinite and montmorillonite (Liu et al. 1986). There is a northwest and southeast

progression in spatial domain of loess from sandy loess to silty loess, and to fine loess, all of which are distinguished from one another in their physical and chemical characteristics. At the same time, vertically in a profile, loess is composed of alternating loess and paleosols with totally four basic units being recognized if the stratigraphy is complete, including Holocene Loess, Upper Pleistocene Malan Loess, Middle Pleistocene Lishi Loess, and Lower Pleistocene Wucheng Loess. As their alternation resulted from shifting climatic regimes, loess and paleosols displays distinct characteristics in physical and geochemical compositions (Liu, 1985).

The SLP has a typically arid and semiarid climate. Water resources in the area are rather limited due to limited precipitation and continuous increasing of water demand. As surface water resource is unevenly distributed and inadequate, groundwater there play an important role in water supply for various purposes. However, high-fluoride groundwater occurs widely across the area (Li et al. 2019). In some localities in the SLP, the endemic fluorosis was attributed to excessive intake of fluoride via drinking high-fluoride shallow groundwater (Zhu et al. 2008). It is the case in the Guanzhong Basin located in the southern SLP, particularly in the east of the basin (Deng et al. 2009b).

Materials and methods

Sampling and analyzing

Four loess profiles in the SLP were chosen for sampling in this study, as shown in Fig 1. They are named Luochuan (LC) profile, Baoji (BJ) profile, Bailuyuan (BLY) profile and Dali (DL) profile, respectively. The LC profile is located in Luochuan County in the north of the SLP with typical loess (silty loess) distributed and the latter three in the south with fine loess distributed. And the latter three profiles lie in the north of Baoji City, the southeast of Xi'an City, and the north of Dali County, respectively. On the regional scale, they are also in the southwest, south-central and southeast of the SLP, respectively. All the profiles are composed of alternating loess and paleosol sequences. Totally 60 loess and paleosol samples were collected from the four profiles. Among them 11 were sampled from the LC profile, 16 from the BJ profile, 15 from BLY profile, and 18 from Dali profile. One or two samples were taken from each layer of loess or paleosol in the profiles.

Fig 1

Samples were first air dried. Then they were sieved through a 2-mm mesh and completely mixed. Soil pH was measured in deionized water with a soil/solution weight ratio of 1/2.5 using a pH meter.

Total F (F_{tf}) content of the samples was analyzed using alkali fusion-selective electrode technique (D'Alessandro et al. 2008). A sequential chemical extraction (SCE) procedure was followed to obtain fluorine speciation in detail (Wu et al. 2002; Yi et al. 2013). Five grams of the sieved samples were put into a 50-ml centrifuge tube. First, water-soluble F (F_{ws}) was leached by deionized water at about 70°C after continuously shaking for 1 hour. The centrifuged leach solution was for determination of F_{ws} . Then the remnant was used to extract exchangeable F (F_{ex}) by adding 1 mol L⁻¹ MgCl solution (pH=7.0) and shaking for 1 hour at room temperature. The supernatant after centrifugation was kept for F_{ex} determination while the remnant was mixed with 0.04 mol L⁻¹ NH₂OH·HCl dissolved in 20% (in volume) CH₃COOH solution and shaken for 1 hour at 60°C to extract F bound to Fe-Mn oxides (F_{fm}). Subsequently, the mixture with the extracted F_{fm} was centrifuged and the supernatant and remnant were for content analysis of F_{fm} and extraction of F bound to organics (F_{or}), respectively. The remnant from the last step was treated with 0.02 mol L⁻¹ HNO₃ and 30% H₂O₂ and then 3.2 mol L⁻¹ NH₄Ac was added. After that, 1-hour shaking was conducted to complete extraction of F_{or} . Suspension was then centrifuged for F_{or} analysis. The supernatant in each step was mixed with TISAB before running on a F ion-selective electrode for F concentration. The detection limit is 1 mg kg⁻¹ and the precision is ±10%. Residual F content (F_{re}) was obtained by a remaining difference method, namely F_{tf} minus the sum of the above four species of F.

