Effect of nitrogen fertilizer on fluorine species and soil pH in fluorine –contaminate soil

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Abstract— In this paper, two kinds of fluorine–contaminate soils, fluvo-aquic soil and paddy soil, were cultivated by nitrogen fertilizer. Then, we studied the various fluorine species in the cultivated soil by sequential extraction method, and study the effect of main components in nitrogen fertilizer on pH of soils. After adding nitrogen fertilizer, the pH value of soil would increase, which consequently led to the water soluble fluoride (Ws-F) increase. The result indicated that the pH value has significantly positive correlation with the content of Ws-F, and high pH value will make the fluorine contamination of soil become worse.

Keywords—nitrogen; fertilizer; fluorine species; fluorine-contaminate soil

I. INTRODUCTION

There are 16 essential nutrient elements for crop to grow up, and many of them must be obtained from fertilizer except carbon, hydrogen and oxygen elements. Fertilizers are divided into many kinds, such as large amount elemental nutrient fertilizer, moderate amount elemental nutrient fertilizer and so on. Nitrogen fertilizer belongs to large amount elemental nutrient fertilizer^[1], so they are used widely in cropland. Recently, there are many reports about the effect of nitrogen fertilizer on crop yield and quality, but there are a few reports about the effect of them on the species of noxious elements in soil (especially for fluorine element).

Fluorine is considered as a possible essential trace element and nutrient by World Health Organization (WHO) and United National Academy of Sciences (UNAS) . It plays an important role in forming of body bone and tooth enamel. Both fluorine deficiency and excessiveness will affect people's health, and the relationship between uptake and reflection presents U-shape curve^[2,3]. In detail, the metabolism of calcium and phosphorus and the formation of calcium fluorophosphates in body will be affected when human body are lack of fluoride, and this leads to osteoporosis. On the other hand, the excessive uptake of this element by human beings will result in fluorosis, which will affect the normal development of bones.

Since Fluorine in human body mainly come from the consumption of food and water, its interactions with soil components are significantly important. The bioavailability fluorides in soil include water soluble fluoride (Ws-F) and

exchangeable fluoride (Ex-F), and they could easily migrate and transform each other. Therefore, the content of fluorine element in soil has significantly positive correlation with its content level in human beings and domestic animals. Whether the fluorine species in soil will be changed after fertilizer added? If yes, what is that? And what are the results if the fluorine species was changed? In order to answer those questions, it is very significant to study the effect of nitrogen fertilizer on fluorine species in fluorine –contaminate soil. This study will give us an instruction about reasonable fertilization in soil to control fluorine –contaminate.

II. EXPERIMENTAL

A. Materials and Reagents

The preparation of fluoride standard solution (500µg/mL): NaF (AR, Chengdu Kelong Chemical plant) was dried at 120 °C for 2h before use, and then dissolved in redistilled water. The solution was stored in a plastic bottle and need to be diluted for further use in analysis.

The apparatus used in these investigations was model JP-303 polarograph (Chengdu instrument Co., Ltd, China) and model PXS-5 pH meter (Shanghai Dazhong analytical instrument Factory, China). The 3-electrode function was used exclusively.

B. Preparation of soil sample

Two soil samples (fluvo-aquic soil, sampling from Wang gang Town, Longjiang County, Shunde city in Guangdong Province; paddy soil, sampling from Da wang Farm, Sihui City, Zhao Qing in Guangdong Province) were selected for this experiment. Briefly, soil samples were firstly taken from the plow layer in 0-30cm depth and air-dried, then passed through a 2-mm sieve to remove the grit and plant residue in soil. Secondly, the samples were cultivated by adding nitrogen (NH₄HCO₃, urea) according to table I. The total volume was kept at 25mL by adding proper amount of distilled water. Thirdly, the samples were swamped and half-swamped in turn at 8-10°C for 3 month, and then air dried and milled. In the end, they were passed through a 0.25-mm and 0.08-mm sieve respectively for further process. The properties of these soils were given in table II.

