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ADSORPTION AND LEACHING OF FLUORIDE IN SOILS OF CHINA

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SUMMARY: Adsorption and leaching of fluoride in typical Chinese soils in relation to physical and chemical parameters of the soils were studied. F-adsorbing capacity of soil can be ranked as Black soil > Purplish soil > Red earth > Dark brown earth > Drab soil > Sierozen. Leaching rate from different soils was Drab soil > Sierozen > Black soil > Purplish soil > Red earth > Dark brown earth. The adsorption of F in soils decreased from humid areas to arid areas and from acidic soils to alkaline soils. The smaller loss of F leaching occurred from acid soil in tropical humid areas and in temperate semi-humid areas compared with arid areas. This would result in enrichment of fluoride in shallow groundwater in northern China.

Keywords: Chinese soils, Fluoride adsorption, Fluoride leaching, Fluorosis, Groundwater fluoride, Soil types.

INTRODUCTION

Endemic fluorosis caused by fluoride in the environment is a global geochemical disease.[1-3] In China, it occurs in more than 30 provinces, municipalities, and autonomous regions affecting a population of 45 million.[4] Endemic fluorosis areas in China can be divided into six types according to the fluoride source: (1) shallow groundwater with high fluoride (> 1.0 mg/L, state criteria of drinking water[5]); (2) deep groundwater with high fluoride; (3) hot springs with high fluoride; (4) abundant fluoride rock formations; (5) high-fluoride coal; (6) high-fluoride tea.[6] Shallow high-fluoride groundwater exists mainly in the vast arid and semi-arid regions of northern China.[6] In these areas, enrichment of fluoride in groundwater occurs from fluoride in rock formations as replenishment sources with relatively poor drainage and high evaporation. The water fluoride concentration is usually about 5 mg/L.

Fluoride content in water depends not only on the geochemical background and climate-biological factors such as hydrological condition, landform, rainfall, and evaporation, but also on the adsorption and leaching of fluoride in soil. The adsorption-leaching process directly affects fluoride migration and exchange from soil to water. Studies on adsorption or desorption of fluoride have shown that the nature of soil or rock relates to the release of fluoride from soils and rocks,[7-15] but to date there has been no study on adsorption and leaching effects of typical soils in China and their relation to fluorosis. In this paper, we present the results of an investigation of adsorption and leaching of fluoride in typical Chinese soils and their relation to physical-chemical soil parameters.

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MATERIALS AND METHODS

Soil samples (0-20 cm depth) were collected from different native landscapes in China. These uncultivated soils without any contamination are representative samples such as Red earth (Hunan Province), Purplish soil (Sichuan Province), Drab soil (Shanxi Province), Dark brown earth (Jilin Province), Sierozen (Gansu Province), and Black soil (Heilongjiang Province).[16] The air-dried, 20 mesh grained samples were used for leaching experiments and 100 mesh grained samples for adsorption studies.

A total of 27 soil samples were collected from arid, semi-arid, temperate, warm temperate, and tropical areas of China. Simultaneously, drinking water samples from shallow groundwater were also collected from the same sampling sites in order to examine the relationship between fluoride in soils and F content in shallow groundwater. Some soil types of these samples were different from the six experimental soils, but they were collected from southern, southwestern, middle, northern, and northwestern parts of China, and therefore they provide additional representative samples for investigation and comparison. The correlation coefficient of F in soils and in shallow groundwater samples was determined by regression analysis.

In the adsorption study, fluoride as sodium fluoride was spiked to soils. Sodium fluoride solutions as 0.0, 5.0, 10.0, 15.0, 20.0, 25.0, and 30.0 mg/L concentration of F^- were added to one-gram duplicates of 100 mesh grained soil in 100 mL polyethylene bottles, respectively, and made up to 20 mL with de-ionized water. Each type of soil suspension was shaken for 4 hours at 25°C. After filtration, fluoride in the filtrate was analyzed by an ion selective electrode.