Methods

Quality assessment with respect to F

In this study, the method introduced by Li et al. (2005) was applied to assess the quality of loess in terms of F. It was established based on statistical relationship between geochemical characteristics of F in high-fluorine soils and local occurrences of endemic fluorosis in China. The assessment is made according to the formula as follows:

$$\begin{cases} C_i < S_1 & \text{soil deficient in F} \\ S_1 \leq C_i < S_2 & \text{soil with normal F} \\ C_i > S_2 & \text{soil with excessive F} \end{cases} \quad (1)$$

where C_i (mg kg⁻¹) is the analyzed concentration of F in soil; S_1 and S_2 (mg kg⁻¹) are the lower and upper limits of standard concentrations of F for the assessment, respectively.

The values for C_i , S_1 and S_2 are taken differently according to pH of soil. If soil pH is acid

(pH<7), F_{tf} concentration in the soil is adopted as C_i . S_1 is the world average F_{tf} content in soil and S_2 is the average F_{tf} content in soil in areas in China where endemic fluorosis highly occurs. The values of S_1 and S_2 are 200 and 800 mg kg⁻¹, respectively (Li et al. 2005; Wang et al. 2012). If soil pH is alkaline (pH>7), however, the measured F_{ws} concentration in the soil is taken as C_i . S_1 denotes average F_{ws} content in worldwide uncontaminated surface soils and its value is 0.5 mg kg⁻¹ (CNEMC, 1990). S_2 is the counterpart in soils in fluorosis prevalence areas of China and generally has the value of 2.5 mg kg⁻¹ according to the statistics from Li et al. (2005). But herein 5.0 mg kg⁻¹ is taken as the value of S_2 under the alkaline condition in accordance with the limit in quality standard for agricultural land stipulated by GB15618-2018 (MEE, 2018).

To make a quantitative comparison, a soil health quality index for fluorine (P_i) was also introduced by Li et al. (2005):

$$P_i = \frac{C_i}{S_2} \quad (2)$$

where C_i and S_2 are the same as those in formula (1). Similar to formula (1), $P_i > 1$ indicates that the evaluated soil is high-fluorine and its health quality associated with F is inferior. And the larger the P_i , the worse the soil health quality of F.

Exposure risks assessment

Daily exposure to soil F (DF) is assessed for grazing animals according to whether acceptable limits of dietary F for grazing animals are surpassed. If DM (kg) is the daily dry matter intake by a certain grazing animal, a safe threshold dietary concentration for F is 60 mg kg⁻¹ DM for breeding ewes and 150 mg kg⁻¹ DM for lambs. And 10-25% of DM intake is for the range of daily soil ingestion (RDSI) (Grace et al. 2003). Then the DF on a dietary basis (mg kg⁻¹) by a grazing animal could be evaluated as follows:

$$DF = \frac{DM \times RDSI \times C_{tf}}{DM} = RDSI \times C_{tf} \quad (3)$$

where C_{tf} (mg kg⁻¹) is F_{tf} content in soils.

Human exposure to contaminants through ingestion of soil may be estimated by the following equation (Bierkens et al. 2011):

$$DI = \frac{IR_{soil} \times F_{soil} \times RBA_{soil} \times C_{soil} \times 10^{-3}}{BW} \quad (4)$$

where DI is exposure through daily intakes of soil (μg kg⁻¹ day⁻¹); IR_{soil} is combined ingestion