C. Determination of total fluorine (Total-F)

Take some soil samples melting with NaOH at 600°C, and then the total content of F could be analyzed according to

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TABLE I AMOUNT OF N, P, K IN SOIL (mg/25g)

Number	1	2	3	4	5	6
<i>nitrogen content</i>	2.5	5.0	10	15	25	40

TABLE II PROPERTIES OF THE TEST SOIL

Number	depth (cm)	Clay (%)	colloidal particle (%)	O.M (%)	CEC mmol/g	pH (H ₂ O)	Eh (mv)	Total Fe (%)	Total Al (%)	Total Mn (μg/g)	Total F (μg/g)
<i>fluvo-aquic soil</i>	0-30	23.00	12.05	2.14	0.12	6.01	221.63	6.085	14.89	511.6	603.8
<i>paddy soil</i>	0-30	30.25	15.75	1.08	0.11	5.79	255.0	6.442	21.80	889.8	851.8

TABLE III SEQUENTIAL EXTRACTION PROCEDURE FOR FRACTIONATE OF SPECIES IN SOIL

Fluorine species	Extract	Condition
<i>Ws-F</i>	distilled water	shake 0.5 h at 60°C
<i>Ex-F</i>	1.0 mol/LMgCl ₂ (pH=7)	Shake 1 h at 25°C
<i>Fe/Mn-F</i>	0.04 mol/L NH ₄ ·HCl	Shake 1 h at 60°C
<i>Or-F</i>	Step1: 3 mL 0.02 mol /L HNO ₃ + 10 mL 30 % H ₂ O ₂ Step 2: add into 12 mL 3.2 mol/L NH ₄ Ac	1 and 2step:shake 0.5 h at 25°C
<i>Res-F</i>	The total fluoride content of soil minus fluorine content in the sum of other species	

the method described as follows.

D. Sequential extraction of varies species of fluorine

Take 2.5g of soil samples (passed through 0.25-mm sieve) and put them into a 50mL plastic centrifuge tube, and then extract varies species of fluorine sequentially through adding 25mL extract solution according to table III^[4]. After every species was extracted, the volume of extract was measured with a 50mL graduated cylinder, and the amount of fluorine in residual fluid would be deducted from the calculating amount of fluorine.

E. Determination of soil pH

Take 1.0g of air-dried soil (passed through 0.25-mm sieve) and mix it sufficiently with 2.5mL of distilled water, then the pH value of solution was determined by pH meter.

F. Determination of Fluorine

Following solutions were added accurately into a 25mL colorimetric cylinder in turn: 3.0mL standard solution of Zr (IV) (10.0 mg/L), 3.0mL HCl solution (2.0mol/L), 3.5mL salicyl fluoronol solution(1.0×10^{-3} mol/L), 1.0mL polyethylene glycol solution (M_w 20000, 0.01wt%) and proper volume of standard fluorine solution or extract solution. The mixture was diluted with distilled water to volume and shaken up adequately. Then, the fluorine content of sample solution could be measured by Polarograph (model JP-303) in a 10mL beaker at room temperature through the second derivative wave. The starting potential, scanning rate and resting time is -0.30V (vs., SCE), 500mv/s and 8s respectively^[5]. The fluorine content of the object sample was the average of three

measurements. In addition, Extract of Organic species should be heated to decompose H₂O₂ before measurement.

III . RESULTS AND DISCUSSION

A. Effect of main components in nitrogen fertilizer on pH of soils

Table IV gives the change of pH value in the two soils after adding nitrogen fertilizer. As shown in table IV; soil pH value decreased with additions of urea from 2.5/25g to 5.0mg/25g and ammonium hydrogen carbonate (NH₄HCO₃) was at 2.5 mg/25g. This indicated that the metathesis between NH₄⁺ and H⁺ in soils is stronger than the neutralization between OH⁻ and H⁺. Then, the pH value increased with the increase of urea and ammonium hydrogen carbonate adding amount, because the neutralization of OH⁻ which is dissociated from the nitrogen fertilizer in soil is much stronger than metathesis between NH₄⁺ and H⁺ of soil. The pH of paddy soil increased more quickly than that of fluvo-aquic soil, as different soil has different properties.

B. Effect of main components in nitrogen fertilizer on species of fluorine of soils

Table V shows the change of the various fluorine species after nitrogen fertilizer added.

