



Vertical distribution of fluorine in farmland soil profiles around phosphorous chemical industry factories

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Abstract

High concentration of fluorine (F) in agricultural soils has got significant attention considering its impacts on human health, but little information was available about F distribution in farmland soil profiles around phosphorous chemical industry factories. In present study, farmland soil profiles and relevant medium samples were collected from farmlands around a main phosphorous chemical base in southwest China. At 0–100-cm profiles, concentrations of soil total F (Ft, 400.9–1612.0 mg kg⁻¹) and water soluble F (Fw, 3.4–26.0 mg kg⁻¹) decreased with profile depth in industrial areas. Industrial activities enhanced F concentration in soil mainly at 0–40-cm profiles. No disparity for both Ft and Fw distributions in paddy-dry land rotation field and dry land indicates short-term land utilization could not affect the F distribution in soil profiles. Correlation analysis showed soil organic matter and wind direction were important factors influencing the distribution of F in soil profiles. The shutdown of factory and government control of industrial emissions effectively decreased the ambient air F (Fa) concentrations in industrial areas. In where Fa and dustfall F concentrations were high, high soil Ft, Fw, and crop edible part F concentrations were found.

Keywords Fluorine · Distribution · Farmland · Soil profile · Crops · Phosphorous chemical industry

Introduction

Fluorine (F) is ubiquitous in the environment, and the amount of F occurring naturally is dependent on the individual geological environment (Harrison 2005; Kahama et al. 1997; Mandinic et al. 2010). Natural and anthropogenic processes contribute to the release of F into the environment and result in accumulation of F in the soils (Pickering 1985). The main natural sources of F in soil derive from volcanic activity and weathering of parent rock (Pickering 1985). In most soils, F concentrations are determined between 20 and 500 mg kg⁻¹

(Ozsvath 2009), with average F concentration in soils to be about 300 mg kg⁻¹ (Arnesen et al. 1995; Larsen and Widdowson 1971). By inputs of artificial materials through industrial and/or agricultural activities, soil F concentrations have increased greatly in certain areas (Polomski et al. 1982). Industries (i.e., aluminum, brick, steel, glass, and fertilizer manufacturing) which use raw materials containing even small amounts of F can release enough gaseous and/or particulate fluorides to the surrounding areas (Cronin et al. 2000; Pickering 1985). In agricultural activities, the use of fertilizers, pesticides, phosphogypsum, and the other soil amendments with high F content increased the farmland soil F concentration (Loganathan et al. 2008).

Fluorine is one of several trace elements receiving much attention in view of its possible beneficial and harmful effects on environment and health (Koblar et al. 2015). Soil F pollution affects the activity of soil microbial communities (Poulsen 2011), inhibits plant growth (Arnesen 1997), and harms human and animal health (Cronin et al. 2000). Fluorine-related adverse effects are considered to be major health and environmental issues in many regions of the world (Koblar et al. 2015). China is a country where soil is enriched in F in many regions and suffered from the fluorosis relatively seriously (Wang et al. 2012). Sichuan Province is one of the

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typical epidemic fluorosis areas in China. In 2012, the endemic disease prevention and control report of Sichuan Province pointed out that epidemic fluorosis covered 61 counties in 14 cities (states) and threatened a population of about 17.34 million. Shifang is a county-level city and a typical epidemic fluorosis area of Sichuan Province. Shifang is also known as “City of Phosphorite” because of rich phosphate rock and thriving phosphorous chemical industry.

Concentration of pollutants in soil could reflect the characteristics of long-term industrial pollution. The establishment of phosphorous chemical factories in Shifang began at the end of the 1850s. However, information about the F concentrations in the cultivated soils in Shifang is limited or unavailable. The objectives of this study are to (1) reveal the vertical distribution characteristics of soil total F (Ft) and water soluble F (Fw) in paddy-dry land rotation field and dry land in agricultural region and industrial areas; (2) discuss the correlation between F (both Ft and Fw) concentration and physicochemical properties of the soils; and (3) identify the F concentration of various media, such as ambient air, irrigation water, and edible portion of main crops etc. The results could support theory development of F migration and transformation in environment and provide information on the pollution control and management of polluted farmland soils due to industry production.

Materials and methods

Sampling sites

Study area is situated in Shifang City, Sichuan Province, southwest China (Fig. 1). The climate of Shifang is subtropical monsoon climate. The mean annual temperature and precipitation of Shifang is 15.2–17.4 °C and 939 mm, respectively. The prevalent wind direction is northeaster. The city covers 86,300 ha, with a total population of 0.44 million. Mountains lie in the northwest in the territory. And the southeast of Shifang is plain while the midland is hilly. Phosphorus chemical factories are situated in both plain and hilly areas. Shifang is one of the six major phosphate rock bases of China, with proved reserves of phosphate rock 170 million tonnes and prospective reserves 300 million tonnes. Meanwhile, Shifang is an important production base of grain and oil. The total annual output of grain, oilseeds, and vegetables is 189.6, 13.6, and 387.6 thousand tonnes, respectively.

Six farmland profiles which were expected to exhibit a wide range of F concentrations were selected for analyzing the vertical distribution characteristics of F in soil profiles (Fig. 1). Located in Jinniu Village, Majing Town, the agricultural region (control, Fig. 1(a)) has no phosphorous chemical plant around 20 km in all directions. Higher concentrations of soil F were expected in farmlands in the vicinity of HD (Fig. 1(b)) and CXD (Fig. 1(c)) phosphorous chemical plants. The HD plant was built

in 1979. The main products and annual productions of the factory were phosphoric acid (0.2 million tonnes), monoammonium phosphate (0.35 million tonnes), calcium hydrophosphate (0.08 million tonnes), compound fertilizer (0.03 million tonnes), sulfuric acid (0.34 million tonnes), calcined gypsum (0.13 million tonnes), electrolytic zinc (0.22 million tonnes), and zinc alloy (0.10 million tonnes). The CXD factory was built in 1975, and the productions of main products were phosphate fertilizer (0.30 million tonnes), compound fertilizer (0.50 million tonnes), sulfuric acid (0.34 million tonnes), and fluorine sodium silicate (1000 tonnes). The CXD plant was closed down at the end of June 2017.

The control and HD areas were in the plain area, while CXD industry was located in the hilly area. The arable land in the plain area was in paddy-dry land rotation, and that in the hilly area was dry land. Therefore, soil profile samples from both dry lands and paddy fields were selected in control and HD area, while only dry land profiles were chosen in CXD area. Considering the location of factories and cultivated lands, farmland profile samples in the prevailing downwind ~ 100 m away from the HD plant were collected, which labeled as HD-dry land and HD-paddy field, respectively. In hill, the dry lands in the prevailing downwind ~ 100 m to CXD plant (CXD-downwind) and in the upwind ~ 400 m to the plant (CXD-upwind) were chosen to evaluate the influence of wind direction on F concentration in soils.