rate of soil (mg day^{-1}); dimensionless F_{soil} is fraction of soil and dust ingestion which is soil; dimensionless RBA_{soil} is relative oral bioavailability in the human body for contaminants in soil; C_{soil} is contaminant concentration in soil (mg kg^{-1}); BW is average body weight (kg). Here children's exposure to F in loess was assessed as they tend to have much more hand-to mouth activities for soils than adults. In the assessment, a representative value of 50 mg day^{-1} is for IR_{soil} (Bierkens et al. 2011). As for RBA_{soil} , its value was not determined alone because of lack of related experiments. Instead, the product of RBA_{soil} and C_{soil} was given a value which was considered as the oral bioaccessible F concentration to the human body. Some researchers reported that F-toxicity risk to plants and humans depended on the soluble soil F concentrations (Gao et al. 1990; Loganathan et al. 2006). Also, Yu et al. (2020) found that there were notable positive influences of F_{ws} on oral bioaccessibility of F. Therefore, F_{ws} in loess was treated as the approximation of oral bioaccessible F concentration of loess and substituted for the product of RBA_{soil} and C_{soil} to obtain a maximum DI estimate. The value of F_{soil} herein is 1 as no dust was considered; 15.9 kg is the BW for children on the basis of local statistics (Xu et al. 2019). The upper intake F levels (ULs) limit for daily intakes is $58 \mu\text{g kg}^{-1} \text{ day}^{-1}$ (Chinese Nutrition Society, 2014).

Results and Discussion

Distribution characteristics of fluorine speciation in loess

Statistical results of fluorine speciation for the loess samples are included in Table 1. Fig 2 also aids in recognizing distribution characteristics of F speciation in loess in the SLP.

Table 1

Total fluorine (F_{tf})

F_{tf} for all the samples vary from 461.45 to 789.72 mg kg^{-1} , with an average of 595.85 mg kg^{-1} (Table 1). It was reported that the average F_{tf} concentration in soils in China was 478 mg kg^{-1} and that in worldwide soils was 329 mg kg^{-1} (Kabata-Pendias and Pendias, 2001; Yi et al. 2013). The average F_{tf} content in the loess is considerably higher than that in nation-wide and world-wide soils. The LC profile in the north has an average F_{tf} content of 540.44 mg kg^{-1} , which is the lowest of all the profiles (Fig 2). In the south of SLP, the F_{tf} content in loess is higher. And the average F_{tf} content for BJ, BLY, and DL profile in the south is 642.84, 587.79, and 594.67 mg kg^{-1} , respectively, with the highest average F_{tf} content in the loess in the southwest and the second highest in the southeast.

Fig 2

Water-soluble fluorine (F_{ws})

F_{ws} is the F extracted by neutral deionized water as a solvent and mainly exists in inorganic forms. It has a profound effect on plants, animals, microorganisms, and humans with highly availability to roots and active involvement in F accumulation in the food chain (Xie et al. 1999; Yi et al. 2013). Overall, F_{ws} accounts for 0.3-6.4% of the F_{tf} in the loess. The range of its content is 1.40-38.97 mg kg^{-1} in the all the loess samples, with an average of 6.14 mg kg^{-1} (Table 1). Average F_{ws} content in loess is far above 2.5 mg kg^{-1} , the corresponding average in soils in Chinese endemic fluorosis prone areas (Li et al. 2005; Yi et al. 2013). The F_{ws} concentrations in loess are nearly one to two orders of magnitude less than that of the F_{tf} . The LC profile in the north has the lowest average F_{ws} content. However, the highest average content of F_{ws} occurs in the DL profile in the southeast that has the second highest F_{tf} content (Fig 2). In this profile, the F_{ws} represents about 4.1% of the F_{tf} on average, which is much higher than that in the other three profiles. The BJ profile in the southwest has the second highest F_{ws} content in spite of F_{tf} in it enriched to the greatest extent (Fig 2).

Exchangeable fluorine (F_{ex})

F_{ex} is the fluoride held by electrostatic attraction and adsorbed on positively charged clay, organic particles and hydrated oxides (Xie et al. 1999). The average F_{ex} content in all the loess samples is only 11.94 mg kg^{-1} although its fluctuation range is between 1.31 and 64.20 mg kg^{-1} much wider than that of F_{ws} (Table 1). As a matter of fact, most of the loess samples have lower F_{ex} content compared to that of F_{ws} (Fig 2). Particularly, average content of F_{ex} in the three profiles in the south is smaller than that of F_{ws} . As shown in Fig 2, the LC profile in the north is the only one enriched more F_{ex} than F_{ws} . Nevertheless, the DL profile in the southeast has the highest average F_{ex} content as well as the highest that of F_{ws} . Similar to the ranking in terms of average F_{ws} content in the profile, it is followed by the BJ profile in the southwest, the BLY profile in the south-central SLP, and the LC profile in the north according to the average F_{ex} content of the respective profile (Fig 2).

