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Effects of long-term Located Fertilization on Spatial and temporal Variation Characteristics of Potassium and Clay Mineral Composition in Brown Soil

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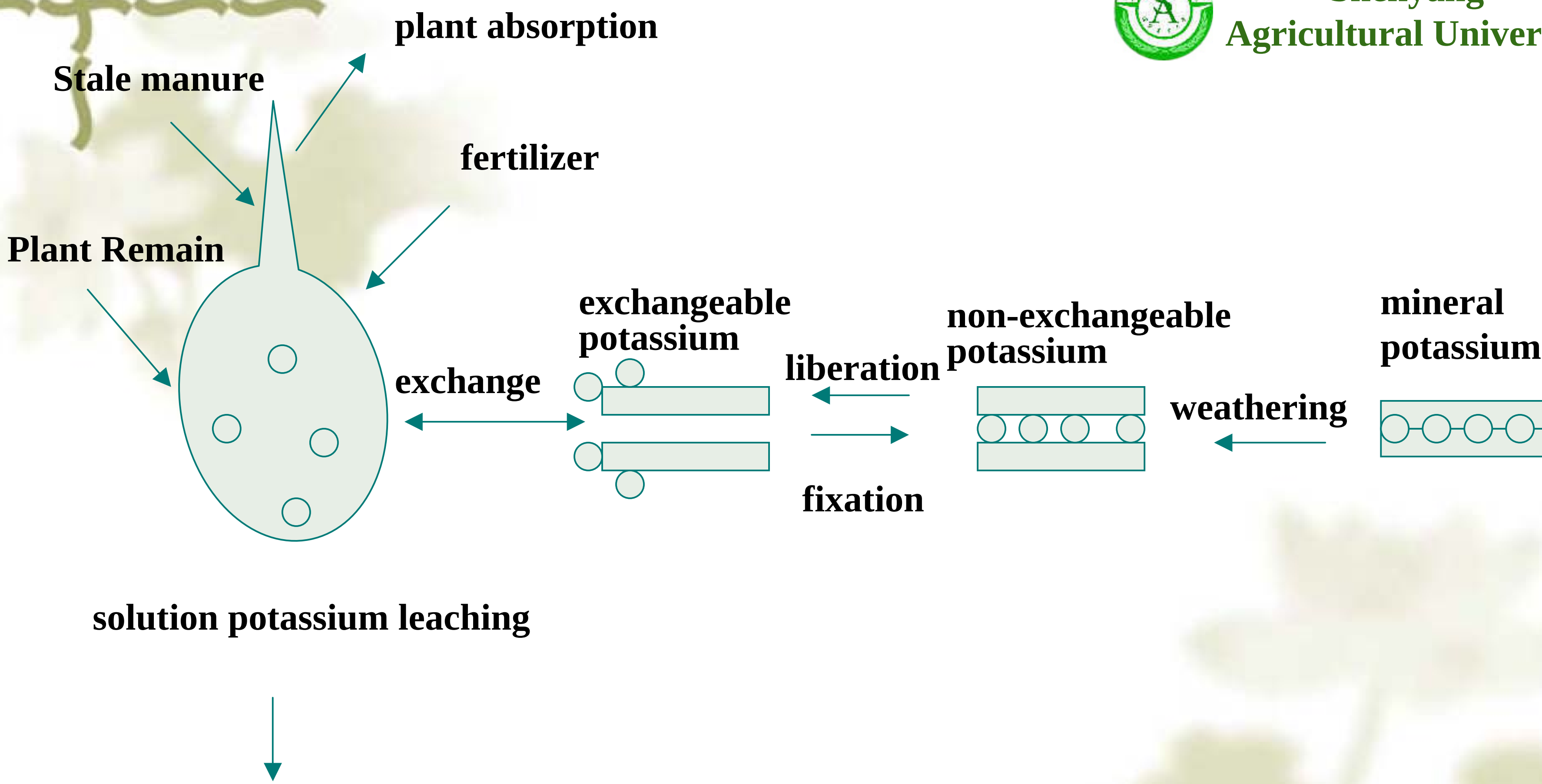
Preface

With the speedy development of the world agriculture and the improvement of multiple crop index ,more and more importance is attached to the research on the changes of soil fertility for the application of fertilizer and organic manure. Especially the evolvement of soil Potassium fertility is an attention issue. From the investigations before we know that there is a dynamic equilibrium exists among different kinds of soil Potassium ,which is affected by outer Potassium application, soil Potassium fixation and release significantly, and then Potassium form, transformation and validity are influenced .



soil potassium pool and soil potassium inversion approach

Research on Soil Clay Mineral Composition and Inversion

The acquaintance of the composition and structure of soil minerals contained Potassium will conduce to acquaint the behavior of soil Potassium and the Potassium supplied potential of different soil. At the beginning of mica weathering, it generally appears hydrated mica, and then weather into Vermiculite and Mt further; oppositely after the absorption of K+ and dehydration Vermiculite and Mt can also transform to illite and micamineral.

Purpose and significance

Our study is based on Brown Soil experimental field of Long-term Located Fertilization of Shenyang Agricultural University, and adopt soil of year: 1979(original soil),1991 and 2004 to conduct our research on Brown Soil fertility variation under different fertilizer applying, and then acquainting Brown Soil potassium form and vertical distribution character ,Clay Mineral composition and inversion and non-exchangeable potassium content variation of each grade when applying proper proportion chemical fertilizer and organic manure in Northeast main plant rotation. And we have a comparison between different treatments, different years, different depths and different grades. By doing this we can expound Brown soil potassium form variation and validity during a long time span ,providing theoretical basis for Brown soil potassium resources continuing and highly efficient utilization, inversion character of potassium resource of organic and inorganic fertilizer and make highly efficient use of potassium fertilizer.

Materials and methods

Materials

- **Adopted soil**: **Brown Soil of Long-term Located Fertilization of Shenyang Agricultural University back hill experimental field.**
- **Adopted treatment**: **CK N_1 N_1P N_1PK M_1 M_1N_1P M_1N_1PK M_2 M_2N_1P M_2N_1PK**
- **Adopted year**: **1979（original soil） 1991 2004**
- **Adopted depth**： **0～20cm 、 20～40cm**
- **Adopted plant**: **corn （with corn –soybean rotation select corn planting years）**

Methods

1. The determination of Soil Potassium Gradation

- **Water soluble potassium (WSK): be extractived with water removed ion,the proportion of soil and water:1:10, constant temperature: 25^{O}C,vibration:30min.**
- **Non-specifically adsorbed potassium (NSAK): be extractived with 0.5mol L^{-1} $Mg(OAc)_2$,the proportion of soil and water constant temperature:25^{O}C,vibration:30min.**
- **Specifically adsorbed potassium (SAK): be extractived with 1mol L^{-1} neutral NH_4OAc, the proportion of soil and water:1:10, constant temperature:25^{O}C,vibration:30min.**
- **Non-exchangeable potassium (NEK): be boiled 10min with 1mol L^{-1} HNO_3**
- **Mineral potassium (MK):be fused with NaOH The extractive liquid of each grade all measured by flame photimeter**

2.The separation and extraction of soil different grades content

Free subsidence and bolting method

Measuring air-dried soil (20#) 30g,using 30% H_2O_2 to make organic matter decomposed completely，expelling superfluous H_2O_2 firstly, then adding 0.5 mol·L-1/$2Na_2C_2O_4$ liquid 30ml and boiling an hour, using ultrasonic to scatter，passing wet (sifter 300#), bolting soil grades which>50um, manufacturing soil outstanding liquid in which soil content <3% and tuning pH=9.5. Making use of Stokes formula, according to extracting time table and room temperature of different grades of soil colloform II ,using siphonage method to extract 0-2um, 2-10um and 10-50um three grades of granular outstanding liquid (waiting for the former extracted outstanding liquid clear,then carrying on next extraction). The granular outstanding liquid which< 2um must be centrifugated, washing-out free electrolyte, using frozen drying method to dry, the others need to be putting in baking box(40℃) to dry the water, and then dried by air, retenting in bottle.

3. The discernment of soil Clay Mineral Composition

Weighing grain of clay 0.05 g(<2um) to 10 ml centrifugal tube, adding DCB solution and heating over bain-marie (80℃)for 15min, dislodging free FexOy, then adding 0.5 mol·L-1 $MgCl_2$solution or 1 mol·L-1 KCl solution to conduct triple exchange to make Mg or K saturated grain of clay. Using Mg saturated grain of clay to carry on centrifugal twice with 1:9 glycerine solution （K saturated grain of clay does not need this treatment）,throwing away clean liquid ,adding 1ml distilled water to mingle ,then pouring out on leveled glass, drying out under room temperature, putting in dryer using $Ca(NO_3)_2$ as saturated solution, waiting overnight and then conducting X-ray diffraction analysis.

Results analysis and Discussion

- The variation character with time of topsoil soil potassium form under Long-term Located Fertilization
- The vertical distribution character of brown soil potassium form under Long-term Located Fertilization
- The variation of brown soil Clay Mineral Composition under Long-term Located Fertilization
- The brown soil non-exchangeable potassium content variation of each grade under Long-term Located Fertilization

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1.Temporal Variatation charracteristics of potassium in cultivated soil under long-term located fertilization

1.1 Effect of long-term fertilization on water souble potassium

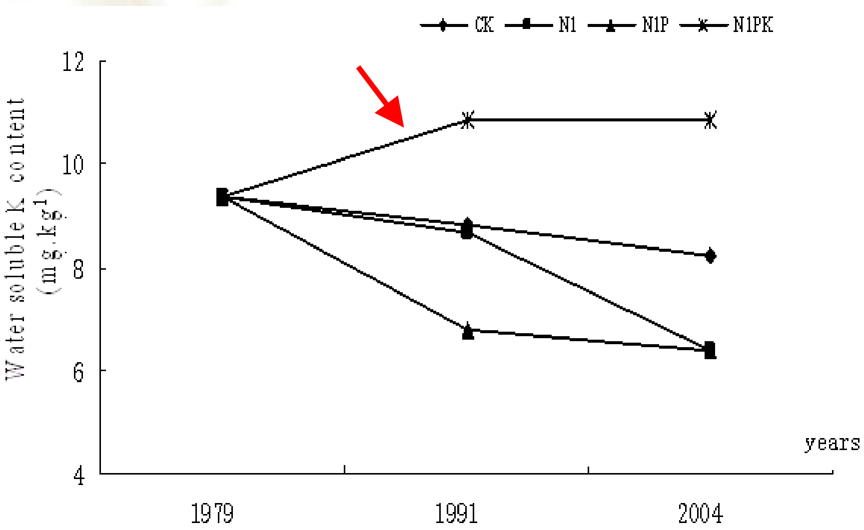

Fig. 1.The change of water soluble K content in soil under Long-term applying fertilizr treatments

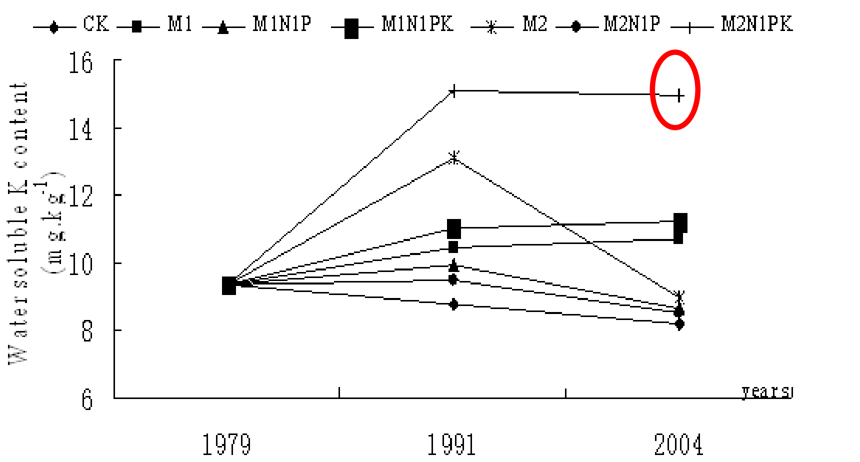

Fig.2 The change of water soluble K content in soil under long-term applying organic manure and fertilizer treatments