1) The change of the water soluble fluoride (Ws-F):

The change of Ws-F amount had the same tendency as that of soil pH value. The amount of Ws-F increased with the increase of soil pH, and there was significantly positive

TABLE IV EFFECT OF MAIN COMPONENTS IN N FERTILIZER ON pH OF SOILS

nitrogen fertilizer	nitrogen content (mg/25g)	0	2.5	5.0	10	15	25	40
<i>pH</i> (urea)	<i>fluvo-aquic soil</i>	6.07	6.03	6.33	6.82	6.81	7.07	7.36
	<i>paddy soil</i>	5.5	6.02	5.8	6.42	6.49	7.05	7.43
<i>pH</i> (NH_4HCO_3)	<i>fluvo-aquic soil</i>	6.07	5.91	6.32	6.63	6.96	7.15	7.55
	<i>paddy soil</i>	5.5	5.18	5.32	5.9	6.67	7.27	7.95

TABLE V EFFECT OF MAIN COMPONENTS IN N FERTILIZER ON DIFFERENT SPECIES OF FLUORINE ($\mu\text{g/g}$)

samples	species	Original soil	Soil cultivate by N as urea (mg/25g)						Soil cultivate by N as NH_4HCO_3 (mg/25g)					
			0	2.5	5.0	10	15	25	0	2.5	5.0	10	15	25
<i>fluvo-aquic soil</i>	<i>Ws-F</i>	6.44	4.63	5.57	7.55	8.00	8.71	10.31	0.882	1.88	3.07	4.32	4.52	4.25
	<i>Ex-F</i>	11.48	11.40	11.07	9.68	10.95	11.45	11.63	3.45	5.04	6.01	4.72	4.85	4.95
	<i>Fe/Mn-F</i>	1.73	1.63	1.25	0.09	0.47	2.07	2.22	2.00	1.38	0.969	1.64	2.51	2.63
	<i>Res-F</i>	584.1	585.6	585.9	586.5	584.4	581.6	579.6	597.5	595.5	593.8	592.3	591.9	592.0
<i>paddy soil</i>	<i>Ws-F</i>	0.792	0.218	0.015	1.67	1.20	3.26	4.48	0.245	0.148	0.340	1.88	3.25	3.67
	<i>Ex-F</i>	6.78	2.08	2.68	2.57	2.93	2.84	2.93	5.66	4.86	6.45	6.37	5.32	6.40
	<i>Fe/Mn-F</i>	4.37	3.91	2.85	2.37	2.59	2.87	3.05	1.88	0.961	—	0.446	0.889	1.25
	<i>Res-F</i>	839.8	845.5	846.2	845.0	844.9	842.5	841.0	843.9	845.7	844.9	843.0	842.2	840.4
	<i>Fe/Mn-F</i>	4.37	3.91	2.85	2.37	2.59	2.87	3.05	1.88	0.961	—	0.446	0.889	1.25
	<i>Res-F</i>	839.8	845.5	846.2	845.0	844.9	842.5	841.0	843.9	845.7	844.9	843.0	842.2	840.4

correlation between each other. Due to Ws-F was in the form of anion and complex ion in soil solution; it was not only affected by soil pH, but also by soil granularity, organic matter and soil components etc.

As shown from table II, the percentage of clay and colloidal particles in fluvo-aquic soil were lower than those in paddy soil, but the content of organic matter in fluvo-aquic soil is higher than that in paddy soil. As a result, the amount of fluorine absorbed on fluvo-aquic soil surface was lower than that on paddy soil surface; but the amount of Ws-F in fluvo-aquic soil was higher than that in paddy soil. Although a certain amount of fluorine could be adsorbed by organic matter, it was relatively lower than fluorine adsorbed by clay and colloidal particle. Despite total-F in fluvo-aquic soil was lower than that in paddy soil, the amount of Ws-F in these two kinds of soil was opposite. It indicated that there was no certain positive correlation between amount of Ws-F and Total-F.

2) The change of the exchangeable fluoride (Ex-F):

There was a big difference in the variation of Ex-F after adding different nitrogen fertilizer in the two soils. Urea could restrain the Ex-F dissolved from paddy soil, while NH_4HCO_3 was more effective to restrain the Ex-F dissolved from fluvo-aquic soil. The properties of soil were changed after using nitrogen fertilizer. Besides pH variation, anions and cations in fertilizer, such as NH_4^+ , CO_3^{2-} and HCO_3^- , could be adsorbed by soil (especially Ca^{2+} on the soil surface would be replaced by NH_4^+), which led to desorption of

fluorine. All the changes affected the amount of Ex-F in soils, and the changing degree depended on the properties of various soils.

