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Fluorine distribution, health risk, and geological and anthropogenic controlling factors in central Guizhou Province, Southwest China

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A B S T R A C T

Fluorine (F)-enriched soils, resulting from geogenic processes or superimposed by anthropogenic activities, have raised significant concerns due to their phytotoxicity and potential threats to human health. Soils in central Guizhou Province exhibit F enrichment, with a mean F concentration of 1067 mg/kg. However, the associated human health risks and geochemical mechanisms driving F enrichment in these soils remain insufficiently understood. In areas with a natural geological background, the average concentrations of F in rice, vegetables, drinking water, and ambient air are 1.54 mg/kg, 0.54 mg/kg, 0.16 mg/L, and 0.29 μg/m^3, respectively. In contrast, samples collected near phosphorous chemical plants demonstrate elevated F concentrations: 1.78 mg/kg in rice, 1.53 mg/kg in vegetables, 0.20 mg/L in drinking water, and 11.98 μg/m^3 in ambient air. Fluorine in soils was immobilized by apatite and clay minerals, and hardly transferred into water and crops. The fixation of F^- by Ca^{2+} in water and by Fe/Al hydroxides and clay minerals in bottom sediment further reduces F concentrations in water. As a result, hazard quotient (*HQ*) values below 1.0 indicate negligible fluorine-related health risk in geological background regions. However, ambient air near phosphorous chemical plant exhibited a 41.3-fold increase in F concentration compared to geological background regions. Fluorine-laden emissions can be directly inhaled or deposited on vegetable leaves and orally ingested into human bodies. Improvement of F-rich waste gas disposal and restricted leafy vegetable cultivation are effective measures to reduce F health risks in phosphorous chemical plant regions.

1. Introduction

Fluorine is an essential micronutrient for humans, which can strengthen both teeth and skeletal tissue (Nielsen FH, 2009; Rafique T et al., 2009). However, excessive F intake can lead to adverse health effects, such as dental and skeletal fluorosis (Hamilton M, 1992; Bassin EB et al., 2006; Choi AL et al., 2012). Millions of people in countries such as India, China, and Mexico have been diagnosed with fluorosis due to prolonged exposure to F-rich groundwater, crops, or ambient air (Teotia SDS, 1981; Grimaldo M et al., 1995; Zhang B et al., 2003; Ayoob S and Gupta AK, 2006; Maheshwari RC, 2006; Currell MJ et al., 2011).

The release and accumulation of F in the environment are controlled by both natural geological processes and anthropogenic activities (Farooqi A et al., 2007; D'Alessandro W et al., 2008; Singh G et al., 2018; Fuge R, 2019; Yang JY et al., 2020; Su CL et al., 2023; Shao YX et al., 2025). The primary natural sources of soils F are volcanic activities and rock weathering (Pickering WF, 1985). In contract, anthropogenic activities, particularly from phosphorous chemical manufacturing, which uses F-rich raw materials, can release gaseous fluorides (e.g., HF and SiF_4) and particulate fluorides (e.g., AlF_3, $NaAlF_6$, and CaF_2) into the atmosphere (Cronin SJ et al., 2000). The hydrofluoric acid emissions from a chemical plant in China were reported to increase F

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concentrations in both air and soil within a 1000 m radius (An J et al., 2015).

The geochemical survey on land quality reveals that the soil geochemical baseline of F in Guizhou Province is exceptionally high, reaching up to 928 mg/kg, the highest reported in China (unpublished data). Soils near phosphorus chemical plants (e.g. wet phosphorus acid plants and phosphate fertilizer plants) exhibit significantly elevated F content (exceeding 7000 mg/kg). Ambient air around these phosphorus chemical plants also shows significantly higher F concentration than other areas. However, it remains unclear whether F transfers from soil/air to water or crops and subsequently results in health risks for residents. Furthermore, the geochemical mechanisms and environmental factors contributing to fluorine-related health risks via soil and air pathways warrant further investigation.

In this study, the central part of Guizhou Province was chosen as a representative area characterized by fluorine-rich soils, with fluorine originating primarily from geological origin (mainly rock weathering) or superimposed by anthropogenic activities. The authors quantify F contents in soil, drinking water, vegetables, rice, and ambient air. Additionally, the authors assessed the associated health risks for residents in both geological background areas and regions surrounding phosphorus chemical plants. Particular attention was given to understand why fluorine-rich soils in some areas pose lower-than-expected health risks. Finally, the underlying causes of fluorine-related health risks were analyzed, and corresponding mitigation strategies were proposed to reduce health impacts in areas affected by phosphorus chemical industry emissions.

2. Materials and methods

2.1. Study area

The study area is located in the central part of Guizhou Province, Southwest China (Fig. 1a). The terrain is characterized by higher elevations in the south and lower elevations in the north, with an average altitude ranging from 1000 m to 1200 m. The region lies within a transitional zone between northern subtropical and southern temperate monsoon climate zones, with a mean annual temperature of 14.5°C and an annual rainfall of 1110 mm.

The rocks in study area are dominated by carbonate rocks, shale, and clastic rocks, with minor metamorphic rocks and basic igneous rocks (Fig. 1b). The F concentrations in carbonate rocks, shale, and clastic rocks are 100–820 mg/kg, 841–1139 mg/kg, and 132–320 mg/kg, respectively. Additionally, several phosphorous chemical plants of varying production scales operate within the study area.

The geochemical data of surface soils are from the 1∶250000 land quality geochemical survey. The F concentrations vary dramatically from 219 mg/kg to 7296 mg/kg (Fig. 2a), with 76% of samples exceeding 800 mg/kg. The high F concentration in soils may be mainly derived from the natural weathering of F-rich shale or secondary enrichment processes during carbonate rock weathering. This

