Spatial and vertical distribution and pollution assessment of soil fluorine in a lead-zinc mining area in the Karst region of Guangxi, China

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ABSTRACT

Soil pollution of fluorine is a serious environmental problem in the world, and the fluorine pollution evaluation of spatial and vertical distribution study in the Karst region is quite limited. In this study, the farmland around lead-zinc mine in the Karst region was chosen as the study area. Ninety-one upper layer soil samples and two soil profiles (one in paddy field, the other one in aerated field) samples were taken. The average concentration of total fluorine of topsoil in the paddy fields is 378 mg/kg, whereas in the aerated field it is 508 mg/kg. The concentrations of total fluorine in all paddy soil samples and 97.87% aerated field soils are higher than that of the background value of Guangxi. The total fluorine contaminations in all aerated field soils are much higher than in paddy soil samples, so the aerated field is contaminated severely. The vertical distribution of fluorine is different in paddy field and aerated field. In paddy field, the content of fluorine increases from 20 to 40 cm, then it decreases rapidly from 40 to 60 cm in depth, and then increases gradually. However, in the aerated field, the content of fluorine rises gradually with the depth of the sampling point. The results of relative analysis and regression analysis between fluorine in soil and soil properties show that the spatial distribution and vertical variation of fluorine in this region are mainly affected by parent rock.

Keywords: soil fluorine; lead-zinc mining area; spatial distribution; vertical variation

Fluorine is an essential micronutrient for both humans and animals. It is present in soils, rocks, water, and the biological chains of animal and plant life. Fluoride is a common constituent in rocks and soils. Its average concentration is 650 mg/l in the continental crust (Fleischer and Robinson 1963, Tripathy et al. 2005) and 300 mg/l in soils (Larsen and Widdowson 1971). Low contents of fluorine are essential components for normal mineralization of bones and formation of dental enamel (Bell and Ludwig 1970). However, exposure to high levels of fluorine through drinking water or air results in skeletal fluorosis in humans. There are more than 20 developed and developing nations where fluorosis is endemic (Meenakshi and Maheshwari 2006). It was found that concentrations of fluorine in some polluted agricultural soils in Chinese coastal areas such as the Ning-Shao Plain and the Jin-Qu Basin reached up to levels between 500 and 1000 mg/kg (Zhou 1995). Environmental fluorine enrichment has both natural and anthropogenic sources (Zhu et al. 2006). The major cause of higher fluorine concentration in soils is weathering of fluorine-rich minerals in the country rocks. Aluminum, calcium, iron, pH, organic matter and clay content of soil are the major parameters that control fluorine fixation through adsorption, anion exchange, precipitation, formation of mixed solids and complexes (Fluhler et al. 1982, Murray 1984). Chemical weathering of some fluorine-containing minerals leads to fluorine enrichment of soils and groundwater (Totsche

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et al. 2000). Various anthropogenic sources do also contribute to high fluorine concentration in soil. Discharges of fluorine from some industries, such as semi-conductors, steel, aluminum, glass, bricks, fertilizers and electroplating, are among the main anthropogenic sources of fluorine pollution (Cronin et al. 2000). Phosphate fertilizers which contain fluorine are another important source of fluorine input to soils (Loganathan et al. 2001). Now, soil fluorine pollution is a serious environmental problem in some areas of China. Contents of fluorine in soil vary between 125 and 983 mg/kg in some farmlands in southern China (Zhu et al. 2007). However, current knowledge of the spatial and vertical distribution of fluorine in soil and its pollution assessment in lead-zinc mining area in the Karst area is quite limited. The southwest Karst area of China is the high fluorine region with typical subtropics Karst landform and the hydrogeological conditions. In this study, the farmland around a lead-zinc (Pb-Zn) mining and concentration plant in the south of the Guangxi Zhuang Autonomous Region, China, was chosen to study the distribution of fluorine in soils and vegetables, which would provide useful information for remediation of the polluted soil. The present work aims at (a) determination of the spatial and vertical distribution of fluorine in soil (b) evaluation of pollution degree of fluorine in soil and vegetables (c) discussion on the influences of ecological factors on soil total fluorine, around a lead-zinc (Pb-Zn) mining and concentration plant in the south of the Guangxi Zhuang Autonomous Region, China.

MATERIALS AND METHODS

Site description. The site is in farmland near a lead-zinc mine and ore concentrating facility in the Karst area of the Guangxi Zhuang Autonomous Region, China. The facility was built in the 1950's, which was employed in lead-zinc ore mining and concentrating. When exploited from underground, the ore was transported to earth surface for comminuting and concentrating with physical and chemical methods. The products were transported outside the site by lorries and the waste residues were stacked nearby. Because of industrial effluent and waste residue discharges without treatment during mining and ore-dressing, the soils have high concentrations of heavy metals (Cd, Pb, Zn, Ni, Hg, Cu, As) around the lead-zinc mine and concentrator (Deng et al. 2009). As a result of source depletion and environmental pollution, the facility filed for bankruptcy in 2001.