Fluorine bound to Fe-Mn oxides (F_{fm})

F_{fm} actually refers to the part of F in soils that may be absorbed by Fe, Mn and Al oxides, oxyhydroxides, and hydrated oxides and precipitated with these chemicals. This F species has little biological effectiveness (Xie et al. 1999; Berger et al. 2016). As shown in Table 1, the F_{fm} content in the loess is rather low, accounts for 0.2-1.1% of F_{tf} . Also, the LC profile in the north contains the

least F_{fm} , with an average content of 1.95 mg kg^{-1} representing 0.4% of F_{tf} . In the other three profiles in the south, the content of F_{fm} falls between 3.17 and 4.10 mg kg^{-1} on average, representing 0.5-0.7% of F_{tf} . Overall concentrations of F_{fm} are similar in the three profiles, with that in the BLY profile in the south-central part being the greatest (Fig 2). The pH condition may be responsible for the relatively small proportion of F_{fm} in loess. The loess is under alkline condition (Table 1), whereas secondary Fe/Mn oxyhydroxides was considered to adsorb F in soils preferentially under neutral to acidic conditions (Loganathan et al. 2006; Borgnino et al. 2013; Berger et al. 2016).

Fluorine bound to organics (F_{or})

Humic substances and organic acids widely distributed in soils are responsible for fluorine capture through complexing actions with fluorine bound to produced organics (Xie et al. 1999). The concentrations of F_{or} in all the samples fluctuate in a relatively wide range from 0.92 to 42.50 mg kg^{-1} (Table 1). The samples with relatively high content of F_{or} almost come from the DL profile in the southeast. The average F_{or} content in the loess from the profile reaches 15.44 mg kg^{-1} accounting for 2.5% of F_{tf} , with 7.28 and 42.5 mg kg^{-1} being the minimum and maximum, respectively. The other three profiles have similar levels in F_{or} content accounting for less than 1% of F_{tf} , which is much lower than the DL profile (Fig 2). Scavenging of F^- by organic matter is reportedly most effective below $\text{pH} = 6.5$ (Berger et al. 2016). Therefore, it is no surprise that there is relatively low percentage of F_{or} in the alkline loess while its proportion in acid soils in southwestern China is much higher (Zhang 2007).

Residual fluorine (F_{re})

Apart from the aforementioned fluorine species, there is residual fluorine existing in mineral lattice in soils, which is unextractable. F_{re} is considered unavailable to biological activities (Xie et al. 1999; Yi et al. 2013). It takes the overwhelming majority of F_{tf} in all the loess samples, ranging from 461.45 to $789.72 \text{ mg kg}^{-1}$ (Fig 2). Its proportion in F_{tf} is between 80.9% and 97.8%, with 93.6% on average (Table 1). The DL profile has an average proportion of 89.8%, which is the smallest in the four profiles. It indicates that the extractable F in the profile is most enriched. In the other three profiles the average proportion of the F_{re} is around 95%.

Relationship between different F species

According to concentrations of different F species in all the loess samples, the content of F_{re} is far higher than that of the other F species. Then the F_{ws} or the F_{ex} is the second in amount or percentage.

In the three profiles in the south, the overall content of F_{ws} is higher than that of F_{ex} , whereas it is the contrary in the LC profile in the north with more F_{ex} . F_{fm} occurs in the least amount except in the BLY profile. All in all, the order of the five-fluorine species, from the largest to the smallest, is that $F_{re} > F_{ws} (F_{ex}) > F_{ex} (F_{ws}) > F_{or} (F_{fm}) > F_{fm} (F_{or})$ if arranged according to overall content of each species in the four profiles.