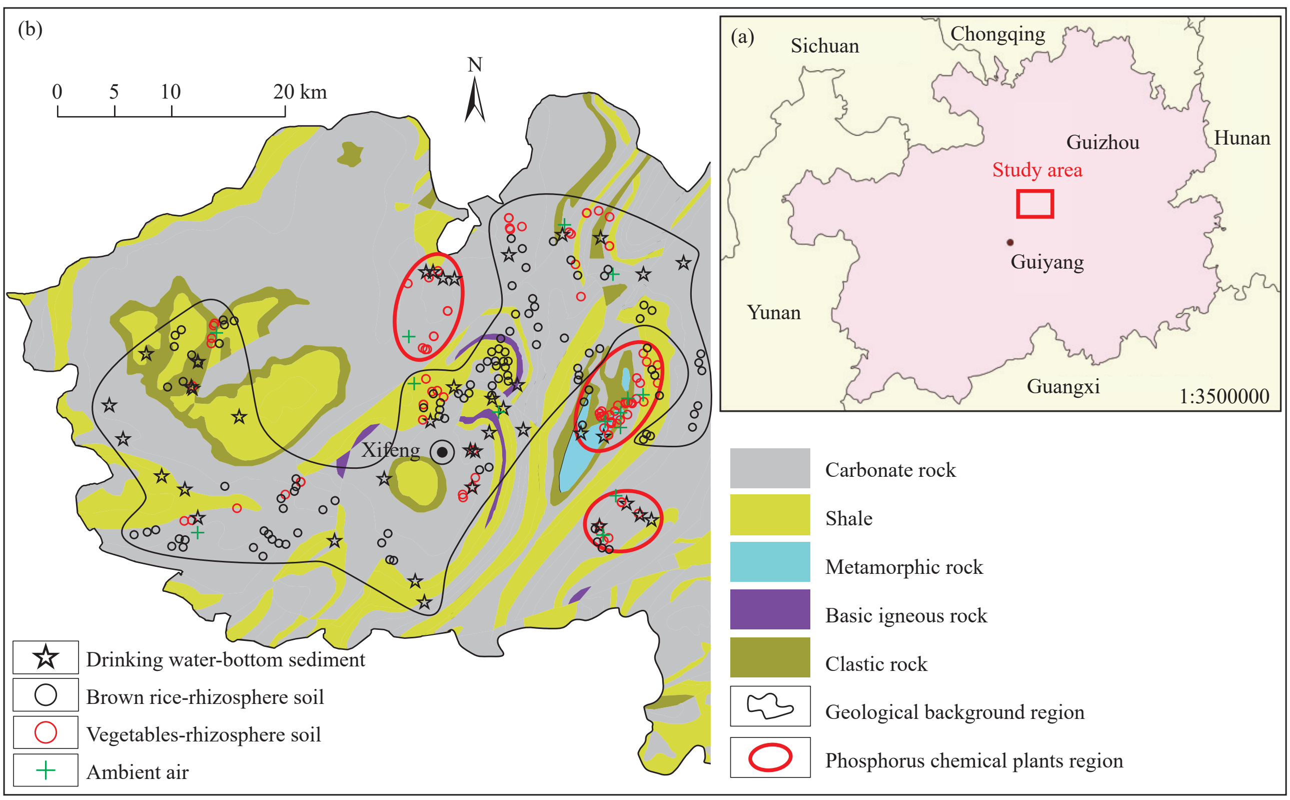

Fig. 1. a–Brief map showing the location of the study area; b–geological map to show the distribution of rocks and phosphorus chemical plants.

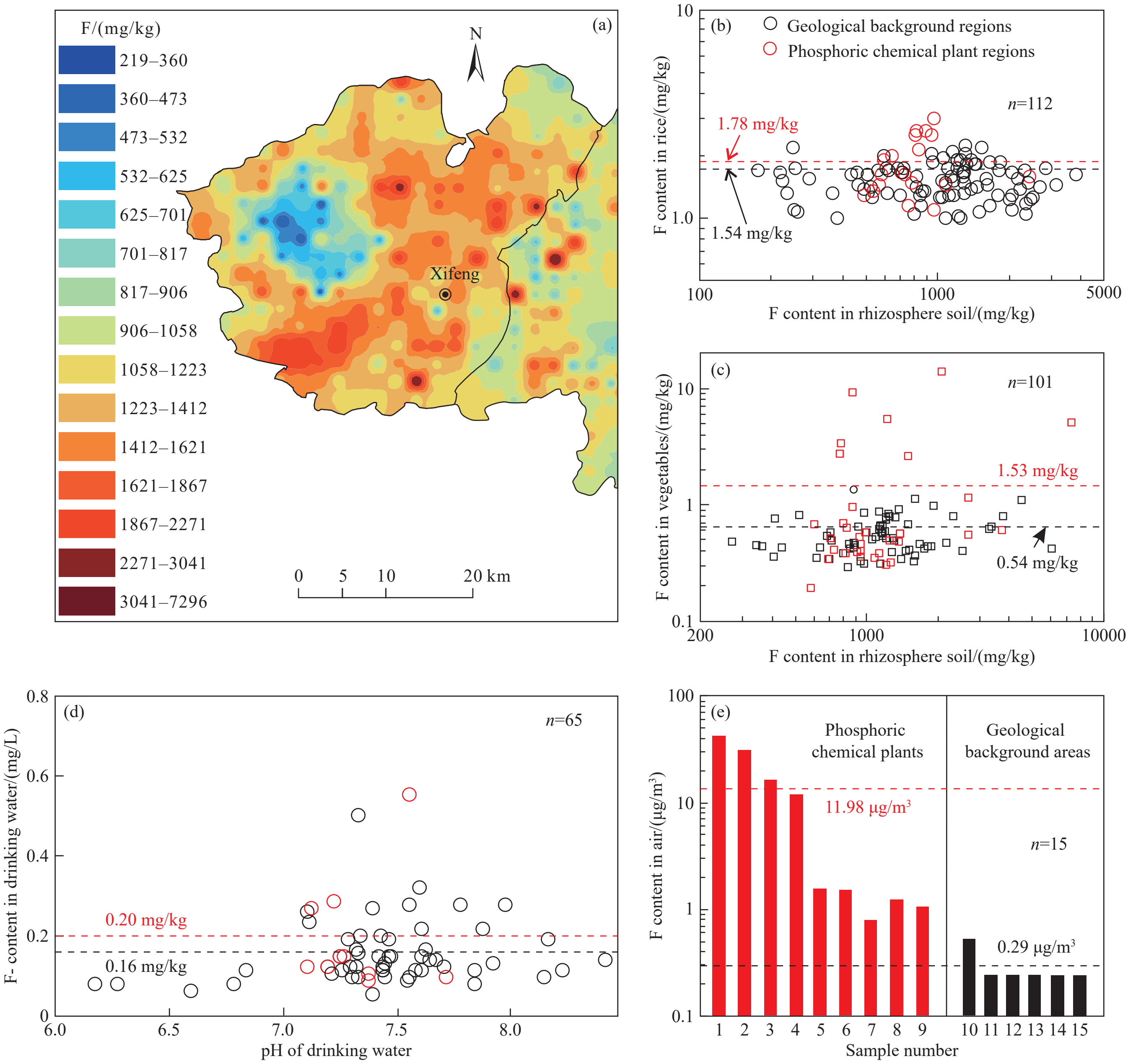

Fig. 2. a–Fluorine geochemical map of surface soil in the study area; b–covariant diagram of F in rhizosphere soil and rice; c–covariant diagram of F in rhizosphere soil and vegetables; d–pH *vs.* F- content diagram of the drinking water; e–F content of ambient air in GBR and PCPR.

type of area is termed the geological background region (GBR; Fig. 1b). In contrast, areas where soil F enrichment is further elevated by F emissions from phosphoric acid or phosphate fertilizer production are designated as phosphorus chemical plant regions (PCPR; Fig. 1b).

2.2. Sample collection

As shown in Fig. 1b, samples of soil, crops, drinking water, bottom sediment, and ambient air were collected from the abnormally high F areas in the study area, Central Guizhou Province. Sampling was conducted during July and August. The crop and rhizosphere soil samples were obtained using a composite sampling approach, whereby multiple subsamples were collected following the multipoint method according to “Specification of land quality geochemical assessment” (DZ/T 0295-2016). Drinking water and bottom sediment samples were gathered from drinking water reservoirs. Ambient air samples were captured as gaseous and particle by filter sampling method. The filter membranes were soaked in dipotassium phosphate and citric acid, respectively, to collect gaseous and particle samples. Meanwhile, blank samples were simultaneously collected. Each air sampling process lasts twenty-four hours, with a flux of 16.7 L/min.