Sample collection

All soil samples were collected in October 2016. Six profiles were prepared at the farmland sites in Shifang (Fig. 1). In CXD-downwind, control-dry land, and HD-dry land farmlands, sweet potatoes have been harvested which leading to the soils of the plow layers fluffy and porous. The control-paddy field and HD-paddy field have raped rice with no water submerging the farmland. The CXD-upwind site has raped corn, and the topsoil was hard. All the topsoil in study area was gray-brown soil. Based on the geological map of China database and the sampling situations, the soil parent materials in control and HD area is fluvial deposits, and that of CXD-downwind and CXD-upwind is gray sandy gravel and yellow sandy clay, respectively. The soil parent materials appeared at diverse depths at different sampling sites. In the two control profiles, the river-sand appeared at 60–100-cm profiles, and the gravel increased with the depth. No pebble appeared in control sites, while pebbles were found at 60–100 cm and 80–100 cm in HD-paddy field and HD-dry land profiles, respectively. The yellow sandy clay layer emerged at 60–100-cm profile of CXD-upwind farmland, but no parent rock was observed in the CXD-downwind profile. According to Zhang et al. (2010), three parallel soil samples were collected for each profile at depth scales 0–20, 20–40, 40–60, 60–80, and 80–100 cm.

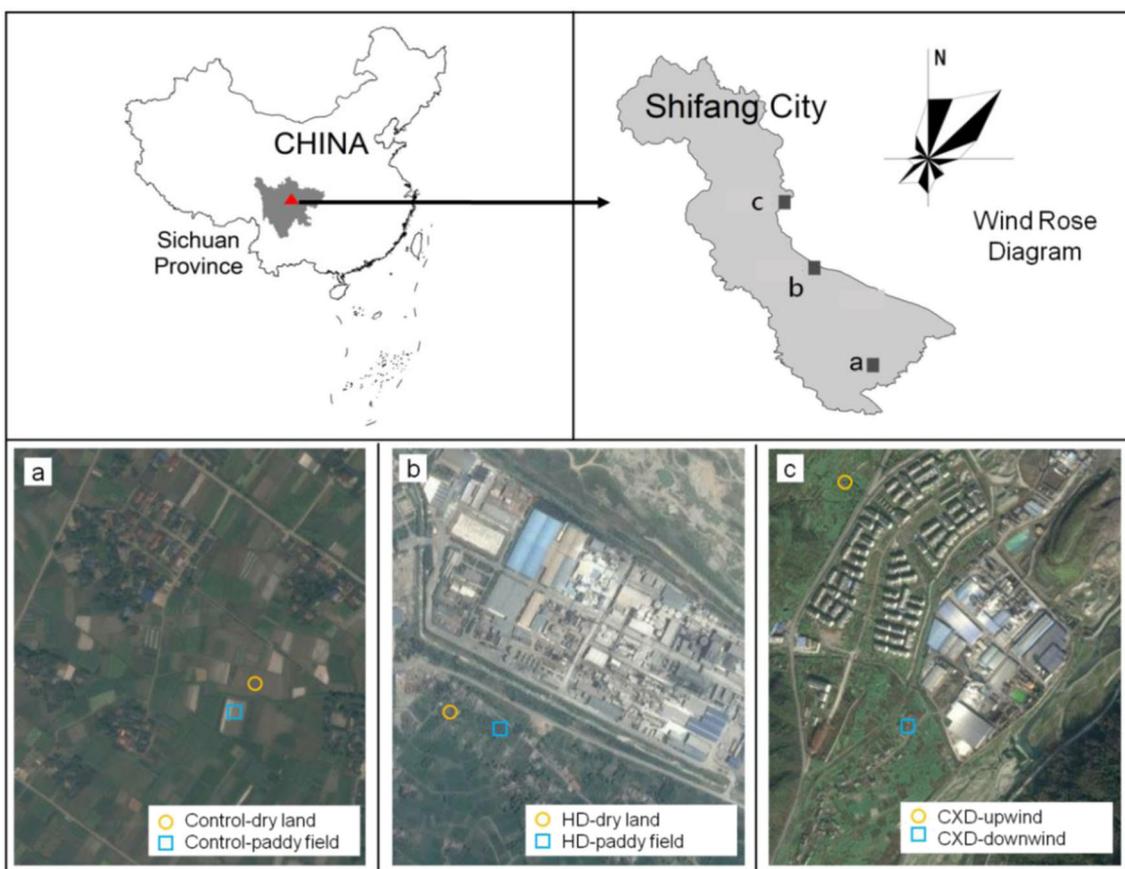


Fig. 1 Location map of the sample sites in Shifang City, Sichuan Province, southwest China. Image from the Google Earth software. **a** represents the control area. **(b)** and **(c)** represent the HD and CXD phosphorous chemical industrial area, respectively

To understand the impacts of local industrial activities on the soil F content around the phosphorous chemical industry factories, the ambient air, dustfalls, and irrigation water samples were collected in study area. The ambient air F (Fa) was collected by lime-paper followed by the guidance of national standards of China (GB/T 15433-1995). The air monitoring sites were arranged in the vicinity of the soil profiles at control and HD- and CXD-downwind. Except the lack of sample in December at control sites, Fa samples from June to December 2017 were collected. Four parallels at each sampling site for each month were collected, and there were 68 air samples in total. After finished the air sample collection, the dustfalls fallen on the raincover were collected. The water in irrigation canals and ditches near the profiles was collected. Each water sample was collected by a 500-mL polyethylene bottles after washing three times with the water. Three parallel phosphate rock samples, the raw materials of the phosphorous chemical factories, were collected from the rock storage stacks. Samples of phosphogypsum, a main by-product of the industrial production, were collected from the HD and CXD plant. Each phosphate rock or phosphogypsum sample included ten subsamples in a total weight of ~ 1 kg. Phosphate fertilizer was unpopular in study area; thus, samples of nitrogen and potash fertilizers which were normally

used were bought from the market in Shifang, and compound fertilizers were collected from the peasant household.

Considering the possible effects of soil F on human health through the food chain, the edible parts of the main crops were collected nearby the profiles during soil sampling. Samples including beans of soybean (*Glycine max*), leaves of rape (*Brassica campestris*), and leaves of Chinese cabbage (*Brassica rapa pekinensis*) were collected based on the random sample method. About 2.5-kg sample of each crop was collected.

Chemical analysis

The soil samples were air-dried and sieved to < 2 mm for soil water soluble F (Fw), pH, and soil available phosphorus (Av-P) analysis. Subsamples were sieved to < 0.15 mm for soil total F (Ft), metal elements, organic matter (OM), and soil total phosphorus (TP) analysis. Soil pH was measured in a water suspension using a solid-liquid ratio of 1:2.5 (g:mL). Soil OM was determined by the Walkley-Black method with K₂Cr₂O₇-H₂SO₄ oxidation (Nelson et al. 1996). Soil Av-P was extracted by NH₄F-HCl or NaHCO₃ (based on pH), and TP were digested by NaOH. Soil Av-P and TP were measured with Mo-Sb colorimetric method following the industrial

standard of Agriculture Ministry of China (NY/T 1121.7-2014). The total concentrations of metals in the soil samples were determined with a portable X-ray fluorescence (PXRF, Thermo Niton XL3t, USA). The limits of detection (LOD) for Ca, Fe, K, Cr, Pb, Zn, and Mn of the machine are 300, 75, 400, 25, 8, 13, and 75 mg kg⁻¹, respectively. The concentrations of As, Cd, and Hg of the samples which were below the LOD of the instrument (7, 8, and 8 mg kg⁻¹, respectively) were neglected in present study. The quality control procedures of metal concentrations were conducted by a comparison with the certified reference material GBW07427 (GSS-14) from the General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China. The recovery rate of the seven metal elements was between 80 and 130% with the PXRF.