The correlation between the different F species is also studied (Table 2). As the F_{re} represents most of the F_{tf} , its content has a strong positive correlation with that of the F_{tf} . The F_{ws} correlates strongly with both the F_{tf} and the F_{or} . The notable correlation between the F_{ws} and the F_{tf} in loess results from the high F_{ws} proportion next to the F_{re} in most loess samples. This relationship between them was also found in other studies on F speciation in soils (Zhang 2007; D'Alessandro et al. 2008). And the F_{ws} and the F_{or} correlates significantly, which was also found in a previous study (Yi et al. 2013). Although the content of the F_{fm} is small, it has positive relationships with the F_{tf} , F_{ws} , F_{re} , and F_{or} . Besides that, there is also a strong correlation between the content of the F_{ex} and the F_{or} . A mechanism explanation can be given for the positive correlation between F_{or} and either F_{ex} or F_{fm} . Multiple functional groups of humic substances matter in soils can bind cations (including Ca, Fe and Al), which in turn provide adsorption sites for F^- while there is already F^- absorbed by the organic matter (Murray, 1983; Berger et al. 2016).

Table 2

Quality assessment of fluorine in loess

Since pH of all the loess samples is alkline, F_{ws} concentrations in loess samples were adopted as the C_i in formula (1) to assess health quality of the loess. As mentioned above, 0.5 mg kg^{-1} and 5.0 mg kg^{-1} were assigned to S_{i1} and S_{i2} in formula (1), respectively. Results show that 56 loess samples were evaluated as soil with excessive F, accounting for 93% of all the samples. Only 4 samples belong to soil with normal F. No sample is classed as soil deficient in F. As a whole, the loess in this study can be assessed as inferior health quality as far as F is concerned. P_i range of the four profiles show that health quality of F for the loess in the north of SLP is relatively better than that in the south (Table 1). Moreover, the loess in the southeast of the SLP has the most inferior health quality of F as it contains the highest F_{ws} content and has the greatest P_i range.

Exposure assessments

Since F is not readily taken up by plants, the F intake of grazing sheep largely comes from soil ingestion, especially during the winter months (Grace et al. 2003). It was found that a safe threshold dietary concentration for F should be satisfied before the long-term F intake results in chronic fluorosis. And grazing animals might be at risk if they ingest high-F soil with high rates (Grace et al. 2003; Loganathan et al. 2006). In Fig 3, DF range exposed to the loess of each profile for grazing animals has been illustrated with 10-25% of DM intake. DF for grazing animals varies from 46-197 mg kg⁻¹ DM if the loess in this study is ingested (Fig 3). Loess in the north, which has the relatively low F_{tf} content, is generally safe for grazing animals as shown by the DF range from the LC profile with most values except two ones are under the upper limits. As a result of the high F_{tf} content, the loess in the southwest might pose a much greater risk to grazing animals in terms of F exposure. It is indicated by the DF range from the BJ profile, in which most values significantly surpass the acceptable limits. Although the F_{tf} content of the loess in the south-central and southeastern SLP is also relatively high, it is generally tolerable for grazing animals if the loess ingested by them. This is because DF range assessed from F concentrations in the two profiles, the BLY and the DL profile, mostly falls below or close to the limits with only a few samples having values far above the limits (Fig 3).

Fig 3

Children's exposure to F via ingestion of loess was assessed according to formula (4). The calculated DI values for all the samples are between 0.004 and 0.123 µg kg⁻¹ day⁻¹. It shows that the exposure is far below 58 µg kg⁻¹ day⁻¹, the upper limited value stipulated by Chinese Nutrition Society (2014). Given the assessed exposure values are two and four orders of magnitude less than the acceptable limit, there is no concern for the children's exposure to F in the loess via ingestion in the present condition. However, there were reports on surge in F concentration in environment caused by application of high-fluorine fertilizers and the resulted adverse impacts on animals or humans (Loganathan et al. 2008; Yu et al. 2020). If application of F-containing fertilizers leads to substantial elevation of F content in some loess strata, it is possible that the exposure to F may also increase greatly. Therefore, the southwest and the southeast SLP might more potentially be F-exposure risk prone regions if the original high background F_{ws} in the loess is coupled with a considerable addition of fertilizer F by human's agricultural activities.