2.3. Sample analysis

The F concentrations of rhizosphere soil, bottom sediment, drinking water, and crops were measured at the Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geological Sciences. The soil samples were air-dried and sieved to <2 mm for soil F fractions analysis. Samples of soil and bottom sediment were sieved to <0.15 mm for the analysis of total F. Both the concentrations of F fractions and total F are determined by the ion-selective electrode (ISE) method. The concentration of F in water was analyzed via the ISE method after filtering through an ash less cellulose fiber filter paper with a pore size of 30–50 µm. The F concentration of ambient air was analyzed by the ISE method at the National Nonferrous Metal and Electronic Materials Analysis and Testing Center.

To ensure analytical accuracy and precision, certified reference materials (GSB-12, GSB-27, GSD17a, GSS71, GSF-2, and ASA-8a) were employed for quality control during sample analysis. Analytical results for these standards showed recovery rates consistent with their certified values. One duplicate sample in each ten samples was analyzed to ensure the reliability of the data. The relative deviations (RSD) for parallel samples were as follows: <5% for soil and bottom sediment, <15% for rice and vegetables, and <10% for water. The qualified rate of standard samples and duplicate samples is 100%.

The backscattered electron observation and electron microprobe analysis were conducted using a JXA-8230 electron microprobe at the Regional Geological Survey Institute of Hebei Province. The minerals in soils and bottom sediments were analyzed using an accelerating voltage of 15 kV, and a beam current of 10 nA. A beam spot diameter adjusted to 1–5 µm, depending on mineral size and stability.

2.4. Health risk assessment of F exposure

The non-carcinogenic risk assessment model has been widely applied to evaluate health risks from fluorine (F) exposure via soil, drinking water, rice, and vegetables (Chavoshi E et al., 2011; Liu RP et al., 2021; Yin NY et al., 2021; Zhang YQ et al., 2021). Noncarcinogenic risk assessment typically follows a margin of safety approach referred to as the hazard quotient (*HQ*), which is derived from Reference Dose (*RfD*) or Reference Concentration (*RfC*) according to the equation *HQ* = Chronic Daily Intake (*CDI*) ÷ *RfD* (*RfC*). The $HQ < 1.0$ indicates negligible risk of adverse effects, whereas an $HQ \geqslant 1.0$ suggests potential health risks In this study, *HQ* value was calculated as the summation of HQ_{Ing}, HQ_{Der}, and HQ_{Inh} to evaluate the effects of F in the following Formula (1):

$$HQ = HQ_{Der} + HQ_{Ing} + HQ_{Inh} = \frac{CDI_{Der}}{R_fD_{Der}} + \frac{CDI_{Ing}}{R_fD_{Ing}} + \frac{CDI_{Inh}}{R_fC_{Inh}} \tag{1}$$

Both RfD_{Der} (adsorbed reference dose) and RfD_{Ing} (oral reference dose) are 0.04 mg/(kg·d) and RfC_{Inh} represents an inhaled reference mass concentration of 0.013 mg/m^3. The *CDI* of F includes dermal contact of soil and water (CDI_{Der}), oral ingestion of soil, rice, vegetables, and water (CDI_{Ing}), and inhalation of ambient air (CDI_{Inh}). According to the method from the United States Environmental Protection Agency (USEPA, 2004; RAIS, 2020), and considering the Chinese regulatory guidelines (HJ/25.3-2014 and WS/T 87-2016), and combining the application of the method used in the previous research (Chavoshi E et al., 2011; Ye QF and Zhou XL, 2015; Wang M et al., 2019), the formulas for calculating *CDI* in present study are given in Table 1.

The parameters for *CDI* calculation are shown in Table 2. The concentrations of F in soil, crops, drinking water, and ambient air are measured in this study. The questionnaire investigation results show the ingestion rates of staple food (mainly rice), vegetables, and drinking water for local adults and children.

2.5. Statistical analysis

The statistical analysis was performed by IBM SPSS Statistics V 28.0. An independent-sample T-test was performed to compare F concentrations in vegetables from PCPR and GBR. When the Sig. (two-tailed) is less than the conventional 0.05, it is suggested that the two means differ significantly.

3. Results

The F concentrations in surface soil across the study area are shown in Fig. 2a. Soil F concentrations range from 219 mg/kg to 7296 mg/kg, with an average value of 1067 mg/kg, which is much higher than the national background value of F in the surface soil of China (837 mg/kg).

The F concentrations of rice and vegetables are shown in Fig. 2b. The rice samples exhibit F concentration of 0.99–3.00

Table 1. Calculation formulas for daily intake of F in different exposure pathways.

Exposure pathway	Media	Formulas
Dermal contact	Soil	$CDI_{der-soil} = \frac{C \times SA \times AF \times ABF \times EF \times ED \times CF}{BW \times AT}$
	Water	$CDI_{der-water} = \frac{C \times EV_{dermal-water} \times ET \times SA \times EF \times ED \times CF}{BW \times AT}$
Ingestion	Soil	$CDI_{ing-soil} = \frac{C \times IngR_{soil} \times EF \times ED \times CF}{BW \times AT}$
	Water	$CDI_{ing-water} = \frac{C \times IngR_{oral-water} \times EF \times ED}{BW \times AT}$
	Grain/vegetable	$CDI_{ing-grain/vegetable} = \frac{C \times IngR_{grain/vegetable} \times EF \times ED}{BW \times AT}$
Inhalation	Ambient air	$CDI_{inh-air} = \frac{C \times ET_{air} \times EF \times ED}{24 \times AT}$

Table 2. Parameters in human health risk exposure of F.

Parameter	Meaning	Reference value		Unit	References
		Adults	Children		
C	F content of soil, grain, vegetables, water, and ambient air	Measured value		mg/kg (mg/L or μg/m^3)	Measured values in this study
IngR_{grain}	Ingestion rate of grain	0.5	0.2	kg/day	Questionnaire investigation in this study
Ing$R_{vegetables}$	Ingestion rate of vegetables	0.4	0.2	kg/day	
IngR_{water}	Ingestion rate of water	1.5	0.7	L/day	
IngR_{soil}	Ingestion rate of soil	100	200	mg/day	RAIS, 2020
Inh	Inhalation rate	14.5	7.5	m^3/day	
SA_{soil}	Skin surface area available for contact soil	6032	2373	cm^2	
SA_{water}	Skin surface area available for contact water	19652	6365	cm^2	
EV_{shower}	Daily exposure frequency of dermal contact event	1	1	/	
ET_{shower}	Daily exposure time to shower water	0.71	0.54	h/day	
ET_{air}	Daily exposure time to ambient air	24	24	h/day	
AF	Absorption factor	0.07	0.2	mg/cm^2	
ABF	Absorption factor of skin absorption	0.01	0.01	/	
EF	Exposure frequency	350	350	day/year	
ED	Exposure duration of adults	24	6	year	
CF	Conversion factor	10^{-6}	10^{-6}	/	
BW	Average body weight	61.8	19.2	kg	
AT	Average time	365 × 24	365 × 6	days	

mg/kg (Fig. 2b). The rice samples from GBR show slightly lower F content than that from PCPR, with average values of 1.54 mg/kg and 1.78 mg/kg, respectively (Fig. 2b). The biological concentration factors (BCF) for rice samples are notably low in both GBR (0.0004–0.0097) and PCPR (0.0006–0.0032). The scattered samples suggest no significant correlation between F contents in rice seed and rhizosphere soil (Fig. 2b).