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1.2 Effect of long-term fertilization on Non—specifically adsorbed potassium

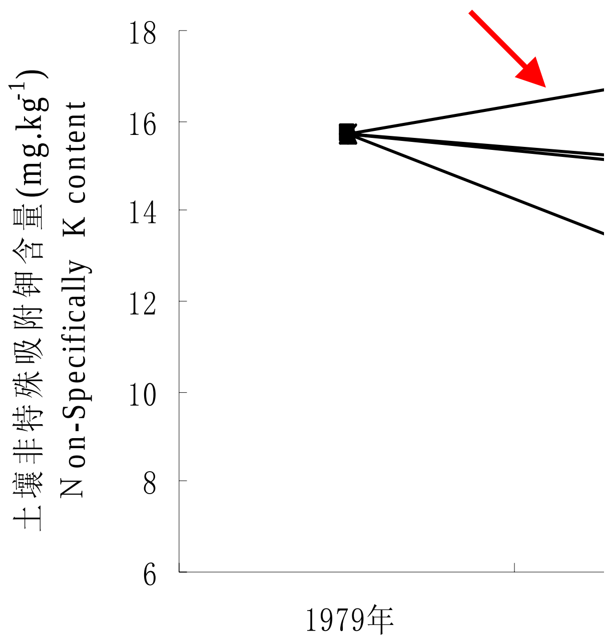

Fig 3.The change of Non- specifically adsorbed K content in soil underLong-term applying fertilizr treatments

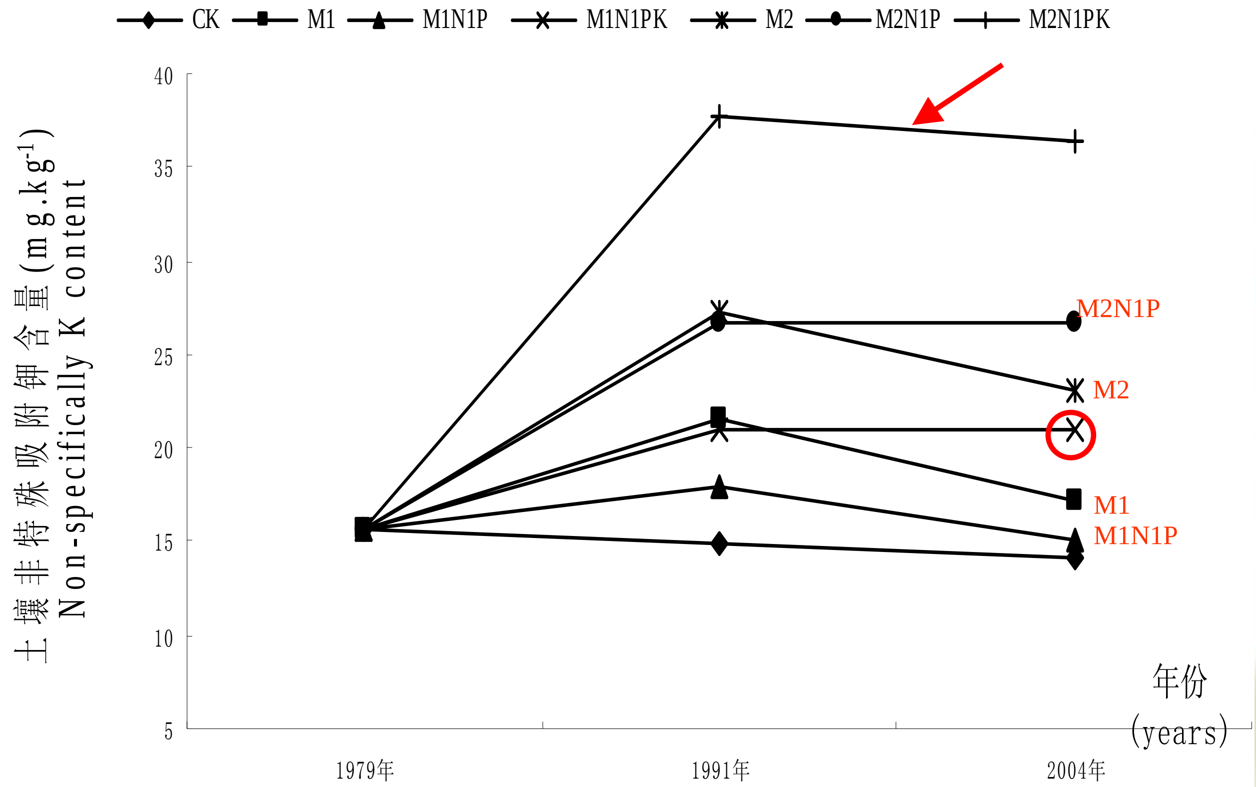

Fig.4 The variation of Non-specifically adsorbed K content in soil under long-term applying organic manure and fertilizer treatments

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1.3 Effect of long-term fertilization on specifically adsorbed potassium

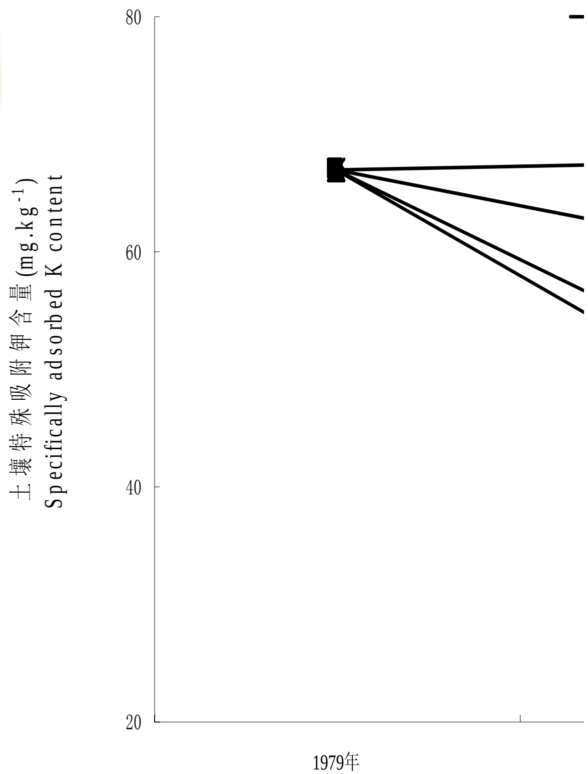

Fig 5.The change of specifically adsorbed K content in soil underLong-term applying fertilizr treatments

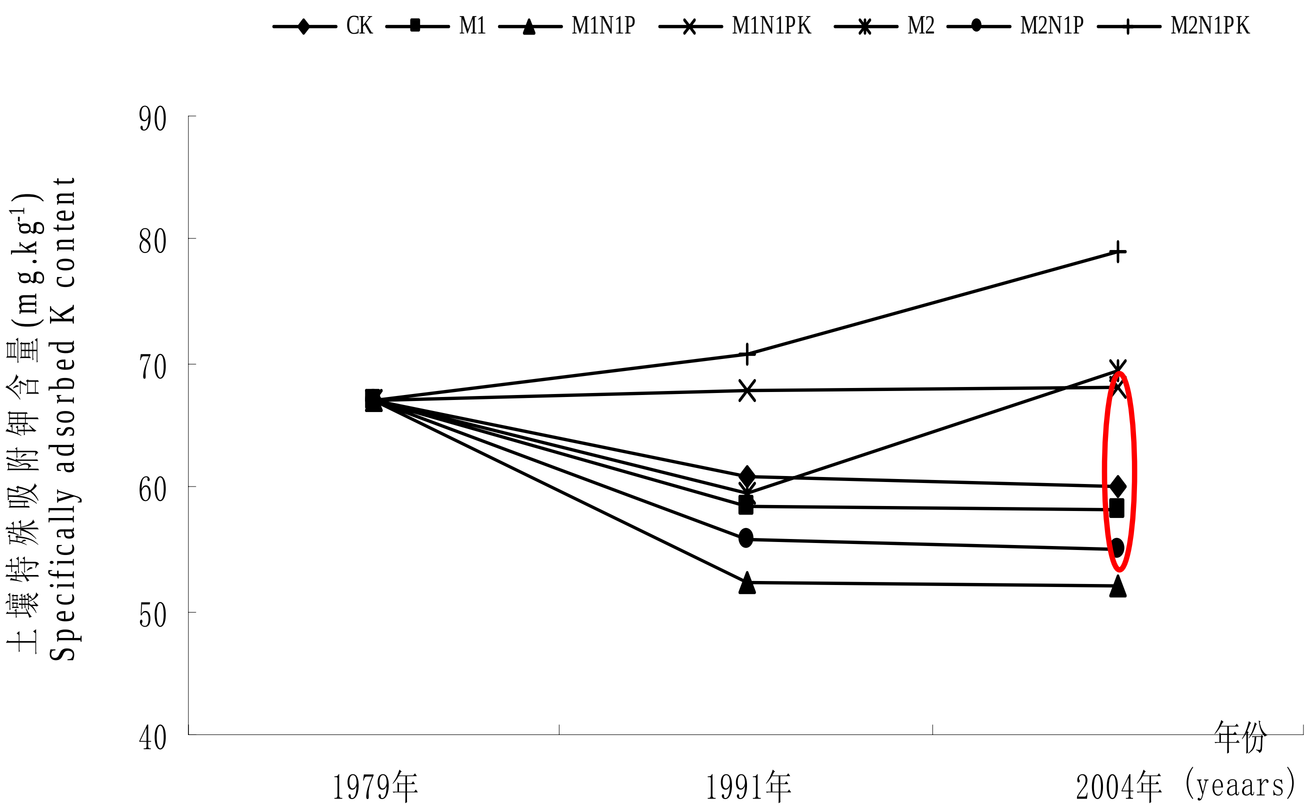

Fig.6 The change of specifically adsorbed K content in soil under long-term applying organic manure and fertilizer treatments

1.4 Effect of long-term fertilization on non-exchangeable potassium

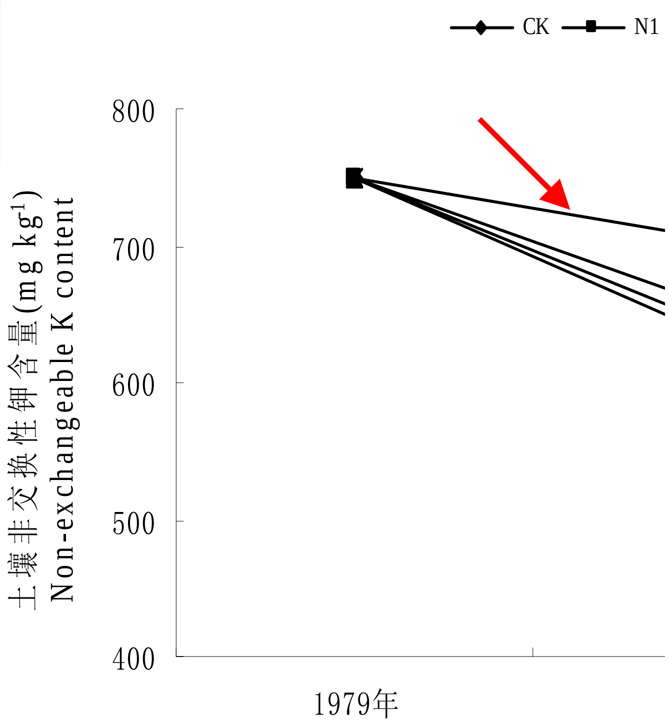

Fig 7.The change of non-exchangeable K content in soil under Long-term applying fertilizr treatments