Risk implication of fluorine speciation in loess on genesis of groundwater fluoride

High-fluoride shallow groundwater is widely distributed in the SLP. The fluoride distribution in groundwater in the SLP, especially in the southern part, Guanzhong Basin, has been studied by some researchers (Zhu et al. 2008; Deng et al. 2009a, b). According to the results, eastern part of the basin, in which the DL profile in this study lies, is a region with the highest occurrence of high-fluoride groundwater. Groundwater around the DL profile generally contains F concentration from 2.0 to 4 mg/L. From the east to the west of the basin, there is an overall trend that the fluoride content in groundwater decreases. In the central part of the basin where the BLY profile is included, the fluoride content in groundwater is overall less than that in the east. To the west of the basin, in which the BJ profile is located, the fluoride concentration in groundwater decreases to the overall lowest level of the basin with almost all groundwater samples having F content less than 1.0 mg/L. In the northern SLP where the LC profile lies, the fluoride content in groundwater is rather low according to unpublished local hydrogeochemical data. Three groundwater samples collected around the LC profile have F concentrations of 0.45, 0.52, and 0.64 mg/L, respectively. With regards to the genesis of high-fluoride groundwater in the southeast SLP, interaction between groundwater and contacting rocks and soils is a critical formation mechanism and fluoride in groundwater primarily originates from F in rocks and soils (Zhu et al. 2008; Li et al. 2014; Xiao et al. 2015; Li et al. 2019; Xu et al. 2019). In the central basin, namely the south-central SLP, however, besides the geogenic origin, fluoride enrichment in groundwater may be partially attributed to the local high-fluoride thermal water, which rises along faults and mixes into groundwater (Deng et al. 2009a, b). Loess is an important groundwater medium in the SLP and comprises such fluorine-containing minerals. Therefore, F in loess might be closely associated with the genesis of local high-fluoride groundwater (Zhu et al. 2008; Li et al. 2019). Combined with the F distribution characteristics in the groundwater, the above F speciation may help to clarify further the relationship. Here discussed is the F speciation in loess and fluoride content in groundwater in the southeast, southwest and north SLP without including that in the south-central SLP as the complication of groundwater fluoride sources there is concerned. Loganathan et al. (2006) has ever pointed out that F-contamination risk to groundwater depended on the soluble soil F concentrations. It means that F_{ws} rather than F_{tf} in loess plays an important role in contributing F to groundwater. It is proved to be true in this study. The loess from the north has both the lowest F_{tf} and F_{ws} content while the groundwater has relatively

the lowest fluoride content. But in the southwest of the SLP, the loess has lower F_{ws} content and higher F_{tf} content than in the southeast, whereas there is much lower fluoride concentration in groundwater than that in the southeast (Deng et al. 2009b). Furthermore, as a matter of fact, the difference between the F_{ws} content for each profile is not so significant compared to that between the total content of extractable F, which is the sum of F_{ws} , F_{ex} , F_{fm} and F_{or} concentrations (Fig. 4). For example, the difference value is 8 mg kg^{-1} between the average F_{ws} concentrations of the BJ and the DL profile, whereas that is 22.4 mg kg^{-1} between the average extractable F concentrations of the two profiles. And the corresponding difference values between the LC and the BJ profile are 10.0 and 17.2 mg/L , respectively. It may suggest that extractable F in loess, not just F_{ws} , is related to the genesis of groundwater fluoride in the loess area. Although rather low is the respective content of the other three types of extractable fluorine species except F_{ws} , the sum of them cannot be negligible for contribution to groundwater fluoride enrichment.