The F concentrations of the edible portion of the vegetables in GBR range from 0.29 mg/kg to 1.12 mg/kg, with an average value of 0.54 mg/kg. In contrast, vegetables from PCPR show high F contents of 0.19–14.08 mg/kg, with a much higher average value (1.53 mg/kg) than that from GBR (Fig. 2c). While, most vegetable samples (e.g., bean, cucumber, pepper, radish, eggplant, and potato) show F level lower than 1.0 mg/kg, but certain scattered samples (such as Chinese cabbage, lettuce, red spinach, and celery) exhibit higher accumulations.

Drinking water in the study area is mainly from mountain springs. The F^- content of drinking water is 0.06–0.55 mg/L (Fig. 2d), with an average value of 0.16 mg/L, which is much lower than that of the WHO guideline (1.5 mg/L; WHO, 2011). No significant difference of F^- concentrations was observed between GBR (0.16 mg/L) and PCPR (0.20 mg/L) drinking water (Fig. 2d).

In terms of atmospheric fluoride, six air samples in GBR show low and uniform fluoride content varying from 0.24 μg/m^3 to 0.52 μg/m^3, with an average value of 0.29 μg/m^3. The total F concentration of the other nine samples near PCPR varies from 1.05 μg/m^3 to 42.33 μg/m^3, with an average value of 11.98 μg/m^3, which is much higher than that of air samples in GBR (Fig. 2e). According to “Ambient Air Quality Standards” (GB3095-2012), four of these samples from PCPR exceed the threshold (7 μg/m^3).

4. Discussion

4.1. Difference of F concentrations between GBR and PCPR

The F concentrations of rice and drinking water in GBR show no significant difference from those in PCPR (Figs. 2b and 2d). The average F concentrations of rice and drinking water in PCPR are 1.16 and 1.25 times higher than those in GBR, respectively.

Some vegetables and ambient air samples in PCPR show abnormally high F concentrations (Figs. 2c and 2e). Specifically, leafy vegetables (including red spinach, Chinese cabbage, celery, and lettuce) in PCPR reaches up to 0.86–14.08 mg/kg, which is 2.83 times higher than those in GBR. Independent-sample T-test results show a significant difference in F contents in leafy vegetables between PCPR and BCR (Table 3). However, non-leafy vegetables (e.g., bean, cucumber, pepper, radish, eggplant, and potato) show no significant inter-regional differences (Table 3). The F concentration of ambient air samples near PCPR is markedly high up to 12.02–42.33 μg/m^3, the average of which is 41.31 times higher than those in GBR (Fig. 2e).

Compared to GBR, PCPR is superposed by phosphorus chemical processes, which produce F-containing gases and release them into the atmosphere. The F-rich air falls on leaves of leafy vegetables through dry and wet deposition and was further adsorbed by leaves. This process accounts for the significantly higher F accumulation in leafy vegetables and ambient air samples from PCPR compared to GBR.

However, rice, as a kind of seed, is not prone to absorb fluorine from the air. The drinking water mainly comes from mountain spring, which is hardly exposed on earth’s surface, and thus was hardly affected by the dry and wet deposition of fluorine.

4.2. Health risk assessment of F exposure

According to USEPA (2004), human exposure to the F in soil, water, crops, and ambient air occurs via three pathways: Dermal contact, ingestion, and inhalation (Fig. 3a). Given the observed differences in F concentrations of ambient air and vegetables between GBR and PCPR, the *HQ* was calculated, respectively, for residents in GBR and PCPR.

4.2.1. Health risk of F in GBR

The average *HQ* values of for adults and children followed the order: HQ_{Ing} >> HQ_{Inh} > HQ_{Der} (Table 4), indicating that the contribution by oral ingestion was much higher than that by dermal contact and inhalation (Fig. 3b). Dermal contact posed the least risk in terms of F exposure. The *HQ* values of children and adults were 0.97 and 0.56, which are less than 1.0, indicating an insignificant health risk. However, children are more susceptible by exposure to F for their *HQ* (0.97) close to 1.0. Crops were identified as the primary exposure medium for F in GBR (Fig. 3c), largely due to their relatively high F concentrations and substantial ingestion rates. The lower effects of soil, water, and ambient air can be attributed to their lesser dermal contact/ingestion dose or lower F contents than those of crops.

4.2.2. Health risk of F in PCPR

The average *HQ* values for adults and children in PCPR are 0.86 and 1.39, respectively, which is substantially higher than those in GBR (Fig. 3). The *HQ* for children exceeds the safety threshold of 1.0, indicating potential health risks, which is consistent with previous studies that children are considered as the high-risk groups in the vicinity of PCPR (Zhu YM et al., 2014; Wang M et al., 2019). The contribution of dermal contact and inhalation to F exposure was far below that of ingestion (Fig. 3b). Most noteworthy is the case that F total daily intake (*TDI*) by inhalation of ambient air by adults in PCPR reaches 0.021 mg/day (Table 4), which exceeds the USEPA-recommended inhalation *TDI* limit of 0.015 mg/day (USEPA, 2004). The excessive daily intake of F by inhalation may cause adverse effects on the health of adults.

Overall, oral ingestion and inhalation are the dominant F exposure pathways in PCPR. The discrepancy of *HQ* values between residents in PCPR and GBR comes mainly from leafy vegetables and ambient air (Fig. 3c). More attention should be given to human health in PCPR.

4.3. Geological controlling factors for low health risk of soil F

In the study area, soils are enriched in F originating from natural weathering processes or superposed by anthropogenic activities. Despite this enrichment, fluorine in soils exhibits limited mobility and does not readily migrate into water or crops, thereby posing no human health risk. The geological

Table 3. Independent samples test of F content in vegetables between PCPR and BCR.