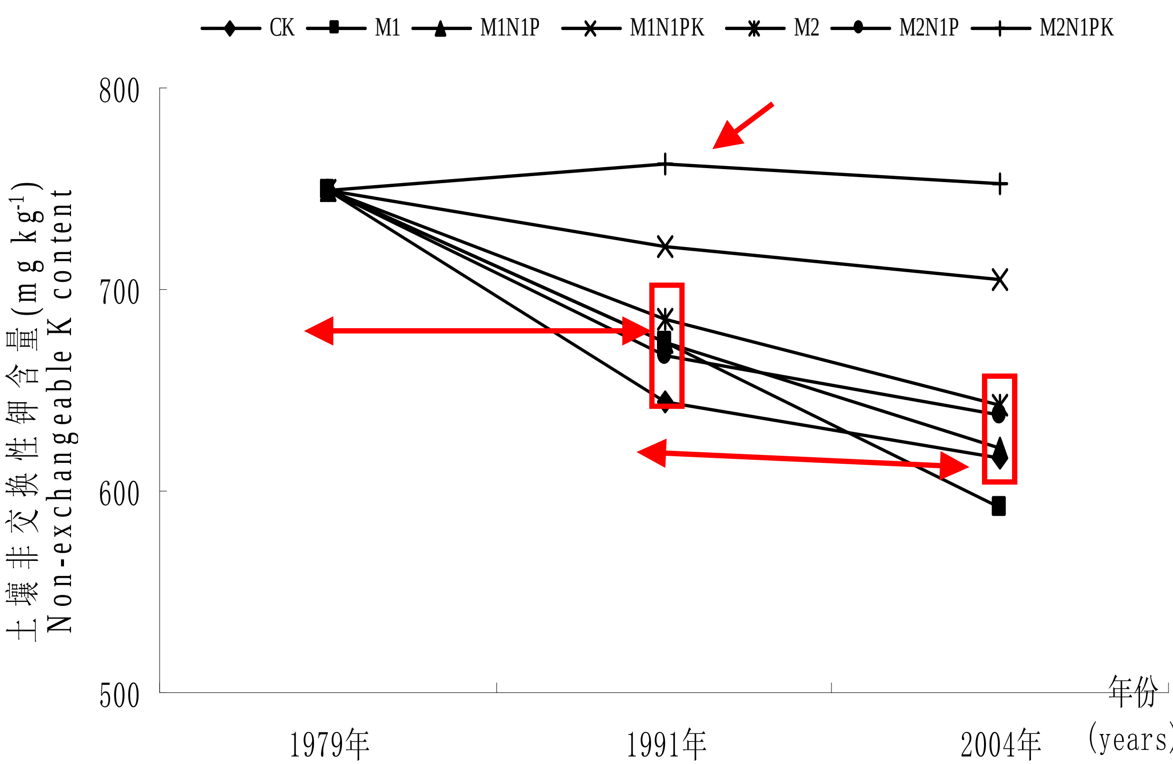

Fig.8 The change of non-exchangeable K content in soil under long-term applying organic manure and fertilizer treatments

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1.5 Effect of long-term fertilization on mineral potassium

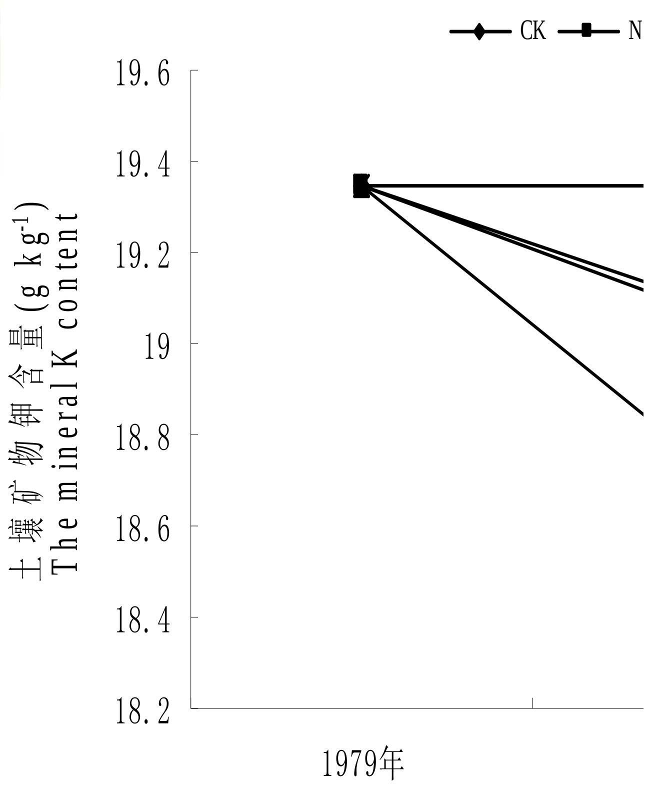

Fig.9.The change of mineral K content in soil underLong-term applying fertilizr treatments

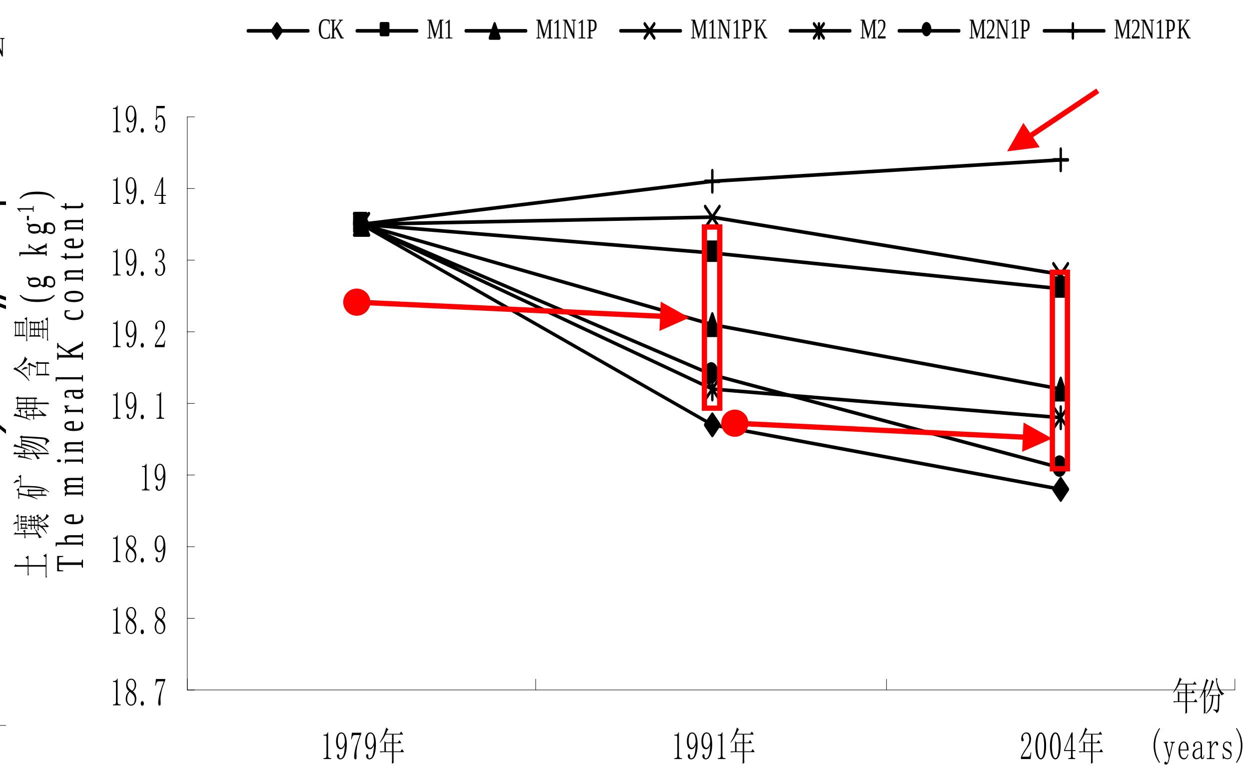

Fig.10The change of mineral K content in soil under long-term applying organic manure and fertilizer treatments

2. Vertically distributing characteristics of soil potassium under long-term located fertilization

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2.1 Effect of long-term fertilization on vertically distributing of water souble potassium in soil

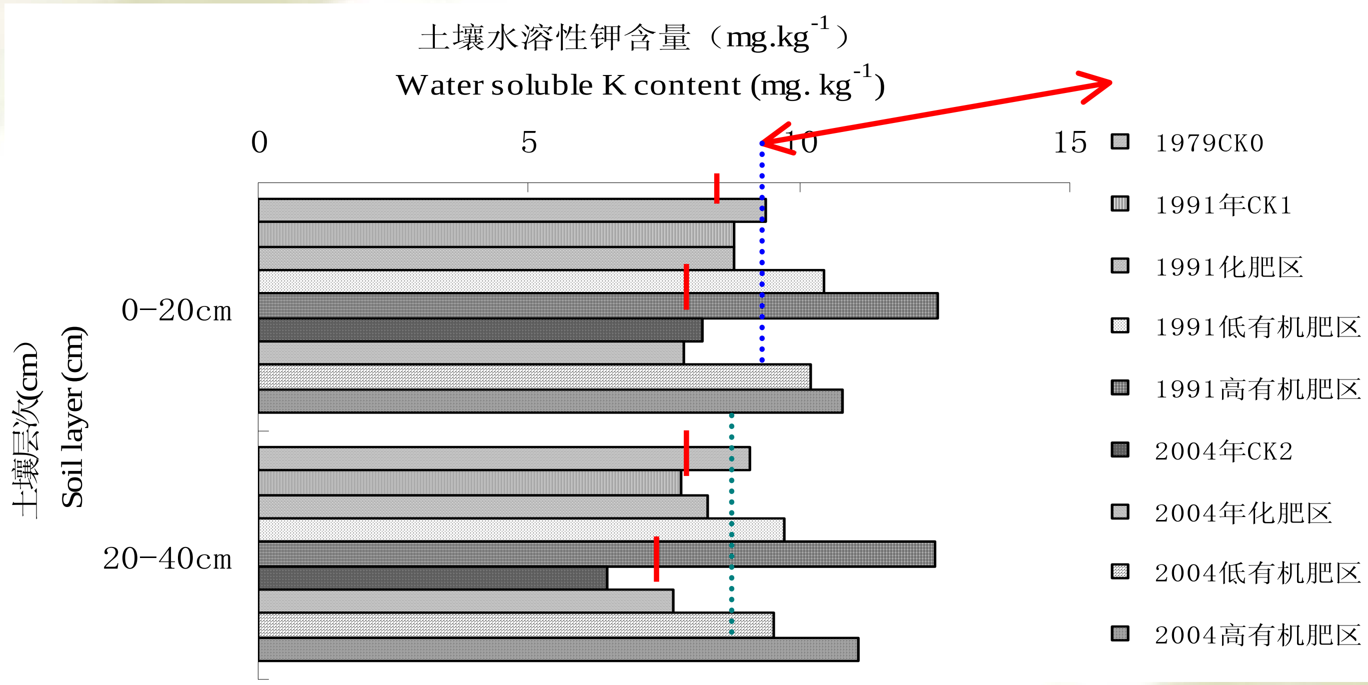

Fig.11.The change of water souble K in soil profile underdifferent fertilizration

As is shown in fig. 11, the content of soil water soluble potassium is higher in 0-20cm than in 20-40cm soil layer with all fertilizations. Also, with cultivation years increasing, the content of soil water soluble potassium in both depths conspicuously decreased compared with original soil with CK and chemical fertilizations, but significantly rose with HM or LM, and which decreased by 22% or 5% respectively in 20-40cm depth, long-term fertilizations increased the water soluble potassium content not only in topsoil, but in 20-40cm depth.