3) The change of the fluoride bound to Fe/Mn oxides (Fe/Mn-F):

The amount of Fe/Mn-F in fluvo-aquic soil decreased and then increased a little comparing with that in original soil. This indicated no-bioavailability fluorine was released. The accumulation of Fe/Mn-F is needed by us. The amount of Fe/Mn-F in paddy soil increased appreciably at 25mg/25g, but on the whole, the Fe/Mn-F was activated by adding nitrogen fertilizer. Therefore, there were different results after being added different nitrogen fertilizer in different soil. The amount of Fe/Mn-F in soil was affected by adding anion and cation. Especially, affection of NH_4^+ is stronger.

4) The change of the residual fluoride (Res-F):

The variation of Res-F content in soil exposed the relation of rose and fell with the other species of F. As can be seen in table V, the Res-F of the two soils was accumulated in a certain degree after using N fertilizers except urea. The latter with high N content could lead Res-F to release in paddy soil, so it can be concluded that the main sources of Ws-F were come from activation of Ex-F and Fe/Mn-F.

C. Correlation of the soil pH and Ws-F in soil with nitrogen fertilizer applied

TABLE VI CORRELATION OF pH AND Ws-F IN SOIL WITH NITROGEN FERTILIZER APPLIED

nitrogen fertilizer	Samples	regression equation of Ws-F and pH	regression proportion (r)
urea	fluvo-aquic soil	$y = 3.1223x - 13.718$	0.9805
	paddy soil	$y = 1.8199x - 10.028$	0.9845
NH_4HCO_3	fluvo-aquic soil	$y = 2.4095x - 13.359$	0.9472
	paddy soil	$y = 1.7951x - 9.8726$	0.9849

Note: $y = \text{Ws-F}$, $x = \text{pH}$

Table IV and V show that: the content of Ws-F in soils has significantly positive correlation with pH value after adding nitrogen fertilizer; the linear relations are shown in table VI. It is learned from table VI, the content of Ws-F increased with increase of soil pH, the main reason is the change of soil pH after using nitrogen, the mechanism of this correlation between content of Ws-F and soil pH can be explained as follows:

Firstly, there are a number of variable charges on the surface of soil clay mineral and hydrous oxide; the charges depend on pH value. Negative charge will be added with increase of soil pH, this will weaken the adsorbability for fluorine, and led to the concentration of F^- increase.

Secondly, the soil pH affects the soil adsorption behavior of fluoride and its dynamic equilibrium, The study by Li bangri^[6] suggest that there is significantly negative correlation between adsorption constant (K_f) of fluorine and pH value, and so is the saturated extent of adsorption (Q_m), it indicates that the adsorbability for fluorine of acid soil is very strong, while that of alkaline soil is much less. Because there is much more OH^- in alkaline soil, which causes some precipitate to form with Ca^{2+} , Fe^{3+} and Al^{3+} . It reduces the opportunity of these cations to complex with F^- and led to fluorine release more from soil. In addition, on the condition of alkalescence, a large amount of OH^- makes an ligand exchange with fluorine which be adsorbed by clay mineral, humus and soil colloid, as the ionic radius of OH^- (0.157nm) and F^- (0.136nm) is similar. Moreover, isomorphism replacement between OH^- and F^- in crystal lattice of silicate minerals will take place. With increase of pH value, the exchanged F^- increased, so the amount of Ws-F increases.

IV. CONCLUSIONS

Soil pH value increased with additions of urea and ammonium hydrogen carbonate (NH_4HCO_3). The amount of Ws-F increased with the increase of soil pH, and there was significantly positive correlation between each other. The main sources of Ws-F were activation of Ex-F and Fe/Mn-F. So, the Ws-F would be released more from soil than original soil after nitrogen fertilizer addition, it would make fluorine transfer from soil, it led to aggravation of the fluorine contamination of the two kinds of soil. On the whole, these

two kinds of soil would be polluted by using of urea and ammonium hydrogen carbonate for a long time without taking some remedial and assistant measure.

As for the specie of fluorine bond to organic matter (Or-F), all of the measured values of the amount of Or-F were lower than the blank value, they were treated as non detected, so there is nothing to discuss.

It was used to cultivate soil by main components of fertilizer in this study, but it is just the first step of research about the effect of fertilizer on the species of fluorine-contaminate soils. It should be continued to study the influence of all components of fertilizer which was used in agricultural production. Further research about the study on the effect of interaction of nitrogen fertilizer with other fertilizer on fluorine species in fluorine-contaminate soil needs to be carried out. It is also needed to simulate agricultural production and study the effect of various components which was used regularly in the farmland on the fluorine species of fluorine-contaminate soils.

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