Fig 4

Conclusions

In the SLP, there is distributed widely typical loess, which is enriched in F. To have a better understanding of F geochemistry in loess, the F speciation of the loess in the SLP was studied. On the basis of that, animal and human exposures to loess F were assessed. And implication of the F speciation of loess on the risk to fluoride enrichment in groundwater was also discussed. The following are the major findings:

- 1) Loess has high F_{tf} content in a range of $461.45\text{--}789.72 \text{ mg kg}^{-1}$, with higher content in the loess from the south SLP than the north SLP. Of the F species in loess, the unextractable F_{re} accounts for most percentage of F_{tf} from 80.9 to 97.8%. Of the four extractable fluorine species including F_{ws} , F_{ex} , F_{fm} and F_{or} , F_{ws} is the most important species in loess as its content in most loess samples is the highest. Except loess in the north SLP that has relatively low F_{tf} content, the loess in the south has much lower content of the other three extractable fluorine species, compared to that of F_{ws} . The average F_{ws} content in the loess greatly surpasses that in soils in Chinese endemic fluorosis prone areas, with an average of 6.14 for all samples and a maximum of 38.97 mg kg^{-1} occurring in loess in the southeast SLP. Although F_{ws} in loess overall has a significant correlation with the F_{tf} , not all loess samples with high F_{tf} content necessarily have high F_{ws} content as shown in the comparison between the BJ profile in the southwest and the DL profile

in the southeast. Loess in the southeast has the highest F_{ws} content in spite of its second highest F_{tf} content.

2) As loess has alkline pH, F_{ws} concentrations were the adopted in the quality assessment of fluorine in loess. As a whole, the loess in the SLP can be assessed as inferior health quality as far as fluorine is concerned. Health quality of F for the loess in the north of SLP is relatively better than that in the south. Particularly the loess in the southeast of SLP has the most inferior quality of fluorine due to its highest F_{ws} content.

3) According to the characteristics of F species in the loess, the exposure to the loess F via ingestion have been assessed for animals and humans, respectively. The exposure to grazing animals was estimated based on F_{tf} content in loess. The assessment results show that F in the loess in the southwest SLP might pose a much greater risk to grazing animals than in other part of the SLP as the loess contains more F_{tf} . F_{ws} content in loess is the basis of exposure assessment for humans. Only children's exposure to F via ingestion of loess was assessed for their special modes of activity different from adults. Fortunately, there is no concern for the children's exposure to F in the loess via ingestion in the present condition.

4) With the F speciation in loess in the SLP and distribution of local high-fluoride groundwater, it can be found that the higher the content of F_{ws} in loess, the higher fluoride content in local groundwater. It proves other researcher's viewpoints on dependence of F^- contamination in groundwater on soluble F in soils. In addition, the other three types of F species including F_{ex} , F_{fm} and F_{or} , although their respective concentration is quite low similar to F_{ws} , also contribute to F enrichment in the groundwater in the SLP. It may indicate that extractable F species, not just F_{ws} , may be responsible for the genesis of groundwater fluoride in the loess area.

Acknowledgments: The research is financially supported by the Natural Science Basic Research in Shaanxi Province of China (Program No. 2019JM-512) and the Open Foundations of State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences (SKLLQG1605). The authors are grateful to Professor Liu Xiuhua, Chang'an University for her help in field sampling.

Author contributions: The study idea and methodology were developed by Lin Deng. Lin Deng, Jiangxia Wang and Xiaoting Yang were involved in the field sampling and laboratory analysis. Bin Xu and Anyan Hu participated in the laboratory analysis and data processing. The first draft of the manuscript was written by Lin Deng. Jiangxia Wang and Bin Xu helped in editing the first versions of the manuscript. Previous versions of the manuscript were discussed by all authors.

Consent to participate and publish: All authors participating in this study agreed to publish.

Data availability statement: Raw data may be provided upon reasonable request.

Compliance with ethical standards and conflict of interest:

The authors claim that they have no relevant competing financial or non-financial interests that would have appeared to influence the work in this paper. And there is no research involving human and animal participants in this study. Besides that, such infractions including plagiarism, data fabrication and/or falsification, double publication and/or submission do not exist at all in this paper.