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2.2 Effect of long-term fertilization on vertically distributing of Non—specifically adsorbed potassium in soil

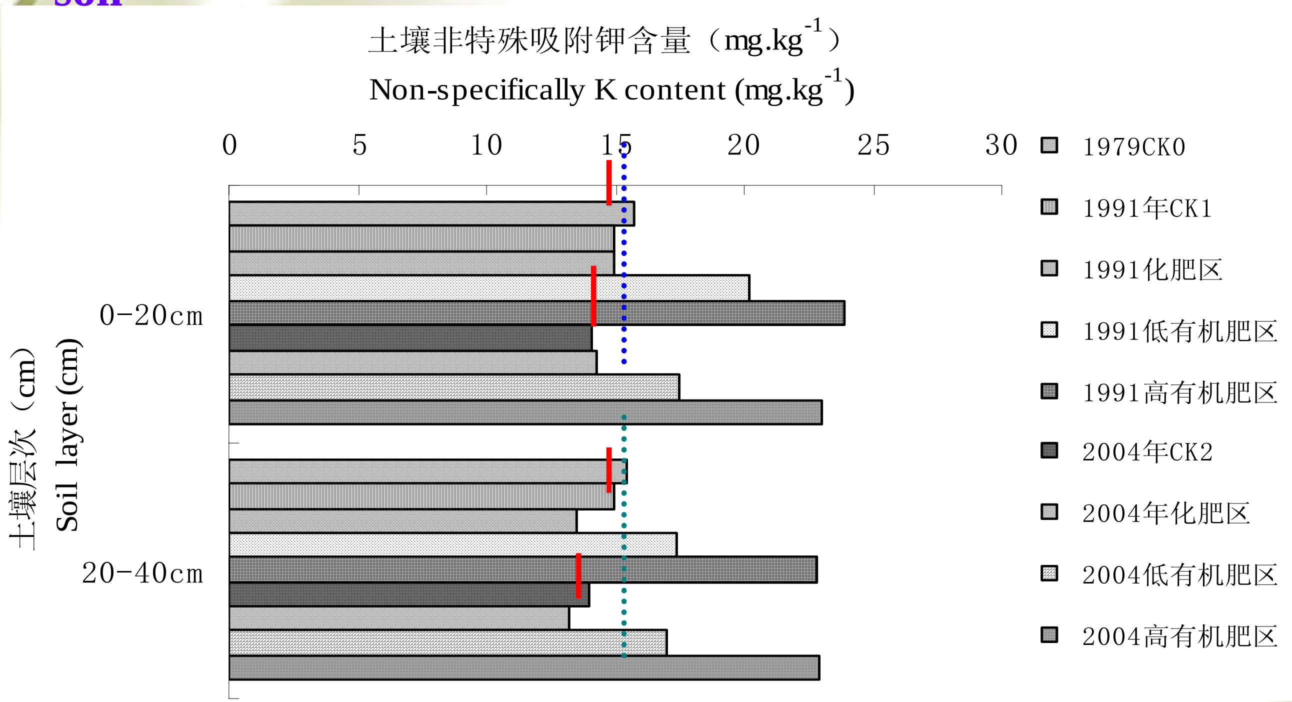

Fig.12.The change of non-specifically K in soil profile under different fertilization

We can see clearly from fig.12, that comparing to original soil, non—specifically adsorbed potassium content declined in both soil layers with CK or chemical fertilizations, but conversely rose with manure treatments. Besides, the quantity as well as relative content of non—specifically adsorbed potassium was lower in topsoil than in 20-40cm layer, mainly due to K+ enriched by crops. To conclude, manure application played a significant role in increasing non—specifically adsorbed potassium content in 20-40cm soil layer

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2.3 Effect of long-term fertilization on vertically distributing of specifically adsorbed potassium in soil

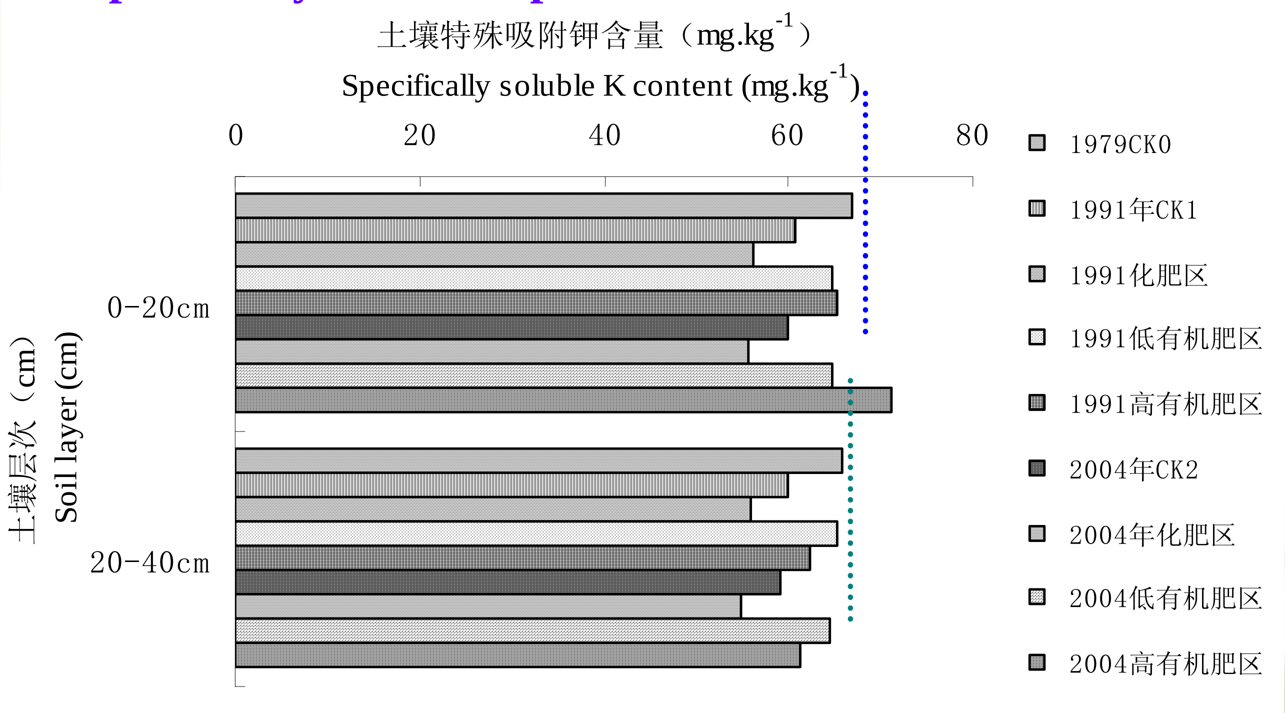

Fig.13.The change of specifically K in soil profile underdifferent fertilizration

Fig.13 showed that,for all treatments, specifically adsorbed potassium content was greater in topsoil than in 20-40 cm depth. Also, pecifically adsorbed potassium contents in both soil layers with all treatments appeared noticeable drop trend with cropping years increasing. Correlation analysis result indicated there was no relationship between the manure level and specifically adsorbed potassium content.

2.4 Effect of long-term fertilization on vertically distributing of non-exchangeable adsorbed potassium in soil

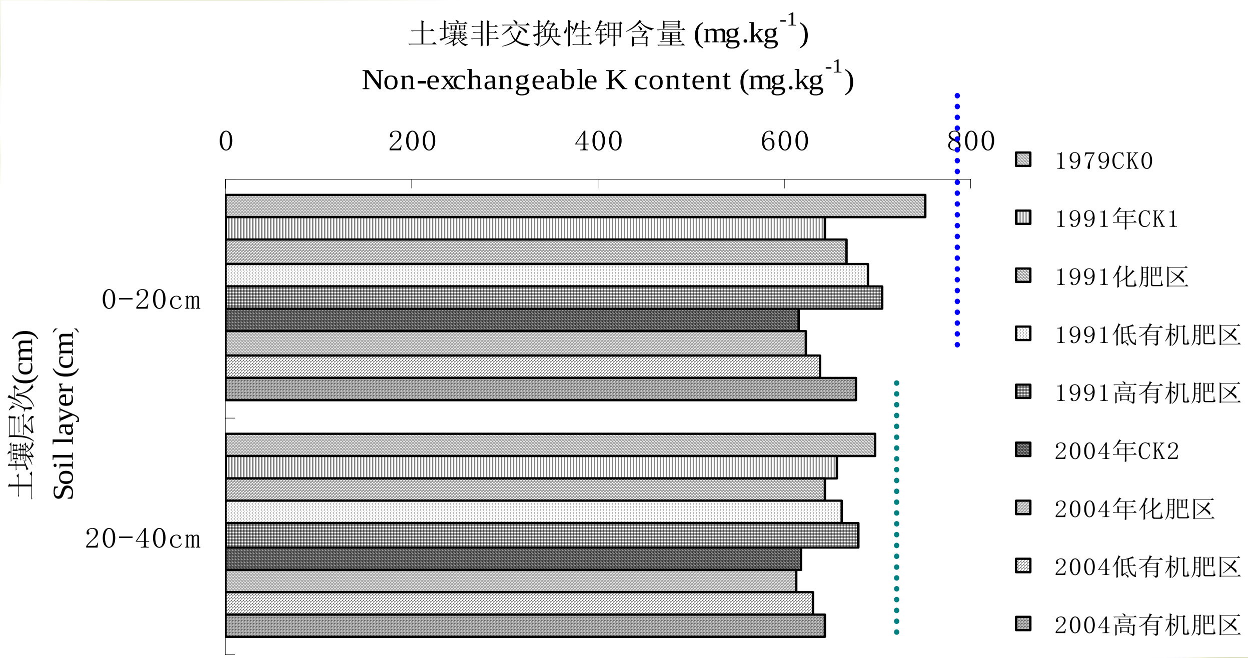

Fig.14.The change of nin-exchangeable K in soil profile underdifferent fertilizration

It can be seen clearly from Fig.14 that, with cropping years increasing, soil non-exchangeable adsorbed potassium contents in both depth with all treatments firstly showed reduction tendency with a greater rate in 0-20cm than in 20-40cm soil layer, then was inclined towards plateau; they were remarkably higher in 0-20cm than in 20-40cm soil layer. We found that long-term manure fertilization alleviated non-exchangeable adsorbed potassium's decline in brown earth.

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2.5 Effect of long-term fertilization on vertically distributing of mineral potassium in soil

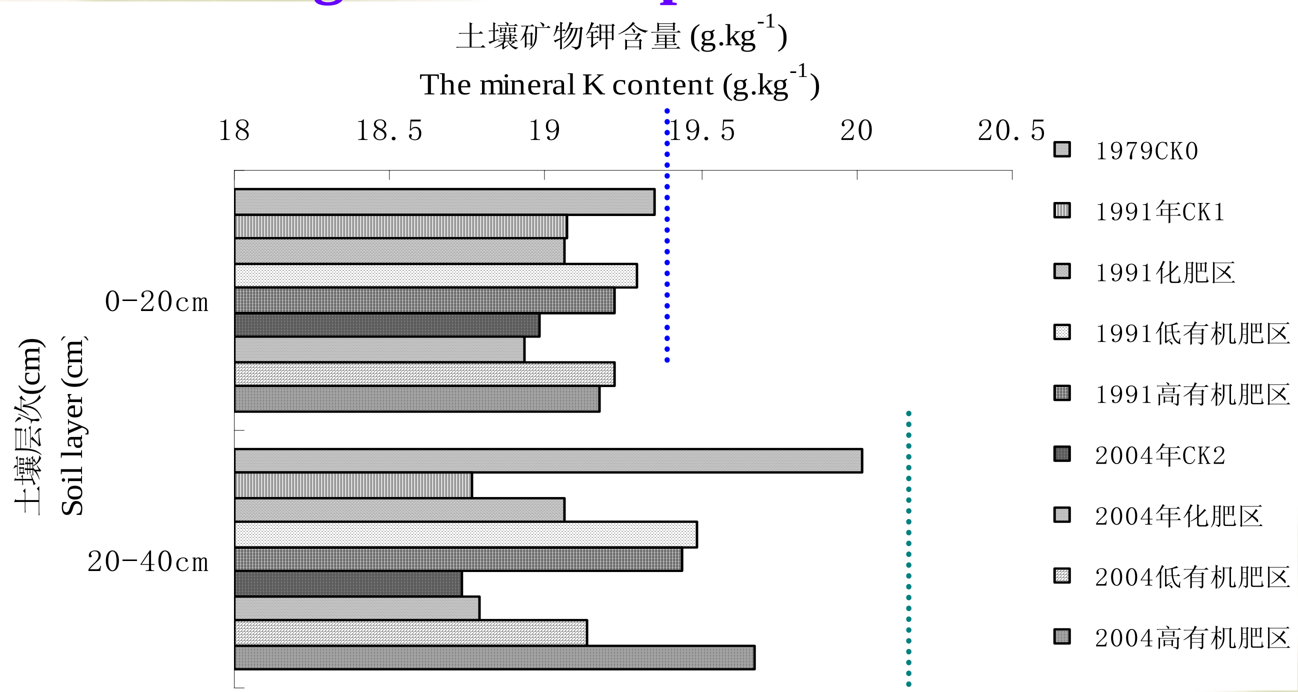

Fig .15.The change of mineral K in soil profile underdifferent fertilizration

Fig 15 showed that, soil mineral potassium presented decline tendency at different degree with different treatments; the decline rate was greater in 20-40cm than in 0-20cm soil layer, possibly because of potassium enriching in crop roots at 20-40cm soil depth, further accelerating mineral potassium effectuation process. In addition, in 2004 for all other treatments, mineral potassium was higher in 0-20cm than in 20-40cm soil layer, except HM with the contrary result. Moreover, according to comparing with soil mineral potassium decline rate with different treatments, long-term manure application contributed to the balance of soil potassium pool.

