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Aluminum extractability in red soils as influenced by land use patterns*

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Abstract: This study on the effect of land use on soil quality in relation to forms and toxicity of aluminum in red soils (Ultisol) in southeast China showed that in general, the extractable order for soil active aluminum by four extractants was: NaOH 0.5 mol/L > HCl 1 mol/L > NH_4Ac 1 mol/L > KCl 1 mol/L. Different uses of the red soils, developed from Quarternary red clay with the similar hydrogeological environment, greatly affected the amount of active aluminum, especially the exchangeable Al^{3+}. The order of exchangeable Al^{3+} (Al mg/kg) in the red soils with different land uses was: barren land (740) > tea garden (663) > peach garden (432) > citrus garden (234) > paddy soil (127). The content of water soluble aluminum in the red soils was highly sensitive to soil acidity.

Key words: Aluminum form, Land use, Red soil, Ultisol, Soil quality
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INTRODUCTION

Red soils (equivalent to Ultisols and Oxisols in the US soil taxonomy) cover 22% of China and support 43% of the Chinese population (Zhang et al., 1994). Crop growth on red soils is often constrained by high acidity and poor nutrient status. Generally, red soils have low pH values and have high content of variable charge clay minerals and iron oxides. In southeastern China, the original subtropical forest was logged since the 1970's and replaced by arable fields with different land uses. The land use change along with cultivation technique may be considered an important causes of soil quality change.

Soil acidification and acid deposition enhance the release of active aluminum from soils and sediments. Attention was paid to aluminum toxicity to aquatic organisms, plants, forests, and mankind health (Pang, 1986, 1987; Norton et al., 1990; Wang et al., 1991, 1992; Flaten et al., 1992; Ma, 1992; Feng, 1993;).

Biotoxicity of aluminum in soil solution and natural water is closely related to the aluminum forms of hydrolysates and is influenced by clay minerals, OH/Al ratio, cations and anions, humus, low-molecular-weight organic compounds, especiadly. organic acids. Although red soils are from the same parent material (Quarternary red clay) in the same place, different land uses can affect the H^+ proton equilibrium, composition of organic and inorganic matters, and hence affect aluminum hydrolysis in soils, leading to much difference in availability, forms, and toxicity of aluminum. The aim of this study was therefore to investigate the influence of land use change on soil quality in relation to aluminum forms and toxicity in red soils in Zhejiang Province of China.

MATERIALS AND METHODS

Soils

Five red clayey soils (Ultisol) (0 – 20 cm

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depth) developed from the same parent material (Quarternary red clay) were collected in Longyou County, Zhejiang Province, China. The land uses of the soils in this experiment are listed in Table 1, including other 3 soils as controls (Soils 6, 7, and 8). The procedure in Standard Methods for the Examination of Water and Waste Water (American Public Health Association, 1971) modified by Pang (1986) was used for the analysis and fractionation of forms of active aluminum in the soils. Organic matter and pH were measured using the conventional methods.

Table 1 Utilization of the soils and characteristics

Soil No.	Soil type	Location	Parent material	Land use	O.M.(%)*	pH(H_2O)
1	Red clayey soil	Longyou	Quarternary red clay	Barren	0.84	4.90
2	Red clayey soil	Longyou	Quarternary red clay	Peach	1.45	4.92
3	Red clayey soil	Longyou	Quarternary red clay	Citrus	2.51	4.93
4	Red clayey soil	Longyou	Quarternary red clay	Rice	3.24	5.04
5	Red clayey soil	Longyou	Quarternary red clay	Tea	4.53	4.64
6	Red sandy soil	Longyou	Red sandstone	Barren	0.65	4.85
7	Blue purple clay	Deqing	Marine deposit	Rice	3.44	6.10
8	Yellow-red earth	Hangzhou	Silty sandstone	Barren	1.44	4.71