The ion-selective electrometry was used to analyze F concentration of all samples. However, different pretreatments were necessary for diverse samples. Before Ft concentration analysis, the soil and crop samples were digested with NaOH following the national standards of China (GB/T 22104-2008) and Mcquaker and Gurney (1995), respectively. Sample for the soil Fw concentration analysis was prepared by shaking 5.0-g samples with 30-mL distilled water for 2 h at 25 °C (Loganathan et al. 2006). The GSS-14 was used to control the determination accuracy throughout the analysis, and the recovery rate of Ft of the standard was 90–116%. The standard soybean sample (GBW 10021), obtained from the Institute of Geophysical and Geochemical Exploration, Langfang, China, was used for the quality assurance. The recovery rate of F of the standard bean varied from 81 to 89%. The pretreatment of dustfall, phosphate rock, and phosphogypsum samples was the same to the soil Ft analysis. The water samples were analyzed after filtering through Whatman No. 40 filters. The chemical fertilizer samples were dissolved with distilled water, and the lime-paper which absorbed Fa was extracted with distilled water followed by the national standards of China (GB/T 15433-1995).

Statistical analysis

Correlation analysis and significance test were carried out by the SPSS Statistics 22.0. Correlations are considered significant and extremely significant on the level of confidence of 0.05 and 0.01, respectively. Origin Pro 8.5.1 was used for creating the figures. The spatial map of sampling sites was performed with ArcGIS 10.2.

Results

Soil properties

The physicochemical properties of the soil samples were presented in Table 1. The pH of all soil samples of 0–100 cm

ranged 4.8–9.0. The pH of the surface soil (0–20 cm) samples were lower than those of the deep layers in all profiles, while the OM content was 3.0–5.6% in 0–20-cm profiles and 0.8–3.8% at 20–100-cm profiles. The contents of Fe, Ca, and K in all profiles were 2.6–4.9%, 0.2–10.6%, and 2.3–3.1%, respectively. The Av-P and TP concentrations were, in large variation ranges, 0.7–199.3 mg kg⁻¹ and 127.1–1255.2 mg kg⁻¹, respectively. The concentrations of Cr, Pb, Zn, and Mn in 0–100-cm profiles were 54.7–142.8, ≤ 32.0, 45.0–127.9, and 302.4–1689.4 mg kg⁻¹, respectively.

Vertical distribution of soil F in profiles

Soil total F

The Ft concentration in all profiles ranged 400.9–1612.0 mg kg⁻¹, and it tended to be constant along the soil profiles in the agricultural region (Fig. 2a), whereas it decreased with depth in the industrial areas (Fig. 2b, c). The Ft concentrations of control profiles were below the Swiss guidance level (700 mg kg⁻¹) of soil protection (Bundesrat 1998) (Fig. 2a), while the Ft concentrations in HD and CXD profiles were higher than the average of value (800 mg kg⁻¹) in Chinese endemic fluorosis areas (Zhang et al. 2010) (Fig. 2b, c). In plain area, the Ft concentrations at 60–100-cm profiles were apparently equal, and the relative mobility of F in dry land and paddy field was similar (Fig. 2a, b). At 60–100-cm and 0–20-cm profiles, the Ft concentrations in the CXD-downwind were higher than those in the upwind soils. However, at 20–60 cm depth, the Ft concentrations in the CXD-downwind profiles were close to those in the upwind profiles (Fig. 2c).

Soil water soluble F

The Fw concentrations in study area were 3.4–26.0 mg kg⁻¹, and it showed a decreasing trend with depth in all profiles (Fig. 3). The Fw concentrations of the two control profiles were below the Swiss guidance level (20 mg kg⁻¹) of soil protection (Bundesrat 1998) (Fig. 3a). The Fw concentrations in the surface soils of HD-paddy field (26.0 mg kg⁻¹) and HD-dry land (24.4 mg kg⁻¹) were three times than those of the control area and exceed the Swiss guidance level. The Fw concentrations of the two HD profiles decreased with depth at 0–60-cm layers and then tended to be stable at 60–100-cm layers (Fig. 3b). The Fw concentrations of CXD profiles ranged 3.4–11.0 mg kg⁻¹. The surface soil Fw concentration of CXD-downwind site was 1.6 times than that of the upwind site, whereas no difference was noted in deeper soils between the two sampling sites (Fig. 3c).

Table 1 The physicochemical properties of the soil. OM, Av-P, and TP represent organic matter, available phosphorus, and total phosphorus, respectively. “—” represents lower than detection limit. Mean value ± standard deviation was shown (*n* = 3)