2.6 Brief Summary

1. Different form potassium contents in 0-20cm or 20-40cm soil layer all **fell** under long-term no chemical potassium fertilization compared to original soil, and this trend become **more and more** obvious with increasing cultivation years.
2. Long-term application of manure contributed to maintain soil available potassium's **balance**, and **decreased** soil r e l i e f Non-exchangeable potassium content, and **increased** active potassium content at 20-40cm soil depth.
3. Long-term application of manure combined with chemical potassium fertilizer played a significant role in **brown** earth's potassium supply, and the role more and more enhanced with the **increasing** manure rate.

3.Effects of Long-term Located Fertilization on Clay Mineral Composition

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Table2 somedominant clay minerals composing and relative content in soil during different years

Treatments	Soil clay mineral relative content （%）						
	Vt-m-Hm	Mt	Vt	Hm	Kt	Q	F
1979yrCK			24.0	39.0	30.0	6.0	1.0
1991yrCK		5.0	20.0	41.0	27.0	6.0	1.0
2004yrCK		10.0	17.0	39.0	31.0	3.0	
1991yrN_1P		14.0	17.0	34.0	31.0	4.0	
2004yrN_1P	13.0		21.0	29.0	28.0	8.0	1.0
1991yrN_1PK				54.0	42.0	4.0	
2004yrN_1PK				54.0	43.0	3.0	
1991yrM_2			16.0	43.0	32.0	5.0	
2004yrM_2		6.0	15.0	47.0	32.0	4.0	
2004yrM_2N_1P		6.0	20.0	41.0	29.0	4.0	
1991yrM_2N_1PK				57.0	39.0	4.0	
2004yrM_2N_1PK				60.0	36.0	4.0	

Most of primary minerals were Q according to identifying clay mineral in this study, because soil clay is produced by strong weathering, under the condition of which some unstable minerals, such as mica, feldspar, et. al, most changed into the smaller particles, forming the secondary minerals, while only the Q with characteristics of unti-chemical and biological weathering were left. Clay mineral is mainly consisted of Hm, still including some Vt, Kt and Mt, and a few Ct.

3.1 The change of clay mineral composition in soil under applying fertilizer treatment

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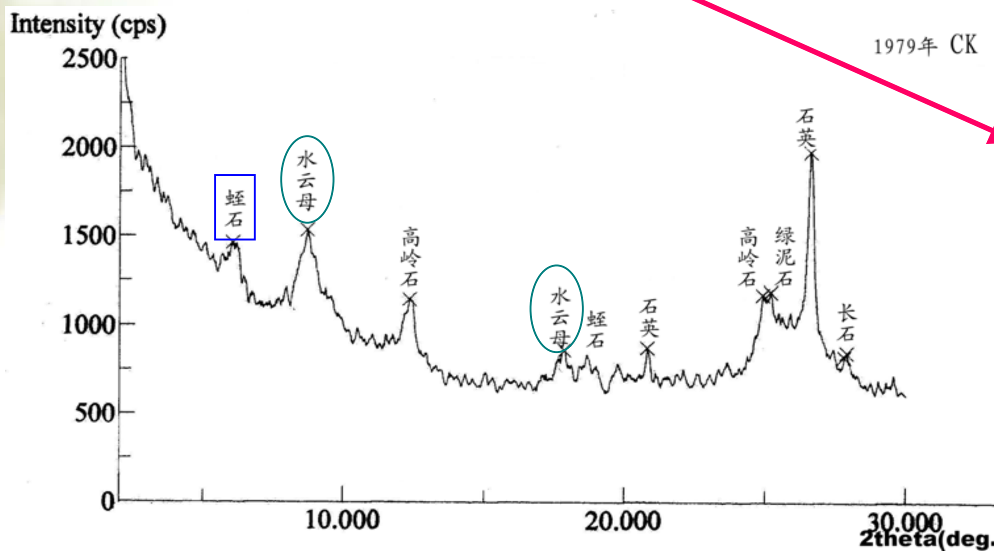
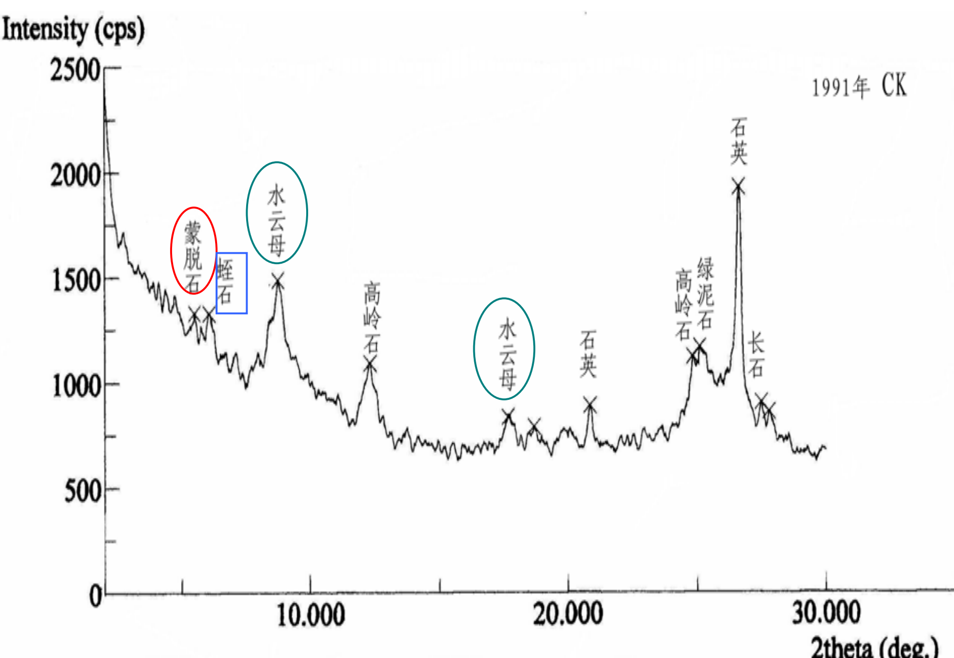
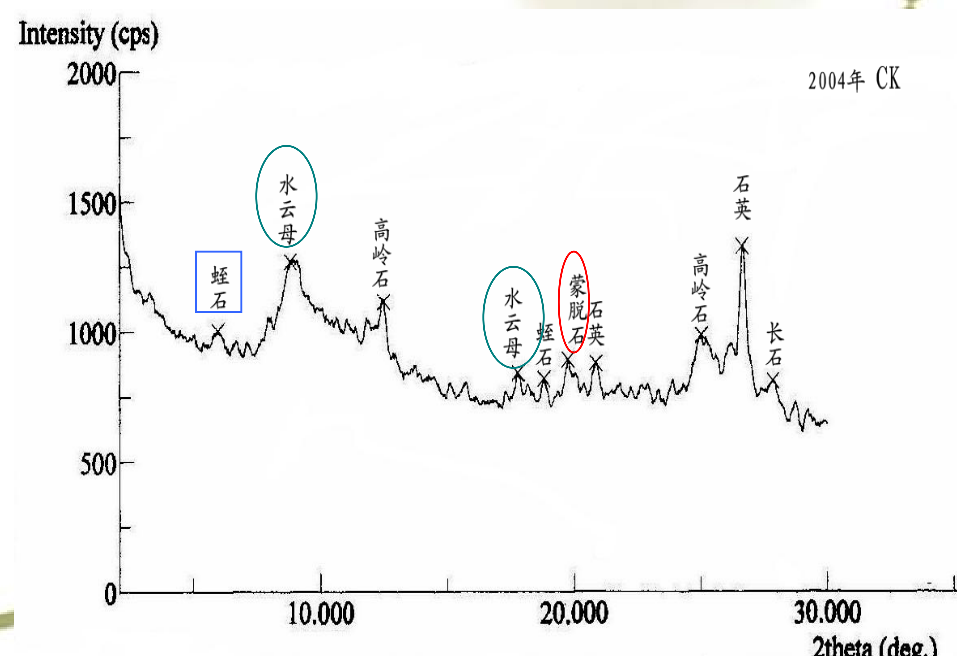


Continuing 26 years exhaungst sowing and planting soil induced Hm→Vt →Mt transform alignment





3.2 The change of clay mineral composition in soil under long-term applying nitrongen phosphorus fertilizer treatment

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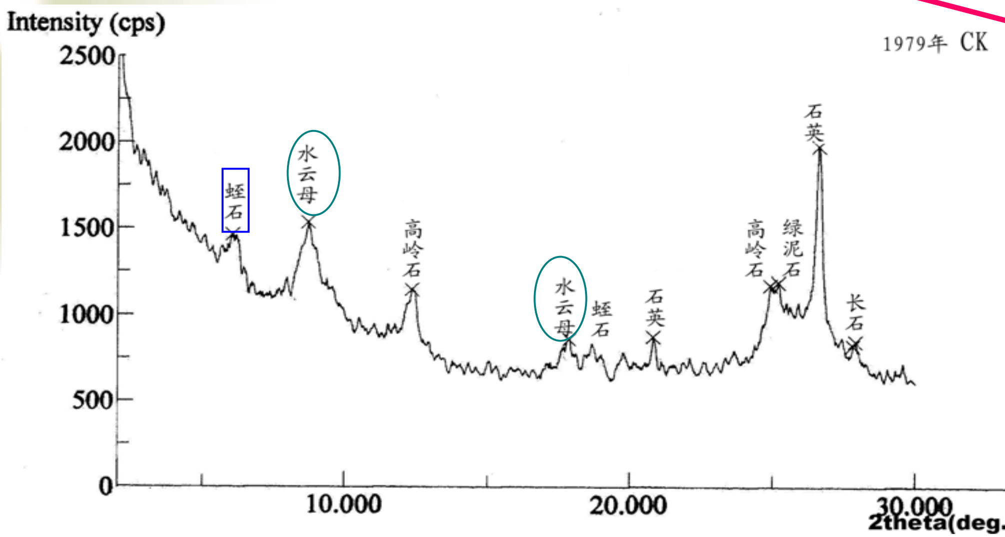
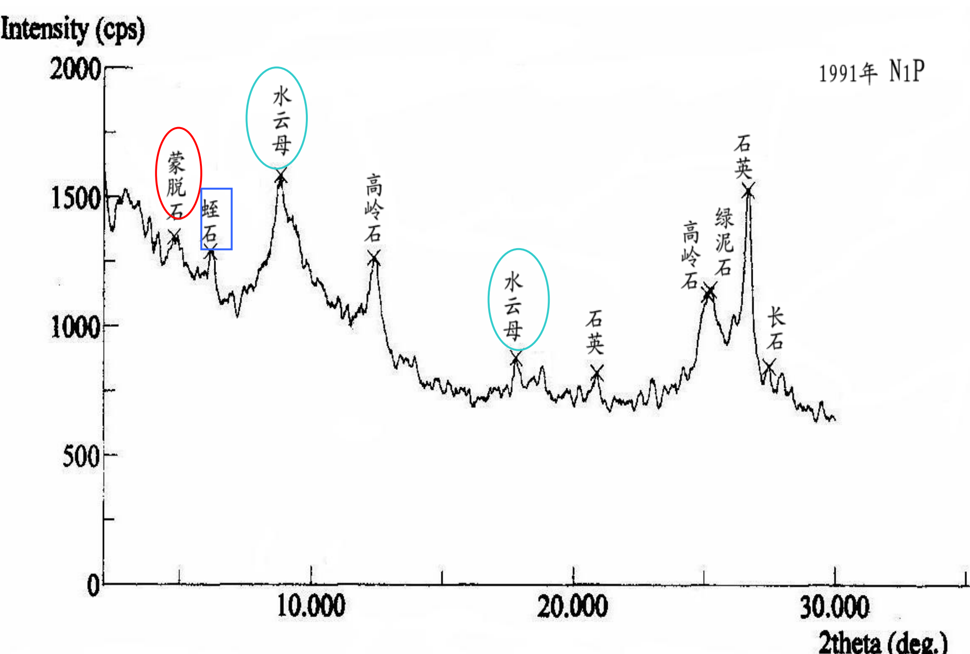
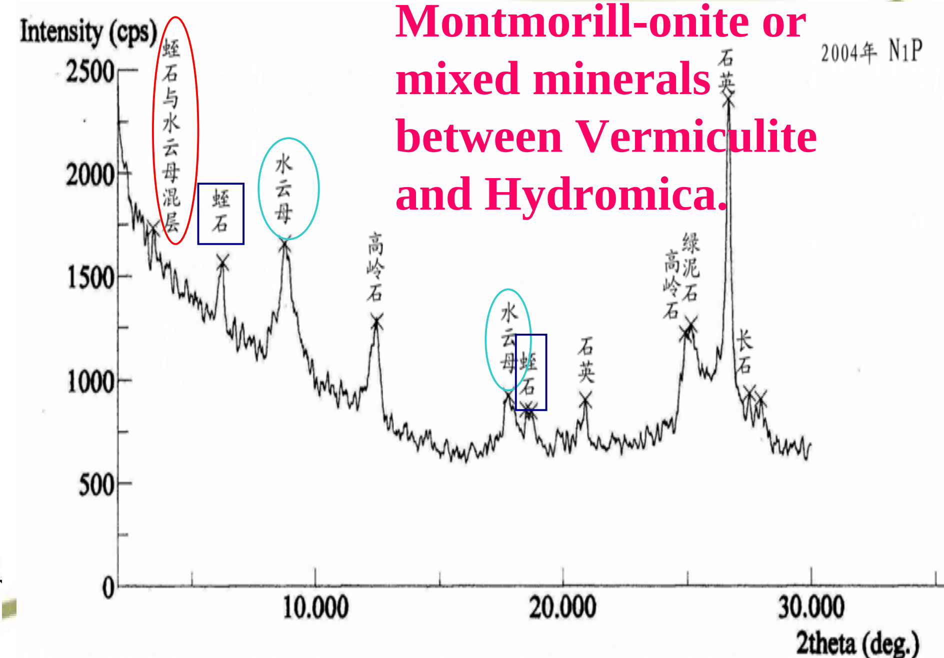