		Levene's test for equality of variances		T-test for equality of means						
		F	Sig.	*t*	Degrees of Freedom	Sig. (two-tailed)	Mean difference	Standard error	95% confidence interval of difference	
									Lower limit	Upper limit
F content of leafy vegetables	Assuming equal variances	41.049	0	−5.812	39	0.000	−4.311	0.742	−5.811	−2.810
	Assuming unequal variances			−2.992	8.01	0.017	−4.311	1.441	−7.633	−0.989
F content of other vegetables	Assuming equal variances	1.364	0.248	−0.452	56	0.653	−0.021	0.046	−0.112	0.071
	Assuming unequal variances			−0.429	39.89	0.670	−0.021	0.048	−0.118	0.077

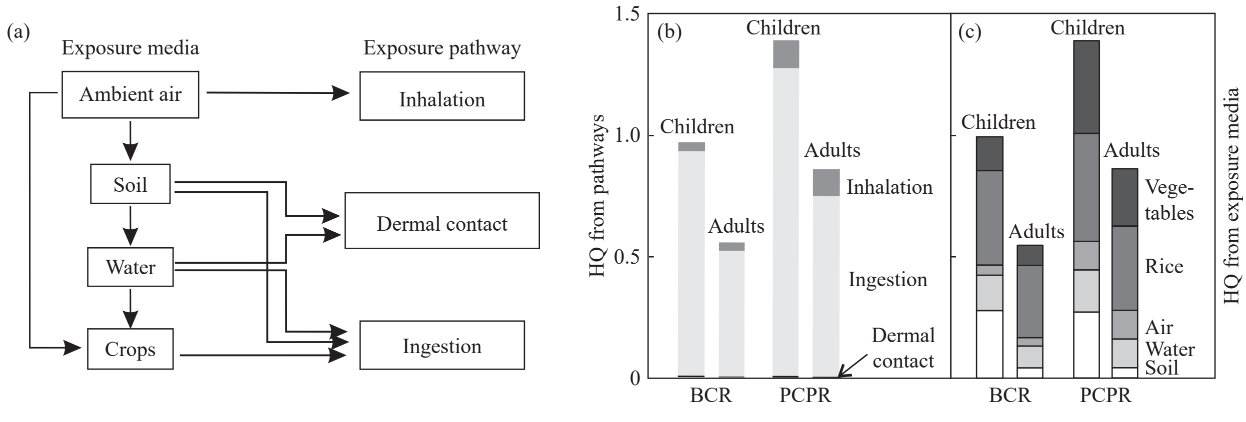

Fig. 3. a–Exposure media and pathways of F; b–*HQ* of F via three pathways; c–*HQ* of F via five media for children and adults in GBR and PCPR.

controlling factors are discussed as follows.

4.3.1. Fractions and occurrence form of F in soil

The F fractions in rhizosphere soil follow the order: Residual F >> Fe-Mn oxide F > organic F ≈ exchangeable F > water-soluble F (Fig. 4). Water-soluble F concentrations are minimal (1.39–22.3 mg/kg), accounting for only 0.12%–1.42% of total F. While residual F content reaches up to 319–2098 mg/kg and the percentage is high to 89.2–97.4%. The Electron Probe Microprobe analysis shows that soil F occurs mainly

in apatite and clay minerals (e.g. talc and illite). The F contents of apatite are 2.73–3.38 mg/kg, and those of talc and illite are relatively low to 1.36% and 0.35%, respectively (Fig. 5).

The soluble F, despite its low abundance, exhibits high biological effectiveness and mobility into water or crops (Loganathan P et al., 2001; Chen W, 2010; Makete N et al., 2022). In contrast, the residual F exists in the lattice of mineral particles and is difficult to become bioavailable (Rizzu M et al., 2020). In studied soils, approximately 94.4±3.2% of fluorine exists in the residual form, primarily due to OH^- substitution within the apatite and clay mineral structures, which substantially limits its transfer into water bodies or crops and minimizes health risks.

4.3.2. Hydrogeochemical type of groundwater

The hydrogeochemical feature is an important factor in controlling the F^- concentration of water. The pH of groundwater in the study area is mainly 6.60–7.63, which is neutral to slightly alkaline. The Ca^{2+} and HCO_3^- are the predominant cation and anion, respectively, with average proportions reaching up to 70.2% and 72.6%. They are

Table 4. *CDI*, *HQ*, and *TDI* values of F exposure to soil, water, rice, vegetables, and ambient air.

Study area	Intake pathway	Medium	Fluorine content	*CDI* /(mg/kg.day)		Reference dose/concent	*HQ*		*HQ* Proportion /%		*TDI* /(mg/day)	
				Adults	Children		Adults	Children	Adults	Children	Adults	Children
Carbonate area	Dermal contact	Soil	1067 mg/kg	0.00007	0.00025	0.04 mg/kg	0.0026	0.0070	0.47	0.72	0.004	0.0040
		Water	0.16 mg/L	0.00004	0.00003						0.002	0.00043
	Oral ingestion	Soil	1067 mg/kg	0.0017	0.0107	0.04 mg/kg	0.52	0.93	92.91	95.48	0.09	0.17
		Vegetables	0.54 mg/kg	0.0034	0.0054						0.19	0.09
		Rice	1.54 mg/kg	0.0120	0.0154						0.68	0.24
		Water	0.16 mg/L	0.0037	0.0056						0.21	0.09
	Inhalation	Air	0.0005 mg/m^3	0.0005 mg/m^3		0.013 mg/m^3	0.037	0.037	6.62	3.80	0.007	0.004
	Total						0.56	0.97	100	100	1.19	0.60
Phosphorus chemical plant	Dermal contact	Soil	1067 mg/kg	0.00007	0.00025	0.04 mg/kg	0.0028	0.0072	0.33	0.52	0.004	0.004
		Water	0.20 mg/L	0.00004	0.00003						0.002	0.0006
	Oral ingestion	Soil	1067 mg/kg	0.0017	0.01066	0.04 mg/kg	0.74	1.27	86.41	91.30	0.09	0.17
		Vegetables	1.53 mg/kg	0.0095	0.01528						0.54	0.24
		Rice	1.78 mg/kg	0.0138	0.0178						0.78	0.28
		Water	0.20 mg/L	0.0047	0.0070						0.26	0.11
	Inhalation	Air	0.0015 mg/m^3	0.0015 mg/m^3		0.013 mg/m^3	0.11	0.11	13.26	8.18	0.021	0.011
	Total						0.86	1.39	100	100	1.71	0.82

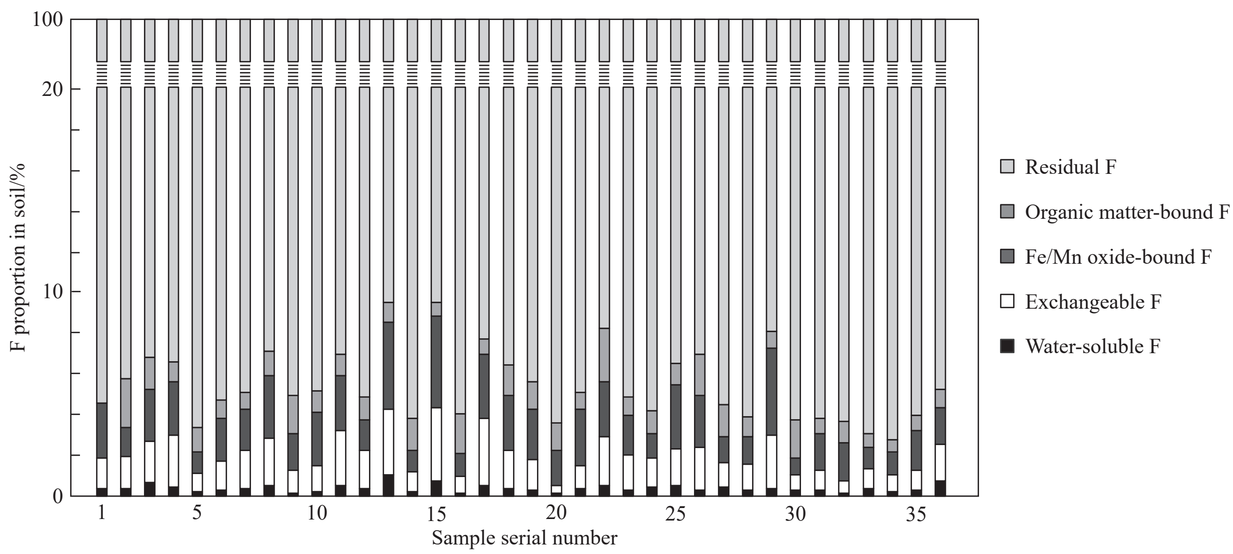

Fig. 4. Proportion of F fractions in soil.