Profiles	Sampling sites	pH	OM (%)	Fe (%)	Ca (%)	K (%)	Av-P (mg kg ⁻¹)	TP (mg kg ⁻¹)	Cr (mg kg ⁻¹)	Pb (mg kg ⁻¹)	Zn (mg kg ⁻¹)	Mn (mg kg ⁻¹)
Control-dry land	0–20	6.0 ± 0.9	3.0 ± 0.3	3.7 ± 0.1	1.5 ± 0.0	2.6 ± 0.1	4.7 ± 0.9	262.2 ± 126.6	97.4 ± 18.9	21.2 ± 3.5	81.6 ± 13.9	304.2 ± 27.7
	20–40	6.9 ± 0.1	1.4 ± 0.4	4.7 ± 0.4	1.6 ± 0.1	2.6 ± 0.2	1.4 ± 0.3	282.0 ± 14.3	78.3 ± 8.3	—	70.4 ± 7.1	992.5 ± 187.1
	40–60	6.8 ± 0.1	1.1 ± 0.2	4.8 ± 0.8	1.9 ± 0.0	2.7 ± 0.1	2.0 ± 0.1	277.6 ± 8.6	75.6 ± 9.2	—	78.8 ± 5.5	650.0 ± 84.5
	60–80	6.8 ± 0.1	2.0 ± 0.0	3.7 ± 0.3	2.0 ± 0.1	2.7 ± 0.1	1.4 ± 0.3	278.4 ± 36.7	77.3 ± 8.9	—	73.5 ± 8.5	417.8 ± 61.4
	80–100	6.9 ± 0.1	1.8 ± 0.2	3.3 ± 0.1	1.9 ± 0.2	2.6 ± 0.2	0.7 ± 0.1	284.1 ± 9.3	142.8 ± 59.8	—	73.6 ± 7.2	352.1 ± 63.1
Control-paddy field	0–20	6.2 ± 0.1	3.7 ± 0.2	3.1 ± 0.1	1.5 ± 0.1	2.3 ± 0.1	12.1 ± 0.4	357.5 ± 32.0	72.8 ± 13.2	19.0 ± 4.0	87.5 ± 5.4	311.8 ± 66.1
	20–40	7.5 ± 0.2	2.3 ± 0.2	3.7 ± 0.3	1.7 ± 0.1	2.5 ± 0.1	5.3 ± 0.5	281.7 ± 32.0	85.9 ± 25.9	—	60.7 ± 10.2	1679.1 ± 112.9
	40–60	6.5 ± 0.1	1.6 ± 0.4	3.6 ± 0.8	1.7 ± 0.1	2.7 ± 0.0	1.8 ± 0.3	289.1 ± 14.6	79.0 ± 8.2	—	72.7 ± 14.5	1294.0 ± 92.0
	60–80	7.4 ± 0.3	1.2 ± 0.3	2.6 ± 0.4	1.9 ± 0.2	2.5 ± 0.1	1.1 ± 0.2	255.9 ± 27.7	72.9 ± 15.0	—	47.7 ± 5.5	379.3 ± 80.1
	80–100	6.8 ± 0.1	1.4 ± 0.2	3.4 ± 0.5	1.9 ± 0.1	2.4 ± 0.1	0.8 ± 0.1	259.8 ± 33.8	65.5 ± 11.9	—	56.1 ± 17.4	369.9 ± 76.4
HD-paddy field	0–20	7.0 ± 0.1	5.6 ± 0.3	3.3 ± 0.1	1.6 ± 0.1	2.9 ± 0.1	75.6 ± 2.3	834.7 ± 101.9	107.9 ± 21.8	27.0 ± 4.4	127.9 ± 6.0	302.4 ± 48.2
	20–40	7.1 ± 0.1	3.8 ± 0.1	3.7 ± 0.1	1.1 ± 0.1	2.9 ± 0.2	11.5 ± 3.2	325.6 ± 79.2	103.2 ± 25.1	19.5 ± 3.8	83.8 ± 10.4	379.4 ± 41.9
	40–60	7.0 ± 0.1	1.0 ± 0.1	4.1 ± 0.2	1.9 ± 0.2	2.9 ± 0.1	5.5 ± 0.8	290.0 ± 26.7	90.9 ± 15.6	16.3 ± 1.7	67.0 ± 10.9	1689.4 ± 92.2
	60–80	7.2 ± 1.2	1.2 ± 0.4	4.9 ± 0.4	5.9 ± 2.1	2.5 ± 0.5	2.0 ± 1.0	307.5 ± 58	61.1 ± 14.7	—	61.5 ± 9.4	1456.4 ± 68.5
	80–100	8.7 ± 0.3	0.8 ± 0.2	3.7 ± 0.0	10.6 ± 2.4	2.3 ± 0.2	1.3 ± 0.6	270.7 ± 23.3	54.7 ± 13.5	—	60.2 ± 12.8	969.4 ± 81.4
HD-dry land	0–20	7.2 ± 0.1	4.7 ± 1.0	3.0 ± 0.1	4.7 ± 0.4	2.8 ± 0.2	59.2 ± 3.7	1088.7 ± 111.5	79.6 ± 12.9	21.5 ± 4.5	110.6 ± 11	549.2 ± 58.8
	20–40	8.1 ± 0.1	3.2 ± 0.2	2.8 ± 0.2	6.7 ± 0.4	2.7 ± 0.2	9.0 ± 1.8	417.2 ± 27.7	90.2 ± 24.6	—	52.8 ± 5.5	416.9 ± 87.5
	40–60	8.6 ± 0.1	2.6 ± 0.2	2.7 ± 0.0	5.9 ± 0.4	2.8 ± 0.1	5.4 ± 1.5	241.2 ± 5.4	99.3 ± 18.1	—	55.2 ± 6.4	476.4 ± 44.9
	60–80	8.6 ± 0.1	1.5 ± 0.1	2.6 ± 0.1	5.0 ± 0.4	2.6 ± 0.1	2.3 ± 0.8	243.2 ± 4.6	75.5 ± 25.1	—	45.0 ± 5.4	433.3 ± 62.2
	80–100	9.0 ± 0.1	1.1 ± 0.4	3.2 ± 0.1	7.9 ± 1.0	2.6 ± 0.1	1.1 ± 0.2	263.8 ± 6.3	80.8 ± 29.4	—	48.6 ± 5.3	471.1 ± 49.3
CXD-downwind	0–20	4.8 ± 0.6	5.2 ± 0.5	3.0 ± 0.1	0.3 ± 0.1	2.5 ± 0.2	199.3 ± 22.7	1255.2 ± 30.9	101.5 ± 21.6	32.0 ± 4.3	98.9 ± 9.1	373.8 ± 41.9
	20–40	5.3 ± 0.3	2.9 ± 0.6	2.8 ± 0.1	0.2 ± 0.1	2.5 ± 0.3	6.0 ± 0.9	455.4 ± 54.3	88.4 ± 20.4	20.2 ± 2.7	95.9 ± 13.2	792.7 ± 91.8
	40–60	6.0 ± 0.3	2.4 ± 0.3	3.1 ± 0.4	0.4 ± 0.1	2.7 ± 0.6	4.2 ± 0.8	277.5 ± 23.9	87.0 ± 22.1	18.5 ± 1.0	80.7 ± 17.7	636.1 ± 81.0
	60–80	6.3 ± 0.1	2.4 ± 0.4	3.3 ± 0.1	0.4 ± 0.1	3.0 ± 0.2	3.0 ± 0.3	251.5 ± 3.1	102.1 ± 14.5	19.8 ± 3.2	81.5 ± 5.9	658.3 ± 69.2
	80–100	6.3 ± 0.1	2.5 ± 0.6	3.4 ± 0.2	0.5 ± 0.0	3.1 ± 0.1	1.6 ± 0.7	213.7 ± 17.2	111.6 ± 13.3	16.3 ± 1.2	77.8 ± 8.2	613.7 ± 53.0
CXD-upwind	0–20	5.4 ± 0.3	3.7 ± 1.8	3.3 ± 0.2	0.3 ± 0.0	2.7 ± 0.2	79.0 ± 6.7	498.3 ± 42.9	108.8 ± 20.8	30.4 ± 3.6	108.2 ± 14.6	593.6 ± 83.8
	20–40	5.8 ± 0.2	2.8 ± 0.4	3.3 ± 0.1	0.4 ± 0.0	2.9 ± 0.2	16.8 ± 1.1	270.3 ± 34.1	87.7 ± 19.4	19.3 ± 1.7	83.6 ± 11.8	740.6 ± 61.7
	40–60	6.7 ± 0.2	1.9 ± 0.8	3.5 ± 0.2	0.4 ± 0.1	2.9 ± 0.3	2.1 ± 0.2	137.4 ± 13.3	122.6 ± 21.7	21.4 ± 9.4	72.1 ± 9.1	848.3 ± 67.8
	60–80	7.0 ± 0.1	1.6 ± 0.0	3.5 ± 0.2	0.3 ± 0.0	3.0 ± 0.2	1.6 ± 0.1	127.1 ± 8.8	125.5 ± 41.8	14.1 ± 2.9	85.3 ± 8.9	829.7 ± 92.0
	80–100	7.2 ± 0.5	1.4 ± 0.2	3.4 ± 0.3	0.3 ± 0.0	3.0 ± 0.2	1.5 ± 0.1	173.1 ± 13.4	114.1 ± 23.2	17.8 ± 1.5	71.5 ± 11.2	902.5 ± 123.2