In the lack of potassium , Hydromica become Vermiculite by decomposing or releasing the potassium ion , and Vermiculite further weathering Montmorill-onite or mixed minerals between Vermiculite and Hydromica.





3.3 The change of clay mineral composition in soil under long-term applying high level organic manure treatment

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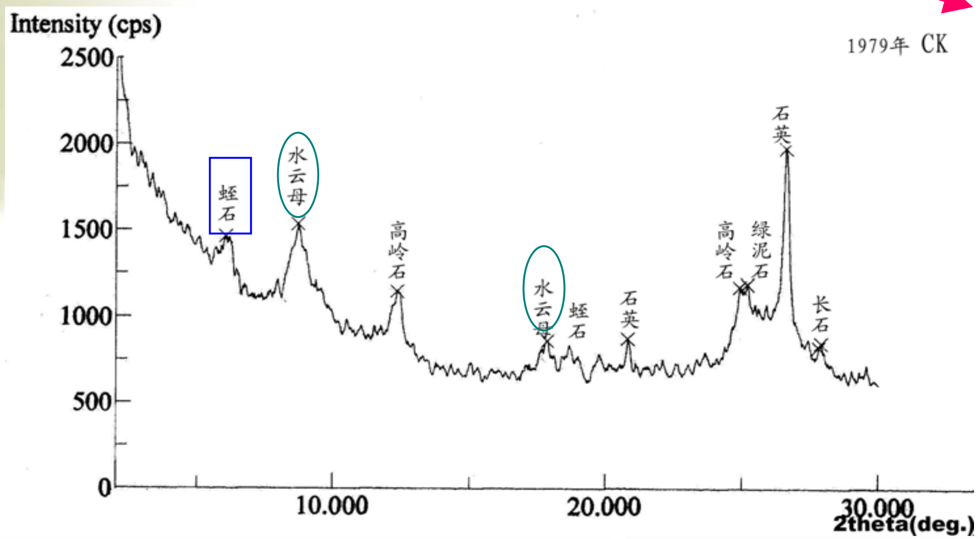
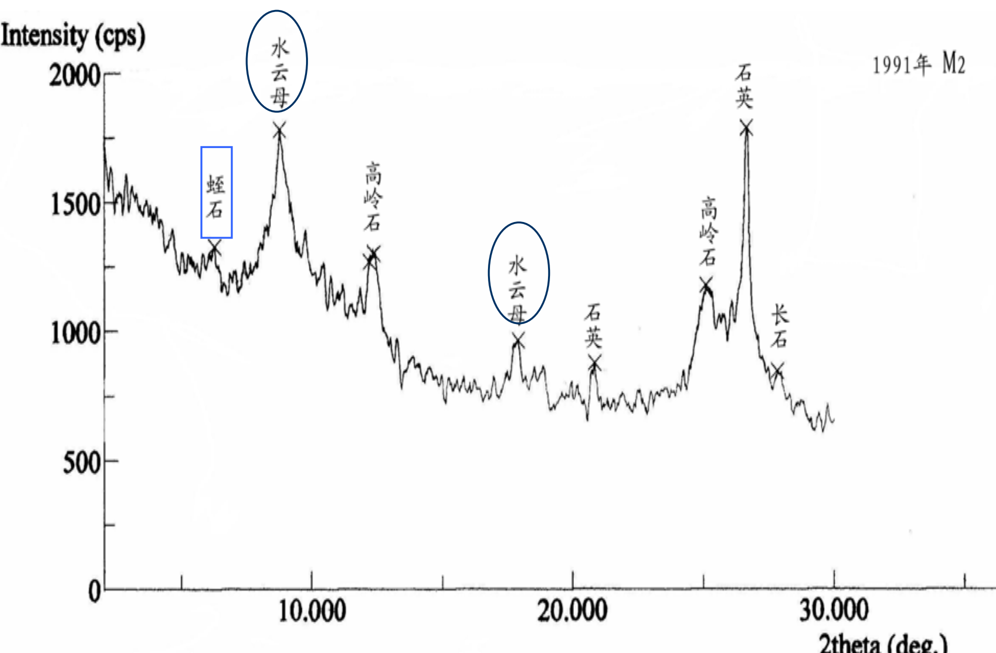
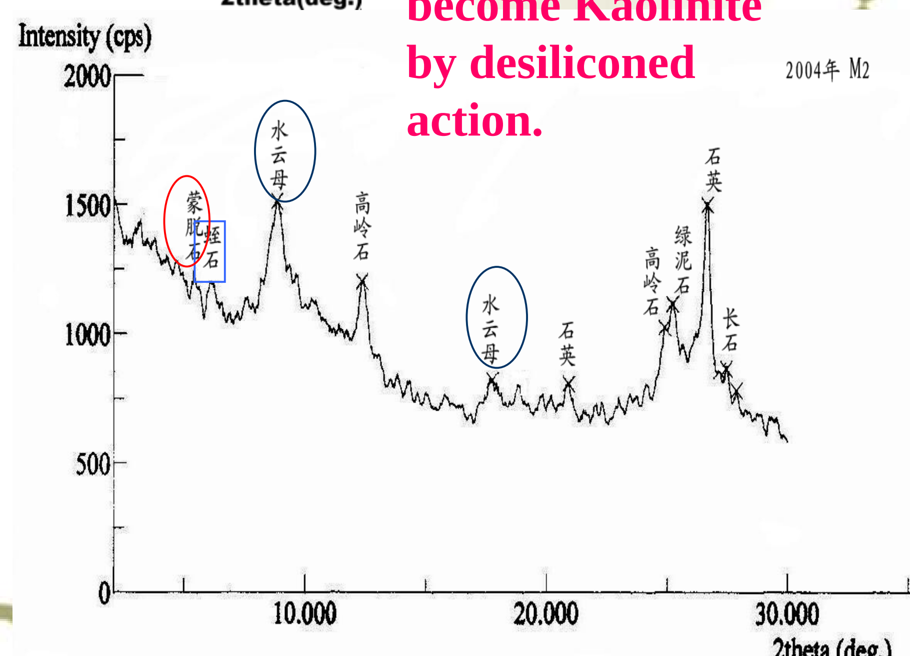


The soil fix some potassium ions in the manure with planting years. In the action of these potassium ions , Vermiculite convert Hydromica, and Montmorillonite become Kaolinite by desiliconed action.





3.4 The change of clay mineral composition in soil applying high level organic manure and nitrongen phosphorus fertilizer treatment

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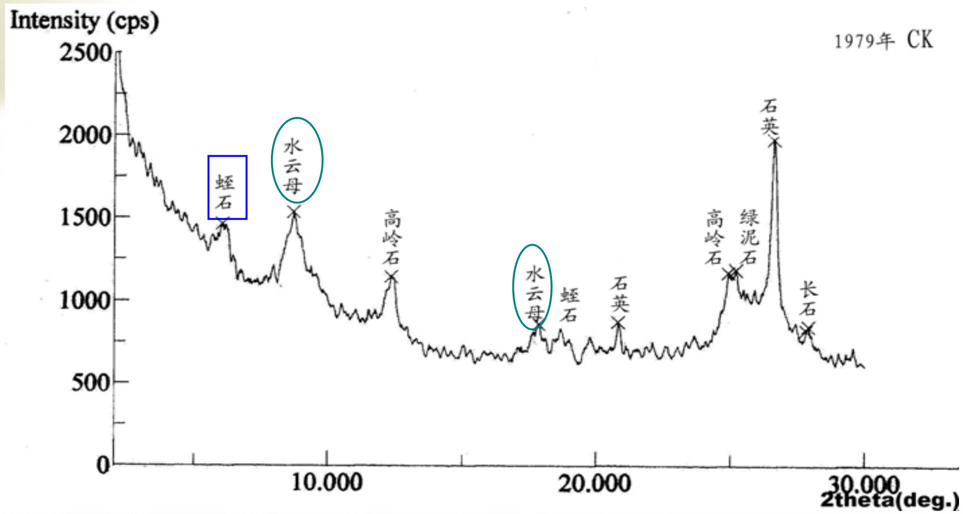