Leaching experiments were conducted at 25°C in a column (see Figure) packed with different soils using 3 replicates. To simulate the top depth of the soil, each experimental soil column was kept at 30-cm depth with 400-700 g of soil depending on different soil gravitation capacity. According to the maximum annual precipitation, as in tropical areas, 2500 mL of de-ionized water for each type of soil was led into the column with a 4-cm water level maintained on the top of column in order to approximate the same rainfall intensity experimentally for 2 months.

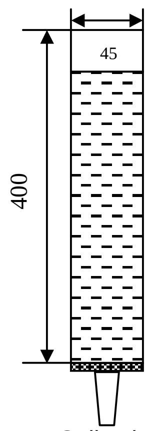

Figure. Soil column for leaching of F.

Total fluoride in soil was analyzed by a fluoride ion selective electrode after digestion of the weighed soil sample with NaOH.[17] Water-soluble fluoride (ratio of soil to de-ionized water = 1:5) was also determined by an ion selective electrode.

The pH was measured by a pH meter, and the soil texture was determined by a Shimadzu granularity analyzer (model RS-1000). The organic matter (OM) was measured by ignition. Metal oxides were analyzed by inductively coupled plasma spectrometry (ICP2070, Baird Co.). All these analytical procedures are documented.[18]

RESULTS

Table 1 shows the physical and chemical characteristics of the soils examined. The adsorption and leaching of F and its content in the major types of Chinese soils are shown in Table 2.

Table 1. Different soils and their physical and chemical properties

Soil Type	Rainfall mm/year	PH	OM %	Texture <0.005 mm, %	Al_2O_3 %	Fe_2O_3 %	CaO %	MgO %
Red earth	2000	4.45	5.35	47.30	19.35	4.38	0.13	0.81
Purplish soil	1148	4.30	2.50	19.75	13.78	4.41	1.33	1.65
Drab soil	614	7.88	4.06	25.79	12.74	4.74	6.00	2.10
Dark brown earth	800	5.45	13.09	33.10	12.38	4.55	2.43	2.13
Sierozen	190	7.90	4.31	21.66	12.40	4.86	6.27	3.53
Black soil	510	5.25	10.67	58.72	13.91	4.50	1.48	1.15

Table 2. Adsorption and leaching of F and its content in major soils of China

Soil Type	Total F µg/g	Water-soluble F µg/mL	W/T[a] %	Q_m[b] µg/g	Leaching rate %
Red earth	439	0.44	0.10	434	0.03
Purplish soil	230	0.62	0.27	476	0.04
Drab soil	374	1.40	0.38	370	0.19
Dark brown earth	225	0.41	0.18	400	0.02
Sierozen	412	2.87	0.70	167	0.16
Black soil	275	0.57	0.21	667	0.05

[a]W/T: percentage of water soluble F to total F in soil.
[b]Q_m: saturated sorption capacity.

The ability of different soils to adsorb F can be expressed as saturation F^-adsorbing capacity (Q_m) ranked as follows: Black soil > Purplish soil > Red earth > Dark brown earth > Drab soil > Sierozen. The results imply that the adsorption of F in soils decreases from humid areas to arid areas and from acid soils to alkaline soils.

The leaching rate of fluoride (percentage of total amount of fluoride in leachate to total fluoride in soil) relates to the mobility of fluoride from different soils. They rank as: Drab soil > Sierozen > Black soil > Purplish soil > Red earth > Dark brown earth.

The results show that alkaline soil from temperate arid and semi-arid areas such as Drab soil and Sierozen leached relatively large amounts of fluoride. On the other hand, the smaller leaching loss of F occurred from acid soils such as Red earth and Purplish soil in tropical humid areas and from Dark brown earth, and Black soil in temperate semi-humid areas.

Some physical and chemical properties of soil such as CaO, Fe_2O_3, Al_2O_3, clay particles, organic matter, and pH impact the binding ability of fluoride[19] and leaching of F. The correlation coefficients are given in Table 3.