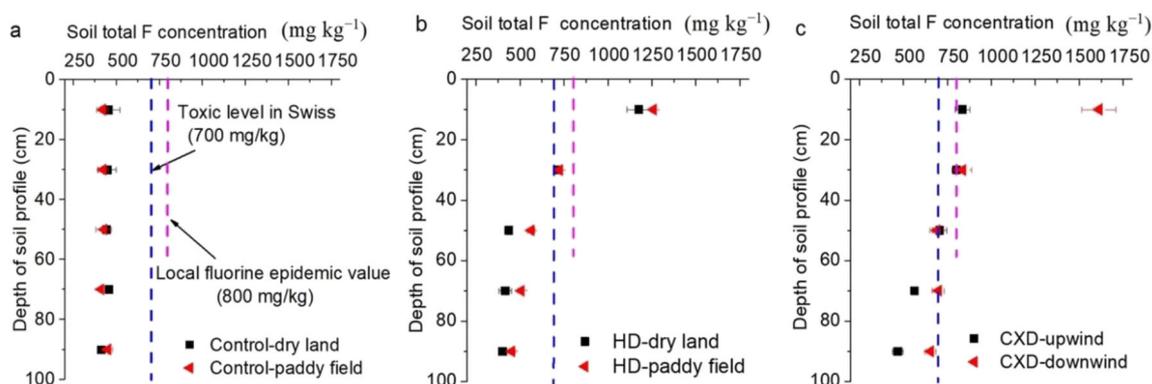


Fig. 2 a–c Total F concentration in soil profiles. Dot at 10, 30, 50, 70, and 90 cm represents soil depth of 0–20, 20–40, 40–60, 60–80, and 80–100 cm, respectively (the same below). The long blue-dotted vertical line represents the Swiss guidance level of soil protection for total F in soil

(Bundesrat 1998). The short pink-dotted vertical line represents the average total F concentration local fluorine epidemic of China (Zhang et al. 2010)

The percentage soil water soluble F to total F

The percentage of Fw to Ft (Fw/Ft) was in the range of 0.5–2.5% (Fig. 4). The mean Fw/Ft values of 1.5% in all soil samples apparently equal to the values of endemic fluorosis area in Yangtze River Delta region, China (Wang et al. 2012), and Iran (Chavoshi et al. 2011). The trends of Fw/Ft with soil depth varied among profiles; however, higher Fw/Ft at 0–40-cm profiles than those at 40–100-cm profiles were normally found (Fig. 4). In plain area, the HD profiles had higher Fw/Ft than control profiles (Fig. 4a, b). The Fw/Ft of CXD-downwind and upwind had no difference. Meanwhile, the Fw/Ft of control profiles was higher than that of CXD profiles (Fig. 4a, c).

Correlation analysis of soil F and soil properties

Correlation analysis was performed to study the relationship between soil F and physicochemical properties at each section in the 0–100-cm profiles (Table 2). The Ft and Fw showed a positive correlation ($p < 0.01$) in both of HD- and CXD-downwind areas (polluted soils), while no significant correlation ($p > 0.05$) between them was noted in control and CXD-

upwind profiles (no or less polluted soils). Pronounced positive correlation ($p < 0.01$) between Ft and OM content in HD and CXD areas was noted, while it was not found in control area. Except in CXD-upwind profile, Fw was positively correlated ($p < 0.01$) with OM and Av-P, respectively. Both the Ft and Fw was positively correlated ($p < 0.01$) with Av-P and TP in the polluted soil profiles. No uniform correlation between soil F (both of Ft and Fw) and soil pH was noted. No significant correlation ($p > 0.05$) between soil Ft and Ca, Fe, K, Cr, and Mn contents was found. The Ft was extremely correlated ($p < 0.01$) with Zn in HD-downwind profile and positively correlated ($p < 0.05$) with Pb in CXD-downwind profile.

Atmospheric F

High Fa concentration appeared in industrial area, and low Fa concentration was found in control area and CXD-downwind area during the shutdown of the factory (Fig. 5). The monthly mean Fa in control area during the sampling period was stabilized at $0.6\text{--}0.9 \mu\text{g dm}^{-2} \text{ day}^{-1}$, lower than the monthly mean limit of air quality standards of China ($1.8 \mu\text{g dm}^{-2} \text{ day}^{-1}$) (GB/3095 2012). The Fa concentration in HD-downwind (1.9 to $4.8 \mu\text{g dm}^{-2} \text{ d}^{-1}$) exceeds the limit

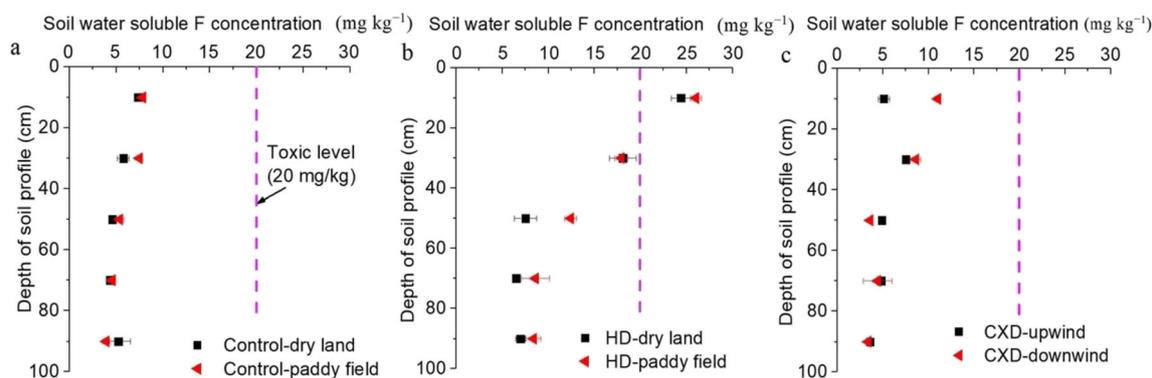


Fig. 3 a–c Soil water soluble F concentration in profiles. The dotted vertical line represents the Swiss guidance level of soil protection for water soluble F (Bundesrat 1998)

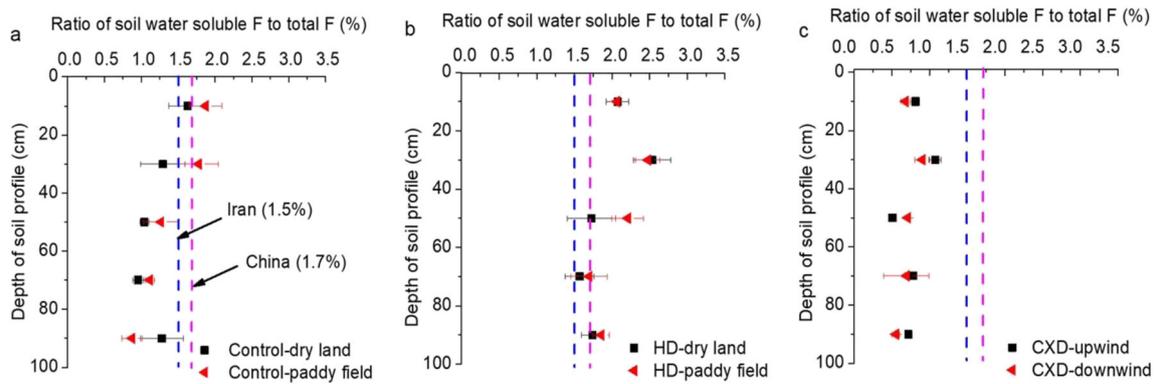


Fig. 4 a–c The percentage of water soluble F to total F concentration in soil profiles. The left blue-dotted and right pink-dotted vertical line represents the average level in endemic fluorosis area of China (Wang et al. 2012) and Iran (Chavoshi et al. 2011), respectively

value of China. Dramatically decrease of F_a concentration appeared after the shutdown of factory from June ($2.3 \mu\text{g dm}^{-2} \text{day}^{-1}$) to July ($0.8 \mu\text{g dm}^{-2} \text{day}^{-1}$) at the CXD-downwind area. And the F_a concentration in HD-downwind area declined in October since the local government tightened inspections on factory emissions at that month (Fig. 5). The dustfall F concentration in control and HD- and CXD-downwind area was 1406 , $14,446$, and 5969 mg kg^{-1} , respectively, which is much higher than the local soil F_t concentration.