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Figure captions

Figure 1 The study area and location of sampling profiles

Figure 2 Distribution of F speciation in the profiles

572 **Figure 3** DF (daily exposure to soil F) range exposed to each loess profile for grazing animals

573 with 10-25% of DM (daily dry matter) intake

574 **Figure 4** Comparison between the content of F_{ws} and all extractable F for the profiles

Table 1 Statistics of fluorine speciation, pH and Pi values of loess samples from the profiles

profile	^a Concentration and percentages	<u>F_{ws}</u>			<u>F_{ex}</u>			<u>F_{fm}</u>			<u>F_{or}</u>			<u>F_{re}</u>			<u>F_{tf}</u>		
		Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean
LC ^b pH: 8.73–10.19 ^c 1.23 (0.28–2.25)	Concentration (mg kg ^{−1})	11.24	1.40	6.14	34.27	1.37	9.21	3.07	1.02	1.95	8.46	2.25	4.27	618.02	450.59	518.86	642.13	461.45	540.44
	Percentages (%)	1.8	0.3	1.1	6.9	0.3	1.8	0.5	0.2	0.4	1.6	0.4	0.8	97.8	91.2	96	–	–	–
BJ ^b pH: 8.50–10.94 ^c 3.23 (1.06–6.40)	Concentration (mg kg ^{−1})	31.98	5.32	16.16	64.20	3.09	13.63	4.93	1.59	3.17	13.02	2.43	5.82	761.13	458.04	604.07	789.72	518.70	642.84
	Percentages (%)	4.8	1.0	2.4	12	0.5	2.2	0.8	0.3	0.5	1.9	0.3	0.9	96.6	85.3	93.9	–	–	–
BLY ^b pH: 7.98–9.03 ^c 2.02 (1.29–2.89)	Concentration (mg kg ^{−1})	14.46	6.47	10.09	15.65	1.31	5.37	7.11	1.58	4.10	6.44	0.92	2.98	733.17	476.83	565.25	761.90	499.50	587.79
	Percentages (%)	2.9	0.9	1.8	2.8	0.2	0.9	1.0	0.3	0.7	1.0	0.2	0.5	97.4	94.5	96.1	–	–	–
DL ^b pH: 8.54–10.76 ^c 4.83 (1.59–7.79)	Concentration (mg kg ^{−1})	38.97	7.97	24.17	56.45	1.90	17.57	6.99	1.95	4.02	42.50	7.28	15.44	618.60	442.06	533.48	744.16	501.92	594.67
	Percentages (%)	6.4	1.5	4.1	10.3	0.4	2.9	1.1	0.4	0.7	5.7	1.2	2.5	93.9	80.9	89.8	–	–	–
Four profiles	Concentration (mg kg ^{−1})	38.97	1.40	15.21	64.20	1.31	11.94	7.11	1.02	3.43	42.50	0.92	7.71	761.13	442.06	557.56	789.72	461.45	595.85
	Percentages (%)	6.4	0.3	2.5	12	0.2	2	1.1	0.2	0.6	5.7	0.2	1.3	97.8	80.9	93.6	–	–	–

^a concentrations of different fluorine species and their percentages in total fluorine in loess samples

^b pH range of loess samples from each profile

^c the average Pi value of respective profile with the range in the following bracket

Table 2 Correlation coefficients between different fluorine species

	F _{tf}	F _{ws}	F _{ex}	F _{fm}	F _{or}	F _{re}
F _{tf}	1					
F _{ws}	0.374**	1				
F _{ex}	0.051	0.013	1			
F _{fm}	0.397**	0.313*	0.046	1		
F _{or}	0.235	0.532**	0.465**	0.323*	1	
F _{re}	0.951**	0.196	-0.197	0.311*	-0.025	1

**The correlation was significant at the 0.01 level (n=60)

* The correlation was significant at the 0.05 level (n=60)

Figures

Figure 1

The study area and location of sampling profiles

Figure 2

Distribution of F speciation in the profiles

Figure 3

DF (daily exposure to soil F) range exposed to each loess profile for grazing animals with 10-25% of DM (daily dry matter) intake

Figure 4

Comparison between the content of Fws and all extractable F for the profiles