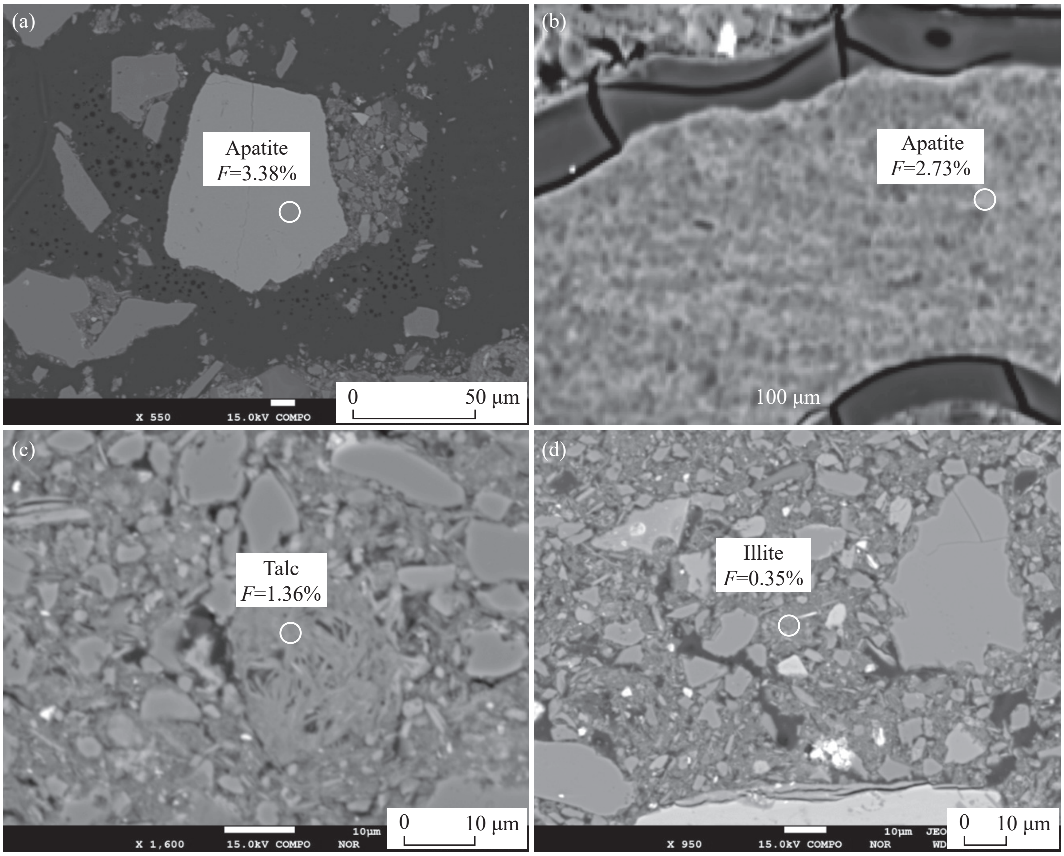

Fig. 5. BSE images showing F content in soil minerals.

predominantly $CaHCO_3$ type (Fig. 6). The chemical type of groundwater in the carbonate rock areas is mainly $CaHCO_3$, which was attributed to both recharge and the weathering of carbonate minerals and silicate (Mamatha P and Rao MS, 2010). This is consistent with the conclusion proposed in previous studies that F content is commonly low in $CaHCO_3$ type groundwater (Chae GT et al., 2007; Wang Z et al., 2021; Lu MY et al., 2023).

Previous studies have shown that alkaline pH, low Ca^{2+}, and high HCO_3^- concentrations promote the release of F^- into the groundwater (Jacks G et al., 2005; Guo QH et al., 2010; Borgnino L et al., 2013; Dehbandi R et al., 2018; Rashid A et al., 2018). The F in studied soils exists mainly in the crystal lattice of apatite and clay minerals, which is prone to be released by the cation exchange process and water-rock interactions in an alkaline conditions for isomorphic substitution of F^- by OH^- (Flühler H et al., 1982), as described in Reactions (1) and (2). The concentration of Ca^{2+} is much higher than that of Na^+ in studied groundwater, and the F^- may precipitate as CaF_2 (Reaction 3). Therefore, the $CaHCO_3$ type of groundwater contributes significantly to the low F^- of groundwater in the study area.

$$\text{Apatite}: Ca_{10}(PO_4)_6F_2+2OH^- \rightarrow Ca_{10}(PO_4)_6(OH)_2+2F^- \quad (2)$$

$$\text{Claymineral}: Na_x(Al,Mg)_2[Si_4O_{10}]F_2\cdot nH_2O+2OH^- \rightarrow Na_x(Al,Mg)_2[Si_4O_{10}](OH)_2\cdot nH_2O+2F^- \quad (3)$$

$$Ca^{2+}+2F^- \rightarrow CaF_2 \quad (4)$$

4.3.3. Immobilization of F by bottom sediment

In the drinking water-bottom sediment system, the total F content in the sediment is notably high (323–3013 mg/kg; Fig. 7), contrasting with the low F^- levels in drinking water (0.06–0.55 mg/L). The soluble F content in sediment is minimal (0.87–12.9 mg/kg), accounting for only 0.07%–1.36% of total F (Fig. 7). The F in sediment occurs predominantly in iron-aluminum hydroxides and high up to 1.18%–2.84% (Fig. 8), while clay minerals contribute less (0.18%–0.53%). These findings are consistent with the conclusion that oxy-hydroxides of Al and Fe, and clay minerals have a crucial role in the fixation of fluorine (Wayne Nesbitt H and Markovics G, 1997; Wang Y et al., 2002; Dehbandi R et al., 2017). Therefore, the F in the drinking water-bottom sediment system is immobilized by iron-aluminum hydroxides and clay minerals in the bottom sediment, and consequently is difficult to release into drinking water.