* organic matter

Principle for fractionation of aluminum forms in soil

Different chemical reagents were used to extract different forms of active aluminum (Pang, 1986) and various forms of aluminum were estimated using the plus-minus method (Table 2). Exchangeable Al^{3+} or Al $(H_2O)_6{}^{3+}$ was extracted with KCl 1 mol/L (pH = 5.5). One NH_4Ac mol/L (pH = 4.8) solution was used to extract exchangeable Al^{3+}, dissolved $Al(OH)_3$, hydroxomononuclear species such as $Al(OH)^{2+}$ and $Al(OH)_2{}^{+}$, polynuclear species tightly adsorbed by soil colloids, and soluble Al-fulvic acids. The fraction of polynuclear aluminum adsorbed by colloids in the supernatant could be removed by the ultrafilter. HCl 1 mol/L solution was used to extract acid-dissolved inorganic aluminum such as soluble and colloidal $Al(OH)_3$, Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_2{}^{+}$, while no Al-humate (including Al-FA) was extracted. All forms of active inorganic and organic aluminum which can form $Al(OH)_4^-$ were extracted with NaOH 0.5 mol/L solution. Therefore, different forms of active aluminum in the soils could be estimated using the plus-minus method from the contents of different forms of aluminum extracted with the above-mentioned 4 extractants.

Table 2 Extraction and estimate of different forms of active aluminum in soil

Extractant (code)	Dissolved form	Main form estimated
KCl (A) 1 mol/L	Al^{3+}	A = Al^{3+}
NH_4Ac (B) 1 mol/L	Al^{3+}, $Al(OH)_3^{2+}$, $Al(OH)_2^{+}$, Al – FA	B – A = $Al(OH)_3^{2+}$ + $Al(OH)_2^{+}$ + Al – FA
HCl (C) 1 mol/L	Al^{3+}, $Al(OH)_3^{2+}$, $Al(OH)_2^{+}$, $Al(OH)_3$	C – B = $Al(OH)_3$ – Al – F
NaOH (D) 0.5 mol/L	Al^{3+}, $Al(OH)_3^{2+}$, $Al(OH)_2^{+}$, $Al(OH)_3$, Al – HA	D – C = Al – HA

* Al – HA includes Al – FA

Eriochrome R cyanine procedure for determination of active aluminum

Replicate samples (1.00 g each) of each soil tested (air-dried and sieved to pass 0.15 mm) were equilibrated respectively, with 50 ml aliquots of 4 extractants as presented in Table 2. The samples were shaken for 30 min at 25 ± 2℃, centrifuged for 10 min (4000 rev/min), and then ultrafiltered by 0.15 μm cellulose nitrate membrane filter. The supernatants were stored in polyethylene plastic bottles for colorimetric measurement using the eriochrome R cyanine method.

After putting 10 ml of deionized water and a series of aluminum standard solutions containing 0, 0.5, 1.0, 2.0, 3.0, 4.0 μg Al into each of 25 ml volumetric flasks respectively, and addition of 0.5 ml of 0.1% ascorbic acid into them, the flask were shaken; and the2.5 ml of 0.01% eriochrome cyanine R as a chromogenic reagent was added to dilute the mixture to 25 ml volume. After 5 to 15 min, the aluminum was measured colorimetrically in a 3-cm colorimetric cup (reagent blank as reference solution) within hrs. The data were used to plot the aluminum standard calibration carve. Aluminum concentrations (mg Al / kg) in the soil were measured using the above-mentioned method.