Crop F

Generally, total F concentrations of all crop edible parts in industrial areas were higher than those of the control area, and the crops grown in the CXD-downwind had higher F

concentrations than those in the upwind (Table 3). The order of crop F concentration of the same area was rape-leaf > cabbage-leaf > soybean-bean. The F concentrations of soybean-bean and rape-leaf in all sampling areas in descending order were HD-downwind > CXD-downwind > CXD-upwind > control area. Concentrations of F in rape-leaf that grows in HD- and CXD-downwind were almost an order of magnitude greater than those in control area. The F concentration of cabbage-leaf in HD-downwind was 6.1 times than that in control area (Table 3).

The cabbage-leaf F content was positively correlated ($p < 0.05$) with soil F_w , indicating that F in cabbage-leaf was major from the soluble F in the soils (Table 4). But no significant correlation ($p > 0.05$) between the F concentration in other crop edible portions and the environmental media which included the soil F_t , F_w , dustfall F, and F_a was noted (Table 4).

Table 2 Correlation coefficient between soil F and soil physicochemical properties. OM, Av-P, and TP represent organic matter, available phosphorus, and total phosphorus, respectively. “–” represents not analyzed because the lack of data. “*” represents correlation is significant at 0.05 level. “**” represents correlation is extremely significant at 0.01 level

Sampling area	Control	HD-downwind	CXD-downwind	CXD-upwind
F_t and F_w	-0.19	0.97**	0.95**	0.80
F_t and OM	-0.08	0.91**	1.00**	0.90**
F_t and Av-P	-0.21	0.96**	0.99**	0.69
F_t and TP	-0.31	0.94**	1.00**	0.80
F_t and pH	-0.38	-0.60	-0.72	0.94**
F_w and OM	0.82**	0.91**	0.93*	0.78
F_w and Av-P	0.81**	0.88**	0.89**	0.53
F_w and TP	0.55	0.86**	0.96**	0.64
F_w and pH	-0.33	-0.64**	-0.97*	0.86
F_w and Ca	-0.87**	-0.55	-0.72	0.78
F_t and Ca	-0.01	-0.51	-0.45	0.46
F_t and Fe	0.58	-0.12	-0.43	-0.60
F_t and K	0.32	0.54	-0.64	-0.83
F_t and Cr	-0.34	0.45	0.07	-0.56
F_t and Mn	-0.14	-0.32	-0.80	-0.84
F_t and Zn	0.23	0.94**	0.80	-0.84
F_t and Pb	-	-	0.99*	0.63

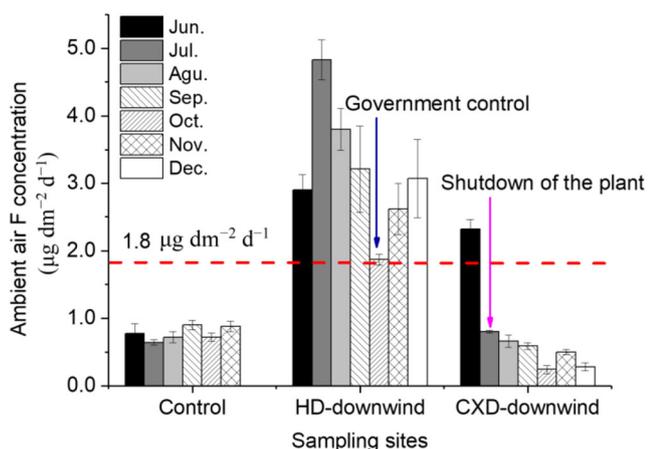


Fig. 5 Ambient air F concentration. The red-dotted line represents the monthly mean limit of ambient air quality standard of China (GB, 3095-2012)

Discussion

Vertical distribution of soil F in profiles

Soil total F

The Ft concentrations in the surface soils (418.2–1612.0 mg kg⁻¹, Fig. 2) were close to or higher than the average values of Chinese A-horizon soil (453 mg kg⁻¹) (Wang and Wei 1995) and far higher than the background value of Sichuan Province which is 280 mg kg⁻¹ and 385 mg kg⁻¹ for A-horizon and C-horizon, respectively (State Environmental Protection Administration and Environmental Monitoring of China 1990). The Ft concentrations were higher than the previous reported F concentration around a phosphorus plant with fluorapatite extensively used where the highest Ft concentration was 909 mg kg⁻¹ (Thompson et al. 1979). The Ft concentrations were in the range of a report which in industrially polluted soils, the soil Ft was 616–2700 mg kg⁻¹ (Polomski et al. 1982).

The distribution tendency of Ft concentration partly agreed with a previous research that Ft concentrations decreased with soil depth in heavily polluted soils, but the F contents usually increased with the depth in unpolluted soils (Arnesen et al.

Table 4 Correlation coefficient between crop edible portion F concentration and F concentration in environmental media. “*” represents correlation is significant at 0.05 level

	Soil Fw	Soil Ft	Dustfall F	Ambient air F
Soybean-bean F	0.92	0.74	0.98	0.99
Rape-leaf F	0.75	0.91	0.85	0.97
Cabbage-leaf F	0.95*	0.17	0.88	0.67

1995). Both natural factors and human activities had effect on Ft distribution in this area. Firstly, the gaseous F (HF and SiF₄) could be released into the environment during the manufacturing of phosphate productions (Czarnowski and Krechniak 1990). Besides, the distribution of soil F in industrial areas may be affected by the redistribution of waste materials over the soil surface (Geeson et al. 1998), such as phosphate rock and phosphogypsum. The F content in phosphate rock and phosphogypsum collected in this study was above 1% and 0.2%, respectively. These materials could be released into atmosphere during industrial activity as wind-borne particles, and F in gaseous and deposits eventually added the topsoil F concentrations by atmospheric dry and wet deposition (Wang et al. 2018). Then, F in the topsoil can transport into deep profile by leaching (Gburek et al. 2005; Haygarth et al. 2013), and digging and deep plowing of soil by agricultural activities probably enhance the concentration of soil F in the 0–40-cm layers in industrial area. The Ft concentrations at 60–100-cm profiles of HD profiles close to those of control profiles, suggesting Ft in deep soil profiles, were weakly affected compared to the topsoil. This was in accordance with the result of a study by Loganathan et al. (2001) which showed that significant quantities of F applied to soils by fertilizers were unlikely move down the deep profile to pollute the groundwater in most pastoral soils. Most of the total quantities of F accumulated in the 0–20-cm profile were similar to those in pastoral soils with long-term phosphorous fertilizer application histories where 33–66% of fertilizer-derived F was recovered in the top 75-mm soil (Loganathan et al. 2001). As for the downward movement of F, analogous to control profiles, the relative mobility of F in dry land and paddy-dry land rotation field of HD was similar (Fig. 2a, b), indicating the short-term land utilization could not significantly ($p > 0.05$) affect the Ft distribution in soil profiles.