4.4. Reasons and prevention recommendations for health risk of F

The primary raw material for phosphate fertilizer, phosphorus acid, and other phosphorus chemical production activities is F-rich apatite, which typically contains over 3% F (Gao S, 2017; Fuge R, 2019; Proidak A et al., 2021). During

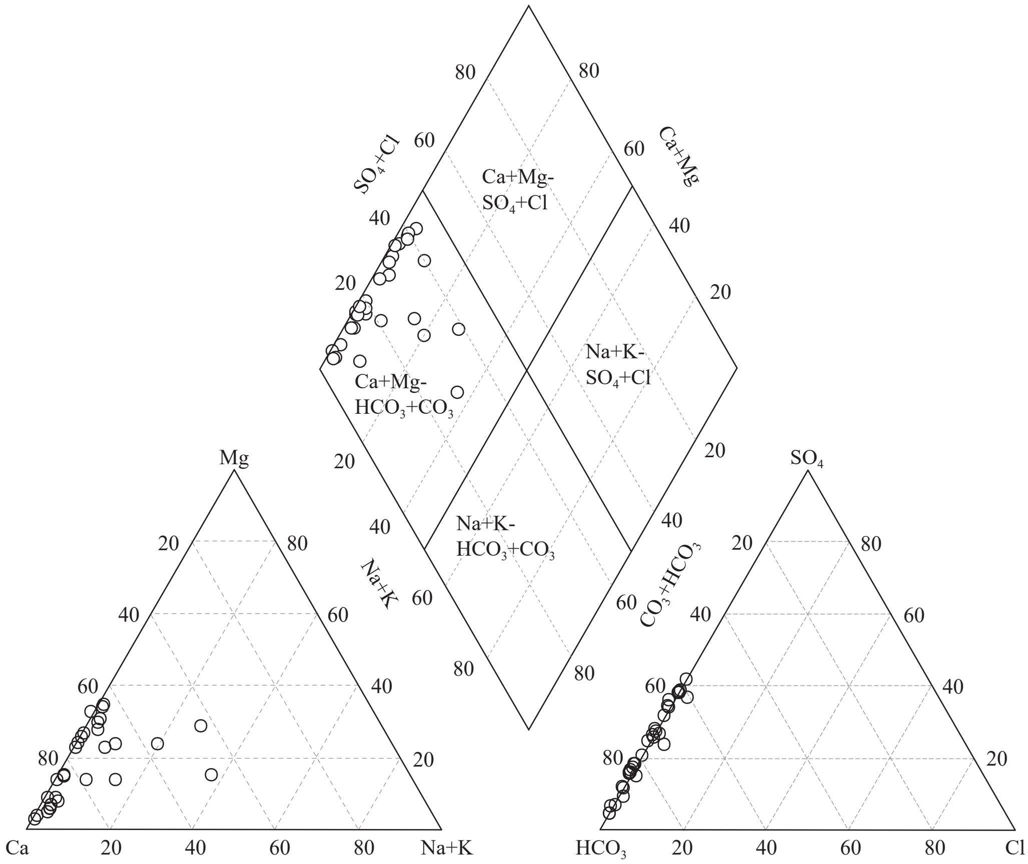

Fig. 6. Piper plots of the major ion compositions of groundwater.

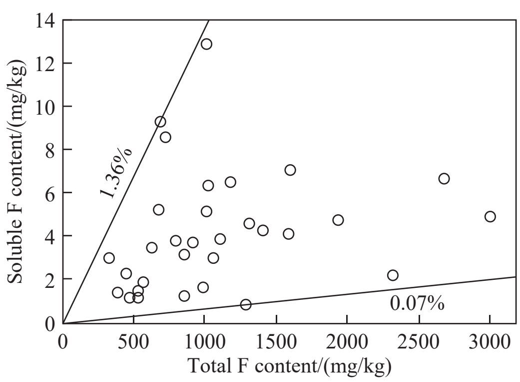

Fig. 7. Total and soluble F contents in bottom sediment of drinking water.

the wet phosphorus acid process, chemical reactions generate HF and SiF_4 gases, which significantly contribute to industrial F emissions into ambient air (Yu YQ et al., 2020). The ambient air in PCPR has a higher F concentration than the national standard (Fig. 4). Fluorine in ambient air may enter the human body directly via inhalation (Fig. 9). Moreover, the atmospheric F can deposit on the surface of vegetable leaves and lead to F accumulation in vegetables (He LL et al., 2021; Wang M et al., 2023). The leafy vegetables in the study area such as amaranth, lettuce, celery, and cabbage in PCPR yield 2.73–14.08 mg/kg, 1.09–5.49 mg/kg, 0.86–5.07 mg/kg, and 2.65–3.34 mg/kg, respectively, which are subsequently ingested by residents (Fig. 9).

Regarding the above reasons for the health risk of F in PCPR, two feasible prevention recommendations are proposed as follows:

(i) Enhance the disposal of F-containing waste gas.

HF and SiF_4 are highly water-soluble, forming hydrofluoric acid, fluosilicic acid, and silica gel. Therefore, the water or alkali absorption is broadly applied in washing F-containing waste gas and recycling F resources. The latest defluorination technologies by Fe/N co-doped microporous carbon or Al/N-doped porous carbon have been confirmed to enhance the efficiency of fluorine removal (Zhang W et al., 2022; Huang QS et al., 2025). The phosphorus chemical enterprise should adopt the “two-level adsorption” defluorination process (water/alkali adsorption+microporous carbon adsorption) to dispose F-containing waste gas, improve the defluorination rate, and minimize the fluoride emission into the ambient air. Meanwhile, government must enforce stricter supervision, including periodic monitoring of ambient air F levels.

(ii) Minimize the growth of leafy vegetables that easily accumulate F.

Due to their large surface area and thin cuticle, leafy vegetables are highly susceptible to airborne fluorine deposition and accumulation (He LL et al., 2021). Therefore, it is not encouraged to grow these leafy vegetables, such as amaranth, lettuce, celery, and cabbage in PCPR. The bean, cucumber, pepper, eggplant, and pumpkin have lower F content than 1.0 mg/kg, which do not easily accumulate F, are