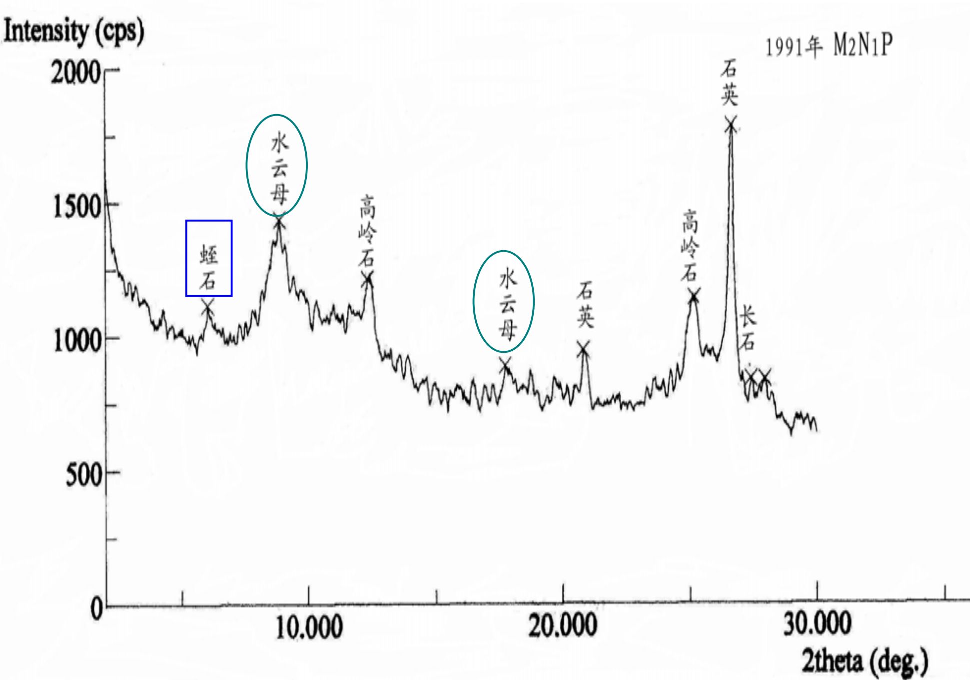

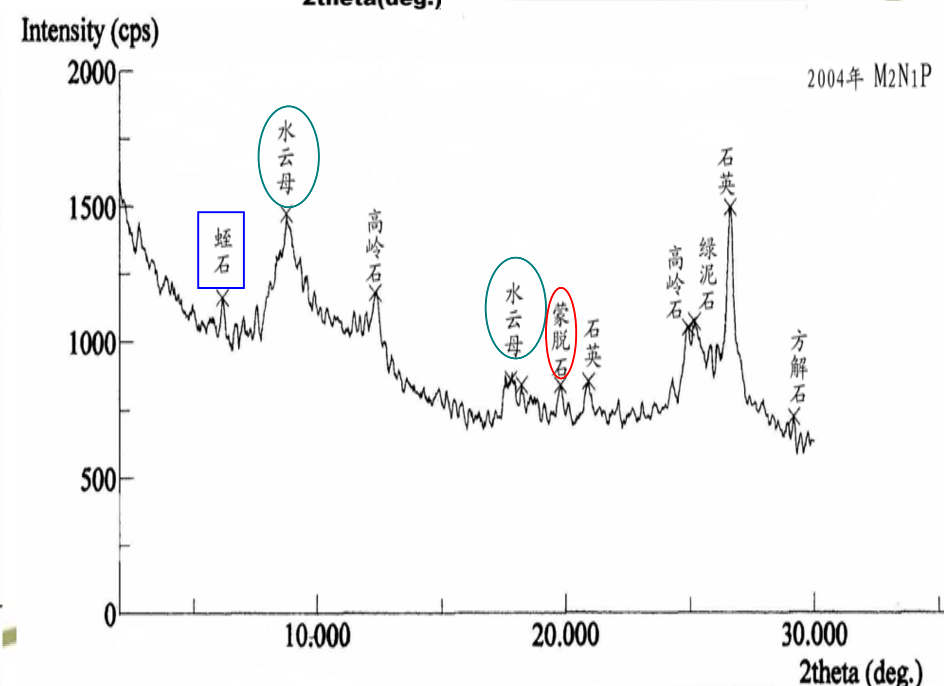

3.5 The change of clay mineral composition in soil under long-term applying nitrongen phosphorus potassium fertilizer treatment

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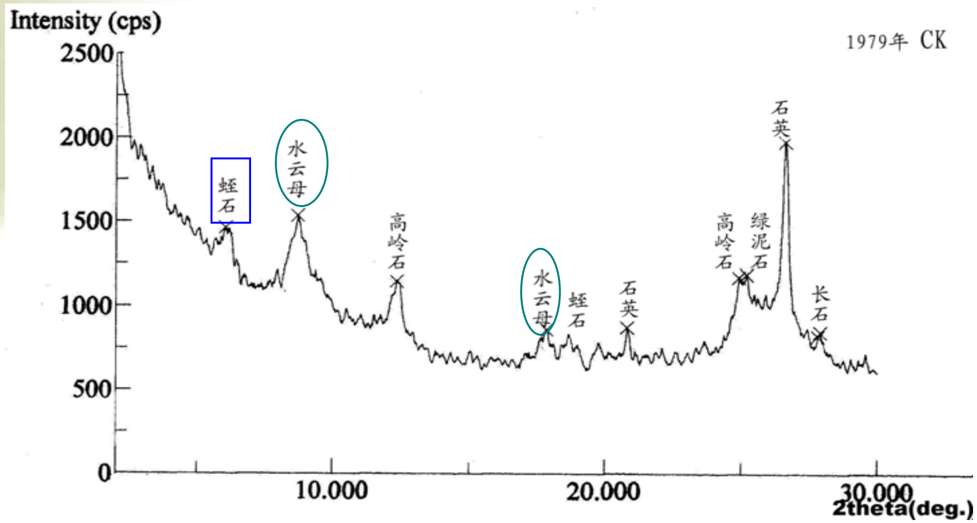

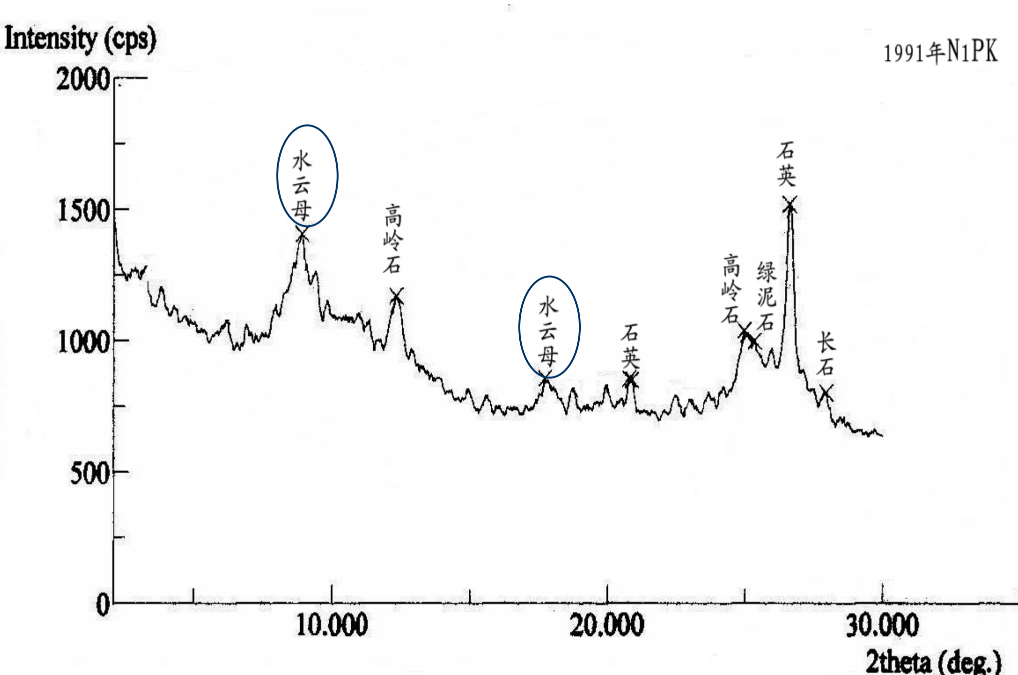

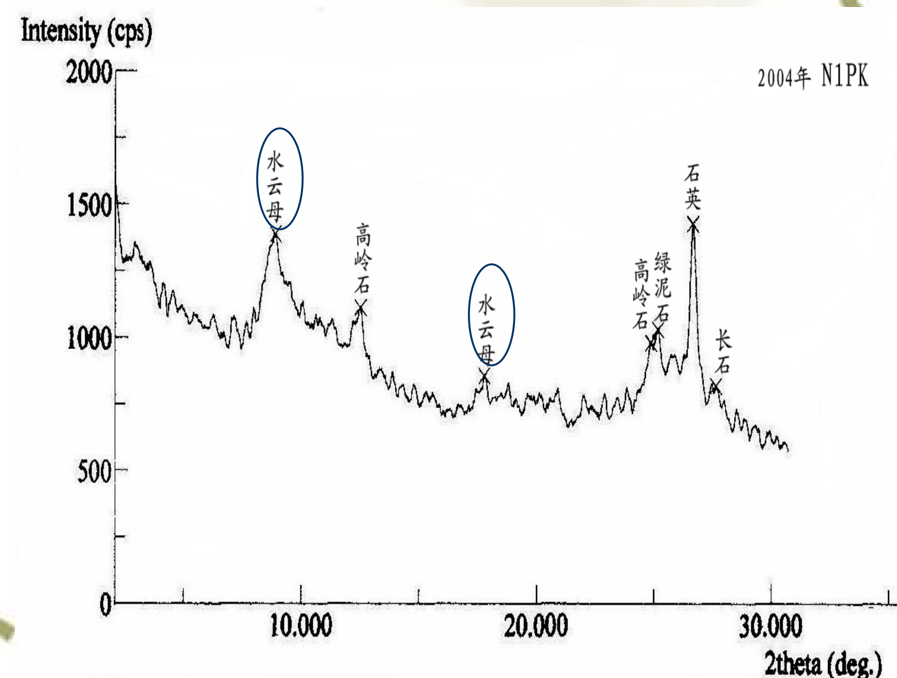

3.6 The change of clay mineral composition in soil applying high level organic manure and nitrongen phosphorus potassium fertilizer treatment