Naturally, F concentration was lower in sandy soils than in clay soils (Fuge and Andrews 1988). The soil parent materials at CXD-upwind and CXD-downwind profiles were yellow sandy clay and gray sandy gravel, respectively. Thus, the CXD-upwind should have higher F content than the CXD-downwind profile. However, higher Ft concentrations in the CXD-downwind profile than those in the upwind profile proved that both spontaneous, such as parent materials and meteorologic conditions, and anthropogenic factors, notably

Table 3 The F concentration in the edible portion of crop. “–” represents no sample was collected. Mean value ± standard deviation ($n = 3$)

Sampling area	Soybean-bean	Rape-leaf	Cabbage-leaf
Control area	12.9 ± 1.2	20.8 ± 1.7	13.7 ± 0.9
HD-downwind	55.0 ± 4.1	177.7 ± 23.6	83.7 ± 9.8
CXD-upwind	23.7 ± 3.0	86.1 ± 11.4	–
CXD-downwind	35.9 ± 2.1	154.7 ± 14.5	–

industrial activities, had an effect on Ft distribution in this area.

Soil water soluble F

Contaminants adsorbed and sequestered onto solid phase components in soil may not be assimilated and therefore are not toxic to organisms (An et al. 2015; And and Alexander 1998). Due to the evaluation of soluble F fraction provides an indication of the mobility degree and the amount of liable to diffuse into waterways, the Fw concentrations may represent the mobile and bioavailable F during a period of continued discharge (Hansen et al. 1958). In light of this fact, the Fw is probably a more reliable indicator of the pollution situation and the availability of F for plants (Arnesen 1997; Bellomo et al. 2007). The Fw concentration (3.4–26.0 mg kg⁻¹) in present study is apparently higher than that of soil within a 1-km radius of the accidental spillage of anhydrous hydrofluoric acid from a chemical plant in Korea, where Fw concentration was 0.1–6.4 mg kg⁻¹ with an average value of 2.2 ± 1.8 mg kg⁻¹ (An et al. 2015). The decreasing trend with depth of Fw concentration in all profiles was consistent with the results from Bellomo et al. (2007) that Fw was higher in topsoil and decreased with depth at the downwind of the volcano's flank. The minimum of F solubility in 60–100-cm profile corresponds to maxima of pH and low OM content, indicating that F solubility is controlled by soil characteristics and the adsorption/desorption processes on OM (Hingston et al. 2010).

Although this area is far away from the industrial factories, the Fw concentrations in 0–40-cm layers of control profiles were higher than 5.0 mg kg⁻¹ which is considered light polluted (GB 15618-2008). From 1986 to 2015, the annual average application amount of nitrogen, potash, and compound fertilizer was 0.50, 0.06, and 0.15 t ha⁻¹ in this area, respectively. The average F concentration of nitrogen, potash, and compound fertilizer was 21.8, 65.9, and 6935 mg kg⁻¹, respectively. Therefore, it is reasonable to deduce that fertilizer application may contribute to the high soil Fw in 0–40-cm profiles. The higher OM content in paddy field (2.3%) than in dry land (1.4%) probably contributes to the difference of Ft concentration in the 20–40-cm layers between the two profiles, in view of that the soil F could be adsorbed onto OM (Cronin et al. 2000; Pickering 1985). Besides, the depth difference of rice roots (mainly distributed in the 0–10-cm profiles) and sweet potato roots (grown in profiles > 20 cm) may lead to the lower Fw concentration at 20–40-cm layers in dry land than that in paddy field by root absorbing of Fw.

The Fw concentrations at 0–100-cm layers of HD profiles were notably higher than those in control area (Fig. 3b), indicating the anthropogenic effect from phosphorous chemical factories was remarkable in this area. The Fw concentrations in deep profiles were affected by the F in topsoil through

rainwater leaching. And the soil pH and Ca content may contribute to the high Fw concentration in the profiles, especially at 40–100 cm. The pH of control and HD profiles was 7.0–9.0 and 6.0–7.5, respectively. The solubility of the fluorides decreased with the increase of pH in the range of pH 4–8 (Fung et al. 1999; Wenzel and Blum 1992). And much higher Ca content at HD sampling site (5.0–10.6%) than at control sampling site (1.9–2.0%) at 60–100-cm profiles was noted. Xu et al. (2010) reported that Ca and F is a pair of antagonistic antibodies in natural, because in the migration of fluorine ion (F⁻), F⁻ can react with calcium ion (Ca²⁺) to give CaF₂ which is difficult to dissolve in water. In alkaline environment, however, Ca²⁺ and OH⁻ would form Ca (OH)₂ while F is in the form of F⁻ in the soil solution. The fact that Fw at 40–60 cm in HD-dry land (7.5 mg kg⁻¹) was significantly lower than that of HD-paddy field (12.4 mg kg⁻¹) may principally affected by the higher Ca content in dry land (5.9%) than in paddy field (1.9%).

Compare with HD profiles, however, the lower Fw concentrations in the CXD profiles may be affected by the relative low pH (from 4.8 to 7.2) and Ca content (from 0.2 to 0.5%) in 0–40-cm profiles. The high CaCO₃ content and alkaline environment are favorable for the migration and enrichment of fluorides (Xu et al. 2010). Conversely, the soil with low CaCO₃ content and pH was tiny conducive to the migration and enrichment of fluorides in soil. That leads to the high Ft content but relatively low Fw concentration in the topsoil of CXD sampling sites. At surface soil, higher Fw concentrations in CXD-downwind than in CXD-upwind profiles suggested that wind direction affected the distribution of F in surface soil around the factory. In the CXD-upwind profiles, interestingly, the Fw concentration in the 20–40-cm profiles (8.6 mg kg⁻¹) was higher than that of surface soil (6.8 mg kg⁻¹). Firstly, F in the surface soils might be leached to the subsurface soil by rain water and irrigation water, while F below 20–40-cm layers was difficult to migrate to the 60–100 cm. Besides, F in soils could strongly be adsorbed onto clay minerals (Kumar et al. 2016). The soil parent materials (yellow sandy clay) of CXD-upwind profile might induce clay mineral at 20–40-cm layers higher than that of the surface soil (sandy loam soil). The distribution of soil F was the result of dynamic balance between transpiration and migration of soil solution.