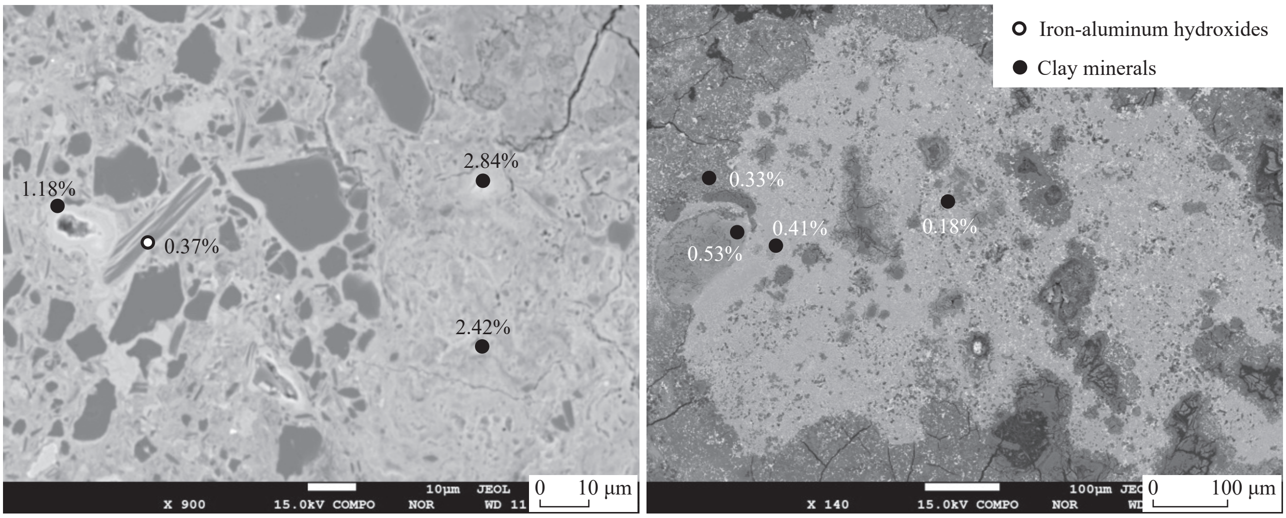

Fig. 8. BSE images showing F content of iron-aluminum hydroxides and clay minerals in bottom sediment of drinking water.

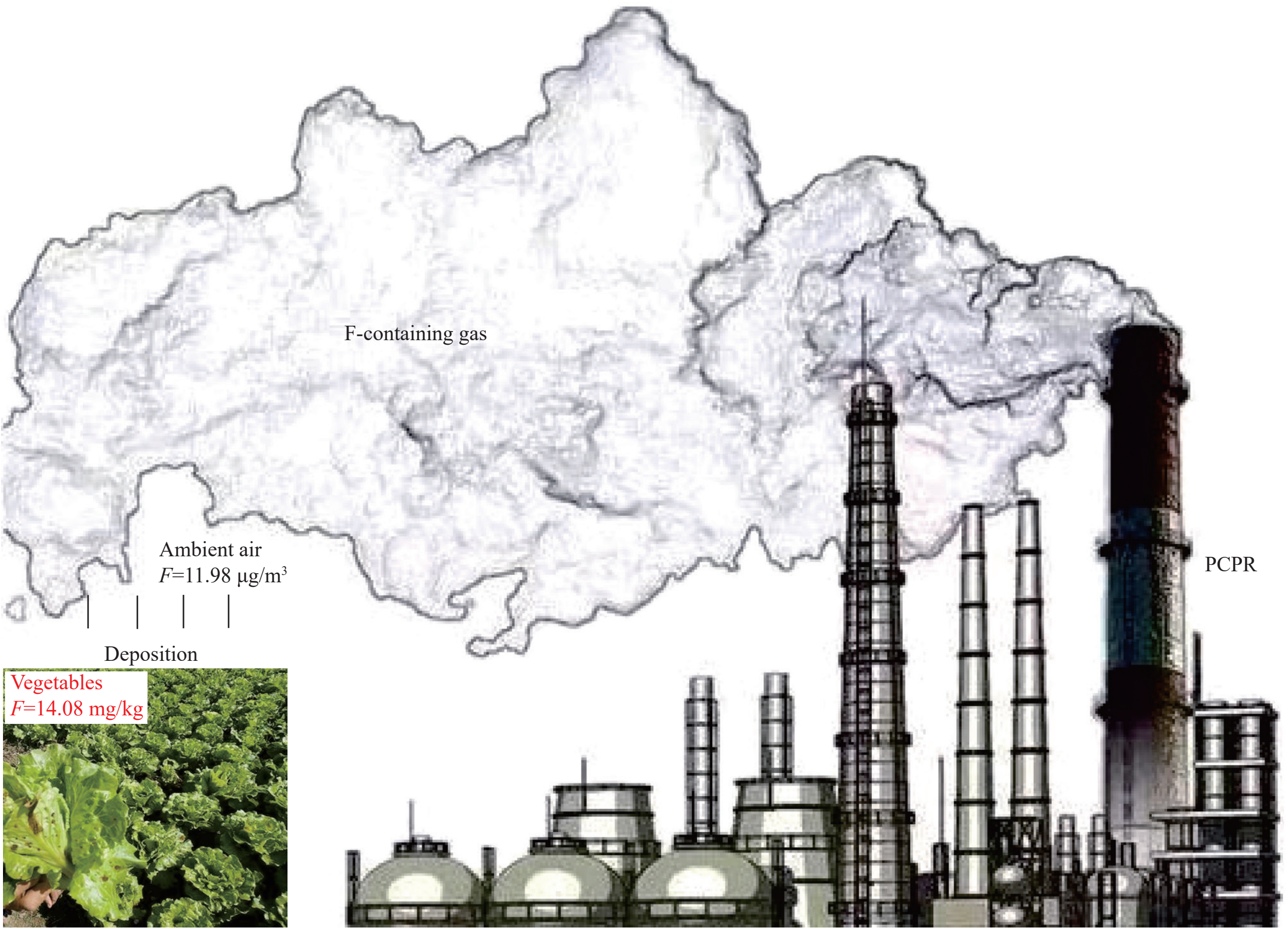

Fig. 9. Picture showing the deposition of F-rich gas on leafy vegetables in PCPR.

more suitable for cultivation in these areas.

5. Conclusions

In this study, the authors present the first comparative assessment of F health risk from soil and air exposure in GBR and PCPR in central Guizhou Province, Southwest China. The results indicate that F concentrations in rice and drinking water do not differ significantly between GBR and PCPR. However, certain leafy vegetables and ambient air samples collected near PCPR exhibit significantly elevated F concentrations compared to those in GBR. These findings indicate negligible F-related health risks in GBR but suggest potential risks to both children and adults in PCPR.

There are three predominant geological controlling factors to prevent F transport from soil to water and crops: (1) Soil F occurs predominantly as residual-F and exists in apatite and clay mineral lattices; (2) the $CaHCO_3$ hydrogeochemical type of groundwater promotes F deposition; (3) iron-aluminum hydroxides and clay minerals immobilize F in bottom sediment. In PCPR, F-rich ambient air is the main cause of human health risks. Improvement of F-rich waste gas disposal and caution of leafy vegetable cultivation are effective recommendations to reduce F health risks in PCPR.

Conclusively, this study contributes in better understanding the health risk of F in PCPR, which may provide the basis for proper management plans to alleviate the adverse effects of excessive F from anthropogenic origin. However, a key limitation of this study mainly lies in the fact that differences in dietary habits of the population were not taken into account in health risk assessment, which may pose a slight impact on the *HQ* value. Future research should focus on elucidating fluorine transport mechanisms within the soil-crops-humans system, especially reveal the bioefficiency of F, to more accurately assess its potential health impacts.

CRediT authorship contribution statement

Xiu-jin Liu, Ya-long Zhou, Min Peng, and Hang-xin Cheng conceived of the present idea. Li Zhang and Zhi-zhuo Liu carried out field investigation and sample collection. Shi-qi Tang, Fei Liu, and Yan-fei Qi processed experiment data and drawed pictures. All authors discussed the results and contributed to the final manuscript.

Declaration of competing interest

The authors declare no conflicts of interest.

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