RESUITS AND DISCUSSION

Extractibility of 4 extractants for aluminum

The extractability of 4 extractants, KCl 1 mol/L, NH_4Ac 1 mol/L, HCl 1 mol/L, and NaOH 0.5 mol/L for aluminum in the 5 different soils, was compared in this experiment. Aluminum by the other 3 extractants extractable as percentages of the NaOH-extractable aluminum are listed in Table 3 showing that in the 3 soils (S2, S6, and S8) with less organic matter (0.65 – 1.45%), the extractable order for the 4 extractants was NaOH 0.5 mol/L > HCl 1 mol/L > NH_4Ac 1 mol/L > KCl 1 mol/L. In the 2 soils (S7 and S4) with higher organic matter (3.24 – 3.44%), the order changed: the amount of HCl-extractable aluminum was higher than that of NaOH-extractable aluminum. This may be related to the high and active contents of organic matter in the paddy soils. Addition of HCl, organic matter esp. organic acids in the paddy soils were activated to reach at $10^{-6} - 10^{-4}$ mol/L (Huang, 1988). The activated organic acids coordinated with Al^{3+} and thus prevented Al3 + from hydrolysis, esp. leading to decrease in aluminum precipitates and decrease in the percentage of crystal aluminum (insoluble in HCl 1 mol/L) in them, i.e., leading to increase in percentage of amorphous aluminum (soluble in HCl 1 mol/L) and to a marked increase in HCl-extractable aluminum amount that surpassed the amount of NaOH-extractable aluminum (Huang, 1988). On the contrary, the concentration of HCl-activated organic acids could not be higher than 10^{-6} mol/L in the upland soils with lower contents of organic matter; and as a result, the amount of NaOH-extractable aluminum was higher than that of HCl-extractable aluminum. These results were rlated to the soil processes of paddy soils, i.e., effects of PH and long submersion on clay minerals in the paddy soil.

Table 3 Relative percentages of extractable aluminum by different extractants

Soil No.	Soil type (land use)	O.M. (%)	KCl	NH_4Ac	HCl	NaOH
2	Red clayey soil (peach)	1.45	9.2	34	83	100
6	Red sandy soil (barren)	0.65	32	38	90	100
8	Yellow – red earth (barren)	1.44	22	32	94	100
7	Blue purple clay (rice)	3.44	0.8	30	237	100
4	Red clayey soil (rice)	3.24	5.9	27	117	100

Effects of different land uses on forms and activity of aluminum in red soils

The effects of barren, citrus, peach, tea, and rice land on aluminum forms and activity were investigated in this study. Active aluminum extracted by 4 extractants and contents of all the forms are presented in Table 4. The content of the most toxic form Al3 + in the barren red clayey soil (S1) was highest, which is related to the soil erosion and lower organic matter. Therefore, attention should be paid to the aluminum toxicity in the newly-cultivated red clayey soils, esp. for barley (very sensitive to Al^{3+} toxicity and widely occurring in Chinese red soils) production. Although the tea garden soil had a higher content of organic matter and higher developmental degree, the active Al^{3+} was accumulated to 663 mg/kg because of the lowest soil pH and the very high content of aluminum (up to 30690 mg/kg) in the old tea leaf which decayed in the soil leading to rich accumulation of aluminum. The amount of Al^{3+} in the paddy soil was the lowest, probably because of the relatively higher pH and organic matter content. The amount of mononuclear hydroxides $Al(OH)^{2+}$ and $Al(OH)_2^+$ increased with a decrease in the exchangeable Al^{3+} in the respective soils. The contents of $Al(OH)_3^0$ in the soils (except for the paddy soil) were almost the same.

Table 4 Effect of land use on activity and forms of aluminum (mg/kg) in red clayey soils

Land use	Contents of dissolved aluminum ($X \pm S$)				Aluminum contents of various forms ($X \pm S$)			
	KCl	NH_4Ac	HCl	NaOH	Al^{3+}	$Al(OH)_3^{2+}$ $Al(OH)_2^+$	$Al(OH)_3^0$	Al – HA
Barren	740 ± 22	955 ± 13	2185 ± 19	2553 ± 32	740 ± 22	222 ± 17	1229 ± 13	368 ± 16
Citrus	234 ± 12	628 ± 6	1893 ± 22	1996 ± 23	234 ± 12	393 ± 10	1261 ± 21	77 ± 16
Peach	432 ± 5	835 ± 8	2066 ± 27	2487 ± 18	432 ± 5	402 ± 3	1232 ± 26	420 ± 18
Tea	663 ± 6	883 ± 10	2126 ± 33	2480 ± 21	663 ± 6	219 ± 9	1243 ± 31	354 ± 9
Rice	127 ± 12	574 ± 9	2488 ± 28	2135 ± 20	127 ± 12	447 ± 3	1914 ± 23	–