Correlation analysis of soil F and soil properties

The average Fw/Ft (1.5%) was higher than the average background Fw/Ft (0.4%) of Chinese cultivated soil (State Environmental Protection Administration and Environmental Monitoring of China 1990). Similar to previous studies, the Fw concentrations were approximately two or three orders of magnitude less than the Ft concentrations because most of the F found in soils occurs within minerals or was adsorbed to clays and oxyhydroxides, with only a few percent or less

dissolved in the soil solution (Cronin et al. 2000; Pickering 1985). Wang et al. (2012) compared the Fw/Ft of topsoil from the Yangtze River Delta region, China, with that of Iran where people also suffer from fluorosis (Chavoshi et al. 2011) and showed that the Fw/Ft was more or less the same as the Yangtze River Delta region (1.7%) and Iranian topsoil (1.5%). Higher Fw/Ft at 0–40-cm profiles than that of 40–100-cm profiles indicates that the effect of human activities on F distribution largely took place in the 0–40-cm layers. Higher Fw/Ft of HD profiles than that of control profiles supported that F released by industrial activities are more soluble than the spontaneous F, and an increase of the F content in soils will lead to higher bioavailability of the element (Singh 1990). There is no difference between the Fw/Ft of CXD-downwind and CXD-upwind. Higher Fw/Ft in control (1.3–1.9%, Fig. 4a) than in CXD profiles (0.7–1.1%, Fig. 4c) were noted. Therefore, it is essential to propose that regarding the Fw/Ft as an indicator of soil F pollution or determination of fluorosis area must basing on similar soil parent materials, geological and topographic conditions.

The correlations between Ft and Fw in polluted soils were stronger than those of none or less polluted soils, which was in accordance with a previous assumption that increases in the soil F contents will lead to higher bioavailability of the element (Singh 1990), with soluble or easily desorbed fluoride being the forms most readily taken up by plants (Cooke et al. 1976). Different from previous reports that the Fw concentration increased with increasing soil pH in surface soil (Arnesen 1997; Li et al. 2017), no uniform positive correlation between soil F and pH was found. This may be influenced by the soil properties, such as OM, CaCO₃, clay minerals, and colloids of soil samples from different profiles. Naturally, soil F⁻ can react with Ca²⁺ to give CaF₂ (Xu et al. 2010). Therefore, the Fw concentrations were extremely significantly negatively correlated with Ca content ($r = -0.87$, $p < 0.01$) in control profiles. In HD-downwind profiles, the good positive correlation between Ft and Zn content is probably because of the high production of electrolytic zinc and zinc alloy of HD factory, which could change the distribution of F and Zn in soil.

Atmospheric F

Anthropogenic sources of F from phosphate chemical plants included the gaseous and particulate fluorides (Ozsvath 2009). The fluorides from air can reach soil and be directly taken in by plants through leaves (Li et al. 2017). High Fa concentration in industrial area was similar to a previous report that atmospheric F concentrations in polluted area were apparently higher than those in other regions in the Yangtze River Delta, China (Wang et al. 2012). Dramatically decrease of Fa concentration after the bankrupt of factory and low dustfall F concentration in the agricultural region indicated that the industrial activity is the vital contribution to the Fa.

Additionally, to bring the construction of ecological civilization into force, the Sichuan local government has tightened inspections on factory emissions throughout Shifang in October 2017. Dramatic low Fa concentrations in October at the industrial area sampling sites affirmed that government controls have great influence on F emission into the atmosphere.

Decades ago, researchers indicated that fluorides can reach soil from atmospheric air, but their content was too low to exert a negative impact on agriculture (Mcclenahen 1976). However, in recent decades, researchers found that the atmospheric deposition was significant in inducing short- to long-term F concentration changes in soils (Egli et al. 2004). In present study, the deposits of F concentration in HD- and CXD-downwind sites were much higher than those in the control area. This was coincided with previous report that the F concentrations of rainfall which contaminated by industrial emissions were an order of magnitude greater than background levels (Ozsvath 2009; Walna et al. 2007). We assume that the high F concentration of deposits probably come from the phosphorous chemical factories basing on the high total F concentration of phosphate ore (above 1.3%), phosphogypsum (above 0.2%), and surface soil (nearly 0.5%) in the factory. The F concentration of the irrigation water samples were below 1.0 mg L⁻¹ in all sampling sites. Similar result is mentioned by Mcclenahen (1976) and Pickering (1985) that wet and dry deposition of various emissions induced the soil in the vicinity of the plant accumulated substantial quantities of fluorides. Meanwhile, at sampling sites where Fa and dustfall F concentrations were high, high Ft and Fw concentrations in soils were noted.

Crop F

The background contents of F in plants are usually lower than 10 mg kg⁻¹, but over uptake of F from soil, water, or air might occur in some species (Koblar et al. 2015). Concentrations of total F in rape-leaf that grows in industrial areas are almost an order of magnitude greater than those in control area which was in accordance with a previous report that rice samples collected from the control and polluted areas contained 41 mg kg⁻¹ and 578 mg kg⁻¹ of total F, respectively (An et al. 2015). In industrial areas, the F concentrations in crops were affected by the environmental F concentration. But the source of F in plants is controversial, and correlation analysis was usually used for the source analysis of F in plants. Loganathan et al. (2003) noted that the total F content in pasture herbage was much less than topsoil Ft and it was strongly correlated with the soil Fw concentration. This was supported by a good positive correlation between the soil solution F and the plant F content (Singh et al. 1995) and by Singh et al. (1979) and Wang et al. (2012) that Fw was the major source of F in wheat grain. But Pickering (1985) and

McClure (1949) pointed out that F contamination of plant was mainly due to direct adsorption from the air. This was supported by the report that the accumulation rate of F in wheat straw was linear to atmospheric F content (Gritsan 1992) and wheat F content significantly correlated with airborne F concentration (Wang et al. 2012). In present study, the significant correlation ($r = 0.95$, $p < 0.05$) between cabbage-leaf F content and soil Fw concentration indicated that the F content in cabbage-leaf was major from the soluble F in the soils. But it was difficult to determine the main source of F in soybean-bean and rape-leaf in the studied areas based on the available data in present study.

Conclusions

Present study discussed the distribution of soil Ft and Fw in farmland profiles around phosphorous chemical factories and the possible sources of high F concentration of soils and crops. The Ft and Fw concentrations in soil profiles ranged 400.9–1612.0 mg kg⁻¹ and 3.4–26.0 mg kg⁻¹, respectively. Roughly, the soil Ft content constantly distributed at 0–100-cm profiles in agricultural region, while the soil Fw and Ft concentrations decreased with depth in industrial areas. The Ft concentrations at 0–40-cm profiles exceeded the “toxic” level in Swiss and were significantly higher than those of the 40–100-cm profiles in industrial areas; thus, we assume that the F contents in soils affected by industrial activities mainly concentrated at 0–40-cm layers. Greatly varied Fw/Ft in plain and hilly areas showed that the identification of fluorosis area by Fw/Ft is not universal. Both the spontaneous factors and industrial and agricultural activities affect the distribution of F in farmland soil profiles around phosphorous chemical industry factories. Detection and analysis indicate that OM content, atmospheric dry deposition from industrial plants, and the wind direction were the most important factors. Dramatically decrease of Fa concentration during the control of government and the closure of factory indicates that chemical production has remarkable effects on the surroundings. In addition, the Fa, dustfall F, and crop edible portion F concentrations in the industrial areas were higher than those in agricultural region. The total crop F concentrations from high to low were rape-leaf > cabbage-leaf > soybean-bean in the same sampling area. Further investigations should be taken on the spatial distribution of soil F in areas farther away from the phosphorous chemical factories and the contribution ratio of the F pollution sources.

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