The farmland is the typical Karst peak cluster-depression rock in a mountainous area with two villages of nearly one thousand people. The cultivated area within the site is nearly 0.60 km^2, including 0.27 km^2 of paddy field and 0.33 km^2 of aerated field, and the soil is mainly formed from sandstone and shale. There are two irrigation ditches which lie to the east and west of the facility (Figure 1).

Sampling and analysis. After considering the distribution of possible pollution sources, topography, soil types, and vegetables (mustard and Chinese cabbage) in the study area, the sampling locations for surface soils were selected as shown in Figure 1. Ninety-one surface soil samples (0–20 cm) were taken according to pre-established gridding in the study area (i.e., 44 in paddy field, 47 in aerated fields) between 2007 and 2008.

At the same time, the samples of soils profile were taken from paddy field locations T1 and aerated field location T2 at the following depths: 0–20 cm, 20–40 cm, 40–60 cm, 60–80 cm, 80–100 cm and 100–120 cm, respectively. In all cases, samples were stored frozen in acid-cleaned HDPE bottles until

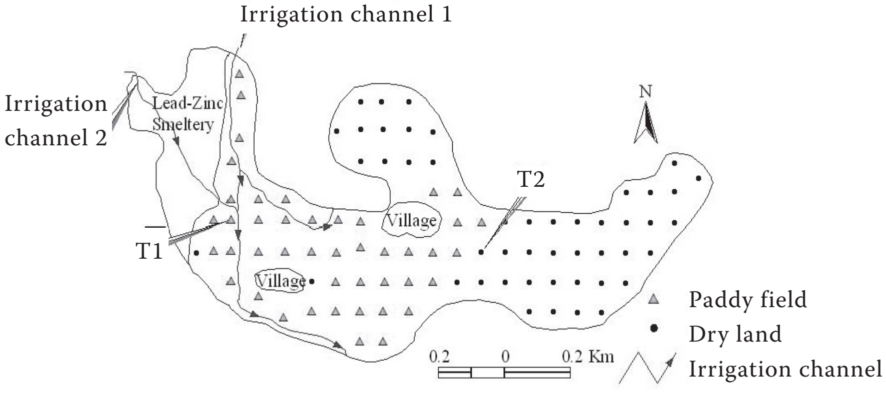

Figure 1. Distribution of sample points

Table 1. Statistical result of fluorine concentrations in Pb-Zn mining agricultural soils (n = 91)

Soils	Range	Mean ± SD	Median	Coefficient of variation (%)	Background value of Guangxi (mg/kg)	Ratio of mean to the background value	Ratio of maximum value to the background value	Local fluorine epidemicvalue (mg/kg)
	(mg/kg)							
Paddy fields	409–1356	712 ± 201	692	28	378	1.89	3.59	800
Aerated field	476–1553	1021 ± 272	1040	27	508	2.01	3.05	800

The number of paddy soils and aerated field soils was 44 and 47, respectively

analysis. Solid waste samples were collected around the lead-zinc mining and concentration plant. Several mustards were randomly collected and mixed to be one sample, the Chinese cabbage as well.

All soil samples were air-dried, crushed by a wooden stick, and the gravel and relict bodies were picked out. They were first sieved through a 20-mesh nylon screen (1 mm aperture size) and then through a 100-mesh nylon sieve prior to analysis. The total fluorine in the soil and vegetables was obtained using the alkaline fusion (McQyajer and Gumey 1997) and the fluorine in leaching solution of solid wastes was measured by fluoride-Ion selective electrode method (GB/T15555. 11-1995). The pH of soil was measured by taking 10 g of sample into 25 ml of reagent water. The soil organic matter content was measured by potassium bichromate oxidation process. Particle size distribution was tested by hydrometer (Liu et al. 1996).

Evaluation of fluorine pollution. To assess the pollution degree of fluorine in soils, single factor pollution index (SFPI) method was used to calculate (EPAC 2005). The formula used to calculate SFPI is: $P_i = C_i/S_i$, where P_i is the single factor pollution index of fluorine, C_i is the content of fluorine in soils at the sampling site, and S_i is the evaluative standard value of fluorine.