Effect of pH on water soluble aluminum in soil

The pH of deionized water was adjusted using 0.01 ml/L H_2SO_4 and 0.01 ml/L NaOH in order to get a series of water extractants with different pH values. After that 50 ml of these water extractants were equilibrated and shaken with 1.00 g of each soil for 24 hours. The supernatants were ultrafiltered for measuring the water soluble aluminum as listed in Table 5. Obviously, the content of soluble aluminum in the soils was highly sensitive to soil acidity. Therefore, increasing soil pH, liming for example is a useful and convenient measure for controlling aluminum toxicity in red soils.

Table 5 Effect of soil acidity on the content of water soluble aluminum (mg/kg)

pH of water extractant	pH of final suspension		Content of water soluble Al	
	Soil 1	Soil 6	Soil 1	Soil 6
7.20	4.93	4.87	0.0	0.0
6.71	4.90	4.85	6.7	5.0
5.90	4.87	4.83	11.7	8.3
4.50	4.85	4.80	25.0	20.0
3.88	4.80	4.77	40.0	28.3
3.58	4.67	4.59	56.7	41.7

* Soil 1: red clayey soil; Soil 6: red sandy soil

CONCLUSIONS

The study yielded the following results:

1. Generally, the extractable order by four extractants for active aluminum in the red soils was: NaOH 0.5 mol/L > HCl 1 mol/L > NH_4Ac 1 mol/L > KCl 1 mol/L.

2. The order of exchangeable Al^{3+} (mg Al/kg) in the red soils with different land uses was: barren land (740) > tea garden (663) > peach garden (432) > citrus garden (234) > paddy soil (127).

3. The content of soluble aluminum in the red soils was highly sensitive to soil acidity.

4. Land use change of red soils in Zhejiang Province of China could influence soil quality in relation to aluminum forms and toxicity.

References

American Public Health Association, 1971. Standard methods for the examination of water and waste water (13th edition), 316p.

Feng, Z. Y., 1993. Effects of acid rains on ecosystem. China Science and Technology Press, Beijing, 289p. (in Chinese).

Flaten, T. P., Garruto R. M., 1992. Polynuclear ions in aluminum toxicity. *J. Theoretical Biology*, **156**, 129 - 132.

Huang, P. M., 1988. Ionic factors affecting aluminum transformations and the impact on soil and environmental sciences. *Advances in Soil Science*, **8**: 1 - 78.

Ma, H. C., 1992. Comparison of forms of active aluminum in coniferous forest soils. Environmental Chemistry, **11**(3), 48 - 54(in Chinese, with English abstract).

Norton, S. A., Lindberg S. E., Page A. L., 1990. Acidic Precipitation (Vol. 4: Soils, Aquatic Processes, and Lake Acidification), Springer-Verlag, New York-Berlin-Heidelberg, 356p.

Pang, S. W., 1986. Study on dissolution and forms of active aluminum in soil using chemical extractants. Environmental Chemistry, **5**(3), 68 - 76(in Chinese, with English abstract).

Pang, S. W., 1987. Effect of acid deposition on soil acidity and dissolved aluminum. Environmental Chemistry , **7**(1):41 - 45(in Chinese, with English abstract).

Wang, W., J. Chen, Q. He, 1991. A study on forms of exchangeable aluminum in acid soils. Science Bulletin , 17(6):460 - 463(in Chinese, with English abstract).

Wang, W., J. Chen, Q. He, 1992. Effect of simulated rain on dissolved aluminum and forms in acid soils. *J. of Applied Ecology*, **3**(2): 184 - 189(in Chinese, with English abstract).

Zhang, T., Zhao Q. 1994. Rehabilitation and sustainable management of degraded agro-ecosystem in southern China. *In*: Pedosphere, Zhao Q. et al., Eds. Nanjiang University Press, Nanjing, p.89 - 93.