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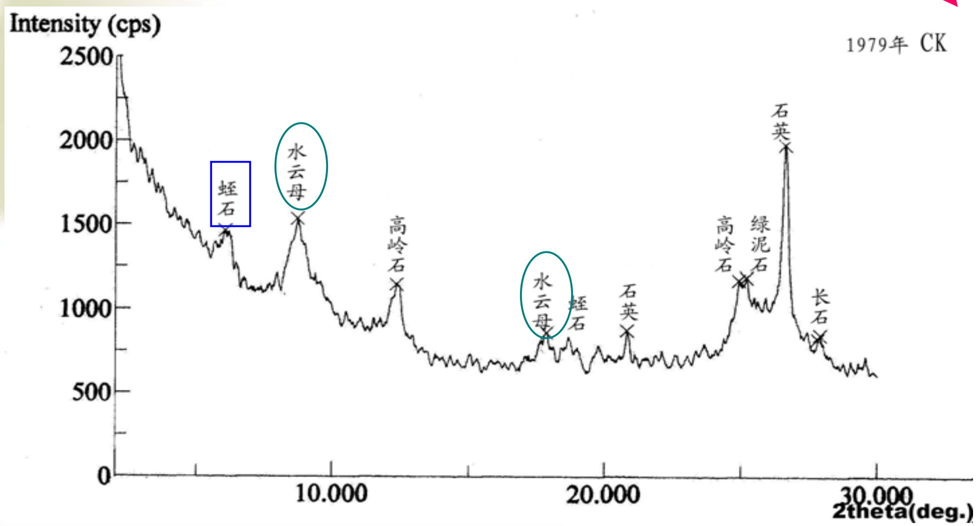
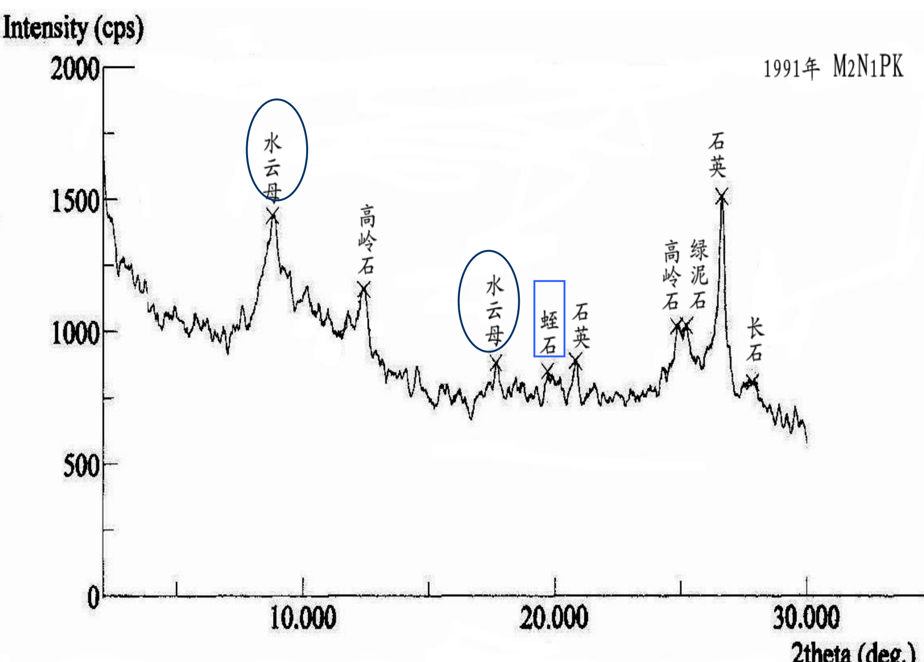
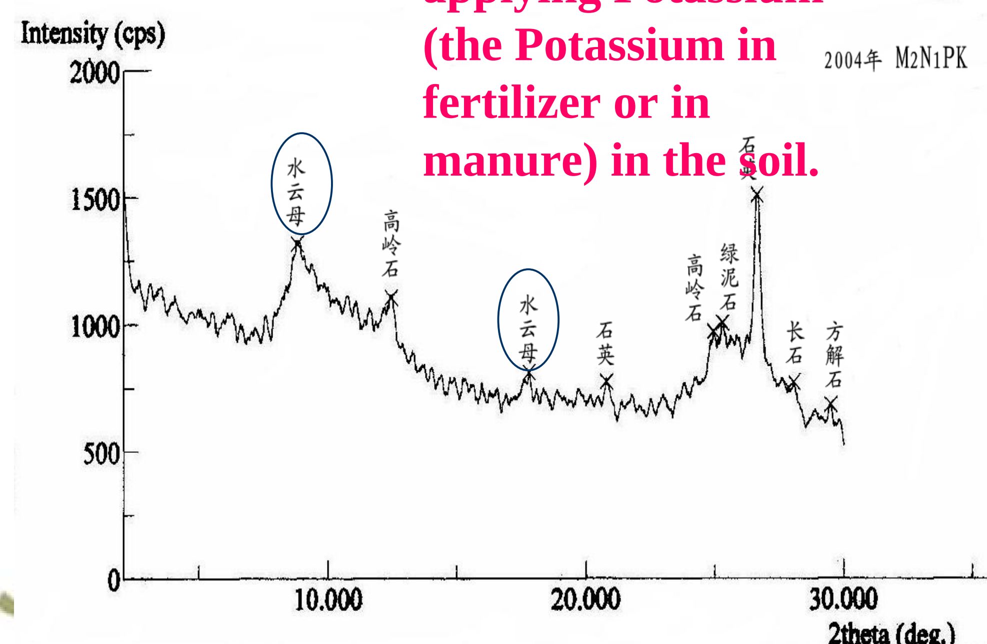
Under the relatively rich of Potassium, potassium ions are apt to fixed by Vermicu-lite,and it makes Vermiculite convert Hydromica.It maybe due to applying Potassium (the Potassium in fertilizer or in manure) in the soil.







3.7 Relationship between the forms of potassium and clay mineral composition in cultivated fertilizer treatment

Correlation coefficient	Hydromica	Kaolinite	Vermiculite	Montmorillonite
Water soluble K	0.901 **	0.594 *	-0.712 **	-0.561 *
Non-specifically adsorbed K	0.769 **	0.454	-0.670 **	-0.392
Specifically adsorbed K	0.854 **	0.598 *	-0.690 **	-0.426
Non-exchangeable K	0.728 **	0.501	-0.524	-0.561 *
Mineral K	0.869 **	0.670 **	-0.644 *	-0.596 *

The condition of potassium in soil can evaluate the ability of providing K to soil.The mineral having potassium are the main source of potassium in soil. From Table 3, we can see that the content of the water soluble K is mainly decided by the contents of Hydromica and Vermicu-lite;The contents of non-specifically adsorbed K and Specifically adsorbed K are respectively related to the contents of Hydromica and Vermiculite;The main clay mineral that influences

the content of non-exchangeable K is Hydromica;and the content of the mineral potassium is related to the content of the main clay mineral in the soil.The contents of every forms of pota-ssium correlate positively with the content of Hydromica, and that means Hydromica have strong ability of adsorbing and fixing or releasing potassium ions. But the contents of every forms of potassium correlate negatively with the one of Montmorillonite and Vermiculite,which reflects the transformation relation of Vermiculite and Hydromica indirectly.The isomorphous replacement capacity of Kaolinite is weak and cation exchange capacity is poor.The fixation and supply of potassium capacity is so poor that the correlation between Kaolinite and all forms of potassium is insignificant.

3.8 Discussion

Clay mineral control the fixation and release of potassium in soil, which lead to mutual transformation among sandwich silicate mineral in soil. The relative content of clay minerals change after the long-term fertilization of 26 years. The contents of Hydromica or Vermiculite is reduced when not applying potassium fertilizer ,and the content of Mortmorillonite or the content of Vermiculite and Hydromica in mixed layer increases;but the relative content of Hydromica increase in soil clay mineral and the content of Vermiculite or Mortmorillonite decrease to some extent for using organic fertilizer only or chemical potassium only or chemical potassium and organic fertilizer.It means that there are a relationship of mutual transformation among Hydromica, Vermiculite and Mortmorillonite.

4. The change of non-exchangeable K in soil different particle size fractions under long-term located fertilization

Generally speaking, the content of non-exchangeable K decides that potassium is provided by soil.In some condition,those K can convert to exchangeable K for plant availing, and they have restricitive fluence of

soil potassium availability. Recently, many scholars develop a lot of research which is based on the research of soil mineral about the distri-bution and transformation of non-exchangeable K in different particle .Developing this research will further know the conversion mechanism of soil non-exchangeable K,and provide obvious evidence to explain the transformation of soil potassium and the advisable application of potassium fertilizer.

4.1The distribution of different particle size fractions in different fertilizer treatments

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		Composition of particle% (Diameter : um)			
Years	Treatments	>50 um	10-50 um	2-10 um	<2 um
1979	CK	11.26cd CD	50.60fF	12.42e EF	25.72hH
1991	CK	10.54eE	50.89eE	12.79cC	25.78hH
	N_1P	8.13 jI	53.47aA	13.04bB	25.36jJ
	N_1PK	9.48 hH	51.94cC	12.33eF	26.25fF
	M_2	11.39 cC	51.02dD	12.72cC	24.87kK
	M_2N_1P	11.85 bB	49.6hH	12.59d DE	25.96gG
	M_2N_1PK	11.02 dD	50.03gG	12.02fG	26.93cC
2004	CK	7.45 kJ	53.48aA	13.62aA	25.45iI
	N_1P	9.75 gG	53.05bB	13.22bB	23.98lL
	N_1PK	8.31 iI	51.83cC	12.02fG	27.85bB
	M_2	10.12 fF	50.82eE	12.68cd CD	26.38eE
	M_2N_1P	12.56 aA	48.37jJ	12.42e EF	26.65dD
	M_2N_1PK	10.13 fF	49.47iI	11.88gH	28.52aA

The changing trend in the contents of above 2um in soil applied by different fertilizer is opposite to the one below 2um.

The content of 0~20um particle grade is decreased every year under long-term not applying potassium fertilizer with planting. But comparing with the original soils, the composition of particle obviously increases with using potassium fertilizer for a long time.

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4.2 Effects of non-exchangeable K in soil different particle size fractions under long-term located fertilization

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Years	Treatments	Different particle size fractions of non-exchangeable K content in soil （K_2O mg. kg^{-1}）							
		Diameter <2um	the percent of total particle grade（%）	Diameter 2-10um	the percent of total particle grade（%）	Diameter 10-50um	the percent of total particle grade（%）	Diameter >50um	the percent of total particle grade（%）
1979	CK	1044.87 hH	53.52	676.82 gG	34.67	125.84 cC	6.45	104.76 gG	5.37
1991	CK	1041.06 iI	54.85	656.67 hH	34.60	115.66 dD	6.09	84.58 jI	4.46
	N_1P	1028.41 iJ	53.41	656.39 iI	34.09	135.97 bB	7.06	104.82 f FG	5.44
	N_1PK	1065.37 gG	54.28	676.71 gG	34.48	115.62 dD	5.89	104.86 fF	5.34
	M_2	1146.58 dD	50.57	839.50 cC	37.02	135.98 bB	6.00	145.46 bB	6.42
	M_2N_1P	1207.76 cC	53.26	798.78 dD	35.22	136.03 aA	6.00	125.14 dD	5.52
	M_2N_1PK	1264.47 aA	53.47	859.53 bB	36.35	135.96 bB	5.75	104.77 gG	4.43
2004	CK	1025.64 kK	55.38	636.18 jJ	34.35	105.44 eE	5.69	84.73 hH	4.58
	N_1P	1014.22 iL	56.98	575.50 kK	32.33	105.48 eE	5.93	84.65 iI	4.76
	N_1PK	1085.76 fF	55.89	656.46 iI	33.79	95.34 fF	4.91	105.02 eE	5.41
	M_2	1126.31 eE	55.09	677.13 fF	33.12	115.69 dD	5.66	125.32 cC	6.13
	M_2N_1P	1146.64 dD	54.72	697.67 eE	33.29	125.83 cC	6.01	125.31 cC	5.98
	M_2N_1PK	1248.36 bB	50.95	920.07 aA	37.55	115.65 dD	4.72	165.88 aA	6.77

Table5 The change of non-exchangeable K content in soil different particle size fractions under long-term different fertilizer treatments

4.3 Discussion

- The contents of every particle fractions in soil applied by different fertilizer change with planting years. The content of 0~2um particle grade is **decreased** every year under long-term not applying potassium fertilizer, but the content of them is **increased** under using organic fertilizer or potassium fertilizer for a long time. The changing trend in the contents of above 2um in soil applied by different fertilizer is opposite to the one below 2um.
- **The content** of non-exchangable K of 0~2um particle grade is maximum,the secondly is 2~10um particle and 10~50um particle grade,the least is above 50um particle grade.The content of non-exchangeable K in soil blew10um particle grade is 88.71% of total amount among them. The influence on the content of non-exchangeable K blew 10um particle grade soil used by organic fertilizer and chemical fertilizer and the function of organic fertilizer is reduced with the increase of particle diameter.

Conclusions

- All forms of potassium in brown soil can move vertically with the influence of parent material, meteorological factors and long-term fertilization by constantly cultivating in the past 26 years.
- With the increase of cultivating time, the contents of different potassium in two-layer soil present obvious downward trend when potassium fertilizer weren't added for a long time. But balance of available K in two-layer soil can be kept, non-exchangeable K downward trend can also be relieved and activation of the mineral K can be fulfilled when using organic fertilizer. So the application of organic fertilizer and potassium fertilizer play the obvious role of fostering potassium fertility and improving the ability of providing potassium in brown soil, and these functions become more obvious with the increase of organic fertilizer.

- X-ray diffraction anlysis results indicate that clay minerals in the cultivating layer of brown soil are 1:1 group minerals and 2:1 group coexisting.The relative content of clay minerals change after the long-term fertilization of 26 years. Because of not applying potassium fertilizer and adsorbing by plants,the content of available K in soil decreases,and the potassium in soil mineral releases.That leads to the transfor-mation from Hydromica to Vermiculite to Montmorillonite. Under applying enough potassium,the shortage of potassium in soil falls off or accumulates indeedly. It also can relieve or stop the transformation. The analysis indicates the contents of every forms of potassium correlate positively with the content of Hydromica and negative-ly with the one of Montmorillonite and Vermiculite,which reflects the transforma-tion relation of Vermiculite,Mortmorillonite and Hydromica.
- The composition of every particle fractions in the cultivating layer applied by different fertilizer change with planting years. The influence on the content of non-exchangeable K blew 10um particle grade soil used by organic fertilizer and chemical fertilizer and the function of organic fertilizer is reduced with the increase of particle diameter.The ability of supplying potassium tosoil is mainly related to the condition of potassium below 50um soil particles.It also is the main contributor in supplying potassium for a long time.

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Thank you!