The local fluorine epidemic value (800 mg/kg) and the background value (200 mg/kg) of the world to determine the starting value and contamination levels of soil were taken as references. Lack of soil fluorine results in body cavities: $C_i < 200$ mg/kg, $P_i < 0.25$; normal soil: 200 mg/kg $\leq C_i < 800$ mg/kg, $0.25 \leq P_i < 1$; contaminated soil leads to local fluorine epidemic: $C_i \geq 800$ mg/kg, $P_i \geq 1$ (Li et al. 2006).

Data analysis. Raw data were analyzed with different software packages. The descriptive statistical parameters were calculated with SPSS 16.0. The geo-statistical analysis was carried out with GS$^+$ (5.1). The map of fluorine spatial distribution pattern was produced by using the Arcview (5.3) software for ordinary kriging interpolation.

RESULTS AND DISCUSSION

The concentrations of total fluorine in topsoil and spatial distribution. The fluorine concentration results are shown in Table 1, regarding original soil samples which were taken from Pb-Zn mining and concentration plant. The average concentrations of total fluorine exceed the background value of Guangxi (GIEP 1992) both in paddy fields and aerated field soils. The pollution situation of

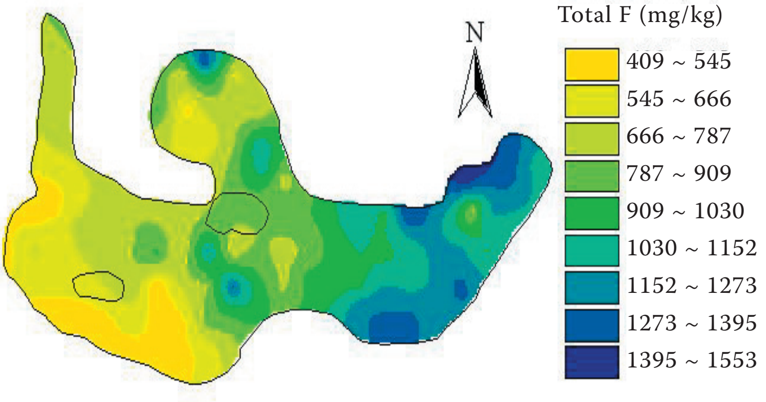

Figure 2. Spatial variation of fluorine

Table 2. The fluorine in leaching solution of solid wastes (mg/l) ($n = 10$)

Item	Range	Mean ± SD	Median (mg/kg)	Coefficient of variation (%)	Evaluation standard limit value (mg/l)
	(mg/l)				
Fluorine	0.08–1.01	0.30 ± 0.32	0.15	107	50

aerated field is much worse than paddy soil. The average total fluorine of paddy field is 1.89-fold of the Guangxi background value, and the total fluorine of aerated field is 2-fold of the Guangxi background value, too. The average value of total fluorine of the aerated field samples is higher than fluorine epidemic of China (Li et al. 2006), and the average value of total fluorine of paddy soils samples is below the local fluorine epidemic value of China. For the paddy soils samples, 23% were out of the local fluorine epidemic value, and 70% aerated field samples out of the local fluorine epidemic value.

In order to depict the spatial variability of soil fluorine in the district, ordinary kriging procedure was used to create the spatial distribution map. From Figure 2, it can be seen that fluorine has distinct geographical distribution, with high concentration in the east and low in the west.

Both natural environmental factors and human activities can impact the pollutants spatial distribution. The studied area is close to the Pb-Zn mining and concentration plant. According to the test results, we can see the low fluorine content in the east of the Pb-Zn mining and concentration plant. According to the results showed in the Table 2, the fluorine content of filtrated solution is much lower than the Chinese evaluation standard limit (GB5058.3-1996). Therefore the fluorine pollution is not caused by Pb-Zn mining and concentration plant.

Vertical distribution of total fluorine in soils. Fluorine is an active moveable substance, and it can accumulate from topsoil to subsoil gradually in natural profiles (Xing and Zhu 2003). The total fluorine content increased with depth in soil profiles in Guangdong (Zhu et al. 2007). Regarding the vertical distribution and profiles of fluorine, please refer to Figure 3. Based on the testing results, we can see that the highest content of fluorine is in the depth of 40 cm, it increases from 20 cm to 40 cm, and it decreases rapidly from 40 cm to 60 cm. The maximum content of fluorine is up to 490 mg/kg in T1 profiles, which locates in the depth of 100 cm in paddy field. And the content of fluorine rises gradually with the depth of the sampling point, reaching up to 944 mg/kg at the 120 cm point of aerated field. This unusual phenomenon is caused by serious heavy metals for the paddy field, and the farmers correct this problem with adding new soil which was not polluted by heavy metal in the 1960's. And the aerated field has not been treated in this way, so the fluorine concentration is increasing with further layer.