Table 3. Correlation coefficients of saturated adsorbing capacity and leaching rate of F with soil properties

	pH	OM	Texture	Al_2O_3	Fe_2O_3	CaO	MgO	Total F[a]	W[b]
Q_m[c] µg/g	-0.658*	0.391	0.718*	0.251	-0.718*	-0.705*	-0.829†	-0.504	-0.791†
L[d] %	0.938‡	-0.483	-0.468	-0.435	0.875†	0.927‡	0.642*	0.517	0.804†

[a]Total F: total F in soils. [b]W: water-soluble F in soils. [c]Qm: saturated sorption capacity.
[d]L: leaching rate. n = 6, *$P < 0.1$, †$P < 0.05$, ‡$P < 0.01$.

In our study, pH is significantly correlated positively with leaching rate and negatively with Q_m. There are no significant correlations between organic matter and Q_m, and with leaching rate. Clay particles are correlated positively with saturated adsorbing capacity Q_m. Al_2O_3 correlated positively with Q_m and negatively with leaching rate, but not significantly. Fe_2O_3 is negatively correlated with Q_m and is positively and significantly related to the leaching rate. The positive correlation coefficient of CaO with the leaching rate is very high, and the correlation coefficient with Q_m is negative. MgO is closely related to Q_m negatively. The total F in soils is not significantly correlated with Q_m and leaching rate. Water-soluble F has a very high negative correlation coefficient with Q_m and positive one with leaching rate.

A comparison of fluoride in shallow groundwater and water-soluble F in soils can be seen in Table 4 and the correlation coefficient between them is significant.

Table 4. Fluoride in shallow groundwater and water-soluble F in soils (mg/L)

Province	Soil Type	Water-soluble F	Water Type	Drinking Water F
Guizhou	Yellow earth	0.27	Well	0.06
	Yellow earth	0.79	Well	0.04
	Yellow brown earth	0.18	Well	0.07
	Yellow earth	0.21	Well	0.05
	Red yellow earth	0.18	Well	0.05
Hunan	Red yellow earth	0.56	Well	0.09
	Red earth	0.37	Well	0.08
Hubei	Yellow earth	0.30	Well	0.16
	Yellow earth	0.17	Spring	0.11
	Yellow earth	0.26	Well	0.13
Henan	Yellow brown earth	1.06	Well	0.16
Beijing	Drab soil	7.85	Well	0.10
	Drab soil	5.60	Well	0.16
Xinjiang	Salinized meadow soil	10.25	Well	0.52
	Salinized meadow soil	10.25	Channel	0.51
	Gray brown desert soil	37.15	Well	1.85
Neimonggu	Dark meadow soil	6.25	Shallow well	0.68
	Chestnut soil	3.60	Shallow well	0.14
	Chestnut soil	6.95	Shallow well	0.28
	Meadow solonchak	19.00	Shallow well	0.74
	Dark chestnut soil	3.15	Well	0.44
Hebei	Chao soil	3.90	Deep well	0.65
	Drab soil	1.85	Shallow well	0.27
	Saline soil	11.90	Shallow well	2.23
	Meadow solonchak	1.95	Well	0.68
	Meadow soil	2.70	Well	0.41
	Meadow soil	8.30	Shallow well	1.07

$n = 27$, $f = 27\text{-}2 = 25$, $r = 0.737$, $r_{0.01\{25\}} = 0.487$, $r > r_{0.01\{25\}}$, $P < 0.01$.

DISCUSSION

Soil clay particles correlated positively with Q_m, illustrating that soil with a high content of clay particles has an intensive adsorption ability. The mineral composition of clay particle consists mainly of kaolinite, vermiculite, and montmorillonite that have very strong sorption capacity. The chemical content of certain hydrous silicates and cations such as Mg^{2+}, Al^{3+}, Fe^{3+}, Ni^{2+}, Mn^{2+}, and Fe^{2+}, impact on the chemical adsorption of F^-. Additionally, the physical adsorption at the surface of clay particles can enable fluoride ions to accumulate in soils. Conversely, relatively high leaching rates of fluoride occur in quartz-sandy soils.[20]