Pollution evaluation of soil fluorine. The pollution degree of soil fluorine in the district was

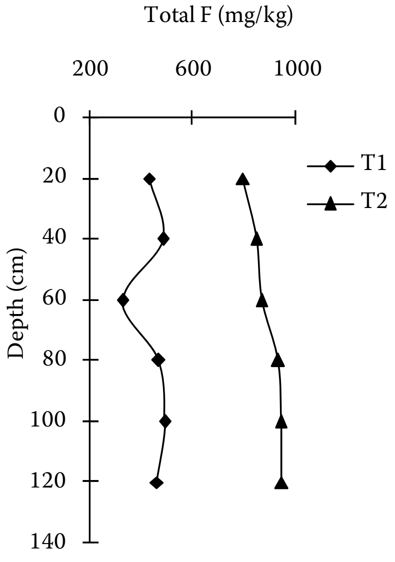

Figure 3. Vertical distribution of fluorine content in different soil profiles

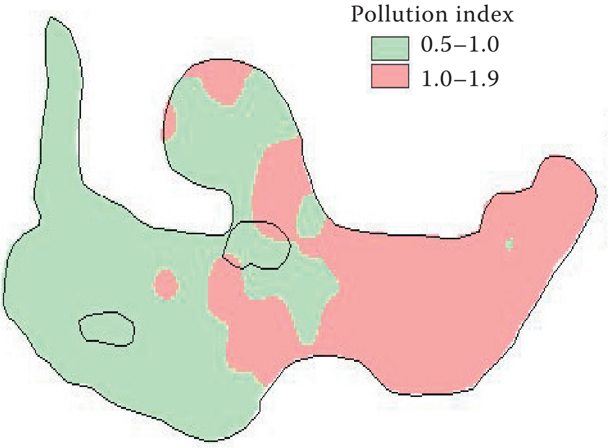

Figure 4. Spatial distribution of fluorine single pollution index

Table 3. Correlation coefficients fluorine and physical chemical properties in soils

	pH	OM	CEC	Grain size (%)		
				0.05–0.02 mm sand	0.02–0.002 mm silt	< 0.002 mm clay
pH	1					
OM	–0.192	1				
CEC	0.660**	–0.139	1			
0.05–0.02 mm	0.006	0.102	–0.205	1		
0.02–0.002 mm	0.102	0.023	–0.028	0.391**	1	
< 0.002 mm	0.237*	–0.278**	0.526**	–0.618**	–0.382**	1
Fluorine	0.433**	–0.183	0.654**	–0.350**	–0.131	0.690**

**correlation is significant at the 0.01 level (2-tailed); *correlation is significant at the 0.05 level (2-tailed)

evaluated by the method of single pollution index. The single pollution indexes of soil fluorine are shown in Figure 4. The pollution indexes of soil fluorine in the west are between 0.5 and 1.0, which indicates that the soils in west are normal according to the soil health quality index ($0.25 \le P_i < 1$). The plants grown in the soils should be therefore safe for people health. However, the contents of soil fluorine in the east exceed the critical value of local fluorine epidemic value (800 mg/kg) so that the pollution index is above 1.0, which indicates that the soils in the east of study areas have been seriously contaminated by fluorine; it may possess risk for human health in this location.

Potential impact for contamination of local crop production. Based on the test data, the vegetables (mustard and Chinese cabbage) have been polluted by fluorine. The concentration of fluorine is between 1.48 mg/kg and 2.11 mg/kg. Both mustard and Chinese cabbage are out of the threshold limit 1.00 mg/kg. According to the tolerance limit of fluorine of foods (GB18406.1), the fluorine pollution in the studied areas has a serious impact on the health of local residents.

Influencing factors. Fluorine distribution is a function of soil-forming process, of which the degree of weathering and clay content are the most pronounced (Zhu et al. 2007). The concentration of soil fluorine had a close relationship with soil parent material, pH value, organic matter, cation exchange capacity and soil texture (Xie et al. 2005, 2006). The correlation between fluorine and soil properties is illustrated in Table 3. It is indicated that fluorine is not significantly correlated with organic matter (OM), sand and silt, however, fluorine is in a significantly positive correlation with pH, cation exchange capacity (CEC) and clay, and the correlation coefficients reach 0.433, 0.654, and 0.690, respectively.

In order to further identify the impact factor of soil fluorine, fluorine was chosen as a dependent variable, and pH, OM, CEC, sand, silt and clay as independent variables. The application of stepwise regression analysis showed fluorine = –213 + 14 clay + 42 CEC. The regression coefficient of the model was 0.771. According to regression equation, the soil fluorine concentration correlated observably with CEC and Grain size, and relativity between fluorine and the Grain size was higher than that of CEC. There data showed that the primary influence on the concentration of fluorine in this district was that of parent rock.

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