Similar to a study[21] on pH and saturated sorption capacity of soil, our experiments show that saturated sorption capacity Q_m of fluoride correlated negatively with soil pH, and the leaching rate of fluoride correlated positively. Smith[22] found that the maximum fluoride sorption capacity was 18.3

meq/100g at pH 6 and 8.6 meq/100 g at pH 7, while others found that adsorption peaked at pH 6-7 in acidified soils. In spite of this, our experimental results on natural soils could be interpreted as competitive sorption,[23] with OH^- in soil solution replacing some F^- from the surface of soil colloids resulting in leaching of fluoride. Therefore, the lower the pH, the stronger is the F adsorption. The leaching rate of fluoride from an alkaline soil is therefore higher than from an acidic soil.

Ferric oxide is a common oxide in soil and usually exists in the forms of goethite, hematite, and amorphous iron. The adsorption of fluoride on ferric oxide is mainly a process in which coordinated OH^- exchanges with F^- as specific adsorption.[24] The negative correlation between ferric oxide and adsorption of F^-, and the positive relationship to leaching of fluoride need to be considered. This is likely due to the small amount of amorphous iron and dominant goethite in the experimental soils. Amorphous iron, the most active form of ferric oxide in soil, is significantly related to the fluoride adsorption. Conversely, goethite[25] has smaller sorption capacity for fluoride.

The main mechanism of aluminum adsorption of fluoride consists as follows: (i) coordination adsorption; (ii) new adsorption site resulting from the broken bridge-connection between hydroxyl and aluminium;[24] (iii) complex adsorption. Different species and fractions of Al such as oxalate-extractable aluminum, pyrophosphate aluminum, and amorphous aluminium[26] in soils impact the adsorption and leaching of fluoride.

The relationship between CaO, MgO, and adsorption or leaching of fluoride due to the hydration of the oxide responsible for higher pH of soils, and resulting calcium hydroxide and magnesium hydroxide react with fluoride. The Drab soil and Sierozen with the highest calcium content have the highest water-soluble fluoride and leaching rate and the lowest F adsorption capacity. Probably the dominant exchangeable cation is sodium rather than calcium, and as a result, the water-soluble fluoride would be higher. Further work on oxide speciation in soils is needed.

Shallow groundwater is usually used as the source of drinking water in rural areas of China. Fluoride in these waters is significantly related to water-soluble fluoride in soils ($r = 0.737$, $n = 27$, $p < 0.01$). The total fluoride in soil is affected by azonal factors such as parent rocks. Water-soluble F in soil, however, is mainly determined by zonal factors, such as climate and soil property. Therefore, water-soluble fluoride in soil will concentrate under intensive evaporation in arid and semi-arid areas.

The conclusions of this work are as follows:

- F-adsorbing capacity of Chinese soils can be ranked as Black soil > Purplish soil > Red earth > Dark brown earth > Drab soil > Sierozen. The adsorption of F in soils decreases from humid areas to arid areas and from acidic soils to alkaline soils.

- The sequence of F leaching rate from different soils is Drab soil > Sierozen > Black soil > Purplish soil > Red earth > Dark brown earth. Alkaline soils from temperate arid and semi-arid areas leach larger amounts of fluoride. A smaller leaching loss of F occurs from acidic soils in tropical humid areas and in temperate semi-humid areas.
- Some physical and chemical properties of soil influence the binding ability of fluoride and leaching of F, and they contribute to a significant relationship between water-soluble fluoride in soils and fluoride in shallow groundwater.
- Acidic and slightly acid soils are mainly distributed in humid areas of southern China and semi-humid areas of northeastern China. These soils have a stronger adsorption of fluoride and a weaker leaching rate of fluoride. Consequently, no fluorosis resulting from drinking water is prevalent in these areas. On the other hand, alkaline soils occur in arid and semi-arid areas of northwestern China. Because of their low adsorption ability and high leaching rate of fluoride, these soils can result in enrichment of fluoride in shallow groundwater where endemic fluorosis is prevalent.

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