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Solid components and acid buffering capacity of soils in South China

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Abstract—The effects of soil solid components on soil sensitivity to acid deposition by sequential extraction method were studied. A multiple regression equation of soil sensitivity was set up on the basis of stepwise regression analysis. The results showed that organic matter expressed dual effects that were decided by soil original pH value and exchangeable cation composition on acid buffering reactions. The hydrolysis of activated oxides was a very important proton buffering reaction when in low pH situation. The crystalline oxides also played a role in the buffering reactions, but the role was restricted by the rate of activation of oxides. Meanwhile, the results by stepwise analysis showed that factors that had significant effect on soil acid buffering capacity were content of montmorillite, soil original pH value, Al_0, Mn_0 and CEC in decreasing order. Finally, sixteen soils were classified into four types of sensitive with single index cluster and multiple fuzzy cluster analysis respectively.

Keywords: acid deposition; acid buffering capacity; soil sensitivity; solid components.

1 Introduction

A complete index system for evaluating soil sensitivity to acidic deposition was not yet been set up and furthermore there are still some different of opinions as to the sensitivity of soils to the south of Yangtze River among Chinese researchers (Norton, 1989; Feng, 1993; Langan, 1994; Wang, 1994). It was thought that soil solid components may be the main factors cause of difference in soil buffering capacity and the essential distinction of divergence in evaluating the soil sensitivity in South China (Liu, 1993; Qiu, 1997a). This paper tried to study the contribution of solid components to acid buffering capacity using a sequential extraction method so as quantitatively evaluate the most influential factors. Multiple stepwise regression analysis and fuzzy cluster analysis were used objective to make a rational classification of soil sensitivity in South China.

2 Materials and methods

2.1 Soil samples

Thirteen soil samples were collected from the main acidic deposition regions in South China and three from other regions for comparison. The main soil types and their physical and chemical properties are shown in Table 1.

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Table 1 The physical and chemical properties of soils studied

No.	Soil type	pH	OH, g/kg	Clay, g/kg	CEC, cmol/kg	Fe_d^a, g/kg	Al_d^a, g/kg	Mn_d^a, g/kg	Fe_o^b, g/kg	Al_o^b, g/kg	Mn_o^b, g/kg	Mon., %	Kao., %	Illi., %	1.4nm mine. %
1	Chao soil	5.01	21.36	365.73	17.29	32.14	7.29	0.56	6.94	0.49	0.16	8.7	34.2	36.1	6.6
2	Latasolic red soil	6.27	4.40	306.32	6.74	5.38	2.27	0.40	1.02	1.78	0.12	0	64.2	16.0	9.5
3	Solonchak	8.55	4.55	24.72	27.84	7.25	0.87	0.37	2.12	0	0.11	0	23.6	35.3	29.5
4	Rendzina	7.06	44.49	573.35	48.36	64.22	2.41	1.36	8.06	0	0.73	10.4	21.8	10.8	50.8
5	Yellow soil	3.90	10.94	168.13	10.25	15.42	10.60	0.27	1.02	4.12	0.05	0	55.8	32.0	0
6	Yellow soil	4.12	4.63	204.49	10.77	32.81	9.37	1.38	0.62	3.20	0.04	0	55.8	32.0	0
7	Yellow limestone	7.22	32.74	404.53	31.02	55.87	8.22	1.57	6.11	2.71	0.71	0	24.6	19.2	44.4
8	Yellow limestone	7.64	34.26	439.31	34.05	55.87	3.07	2.13	9.00	0.89	1.04	1.6	24.6	19.2	44.4
9	Red limestone	7.98	22.67	320.84	32.10	334.8	1.56	1.44	4.39	0.29	0.64	0	43.5	36.5	18.3
10	Latasolic red soil	4.23	9.86	340.11	5.24	47.73	17.02	0.20	1.88	6.75	0.04	0	77.9	1.8	5.9
11	Red soil	4.26	43.88	526.44	11.20	19.21	9.45	0.32	5.25	4.66	0.07	0	55.5	17.3	17.6
12	Latosol	5.06	26.74	220.24	3.54	22.77	17.22	0.69	1.83	6.89	0.23	0	56.8	23.6	4.3
13	Latosol	4.66	14.34	313.14	3.30	37.30	19.25	0.27	5.44	7.76	0.05	0	64.2	0	35.8
14	Latosol	5.44	19.81	549.41	4.35	178.0	12.86	3.56	9.94	5.22	1.40	0	70.1	0	12.5
15	Udic vertisol	8.16	37.70	631.80	53.84	53.43	8.72	1.96	4.36	1.91	1.77	50.9	19.9	19.3	9.9
16	Paddy soil	7.42	10.40	489.00	13.03	29.14	8.03	1.12	2.51	3.33	0.96	0	10.0	72.2	17.8

a: free oxides extracted by dithionite-citrate-bicarbonate buffer solution; b: activated oxides extracted by acid ammonium oxalate; Mon. = Montmorillite; Kao. = Kaolinite; Illi. = Illite; mine. = mineral

Five soil groups were made by a selective removal of soil constituents. Firstly, 30% H_2O_2 was added into Group A (original sample) to remove organic matter by repeated oxidation. Soil samples of Group B (removal of organic matter) were obtained after the removal of surplus H_2O_2 through heating. Then 0.2 mol/L $H_2C_2O_4$-$(NH_4)_2C_2O_4$ (pH = 3, solution/soil ratio = 25:1) was added into Group A and Group B respectively. After a two-hour shaded vibration, soil samples were centrifugalized and Group C (removal of activated oxides) and Group D (removal of organic matter + activated oxides) were obtained. Finally, 0.2 mol/L $H_2C_2O_4$-$(NH_4)_2C_2O_4$-Vc (pH = 3, solution/soil ratio = 25:1) was added into Group D and soil samples of Group E (removal of organic matter + activation oxides + free oxides) were obtained after a two-hour shaded vibration and centrifugation. Prior of sensitivity study, the soil samples of each group were washed with deionized water and made homoionic with respect to Ca by saturating with 1 mol/L $CaCl_2$ solution. Excess salts were removed by repeated washing with deionized water until free of Cl^- in the $AgNO_3$ test and samples were ovendried at the temperature below 60℃ and passed through a 1 mm sieve.

2.2 Determination of acid buffering capacity

10g soil sample of each group was placed in a 50 ml beaker and 25 ml deionized water without CO_2 was added. The soil solution was adjusted with 0.1 mol/L H_2SO_4 to a pH value of 3.0 after the original pH was tested. After 24 hours' equilibrium, the suspension pH was tested and adjusted again to 3.0 with 0.1 mol/L H_2SO_4. Above procedures were repeated until the suspension pH value was lower than 3.15 after 24 hours' equilibrium.

2.3 Mathematical treatment

The multiple stepwise regression analysis and fuzzy cluster analysis were conducted in FACOMM 340S medium-sized computer with ANALYST software bag.

3 Results and discussion

3.1 Soil apparent acid buffering capacity

Table 2 showed the considerable differences of accumulated volume of input acid (Q) among soils studied with a descending sequence of vertisols, calcareous soils (rendzina, yellow limestone soil and red limestone soil), coastal solonchak, anthrosols (paddy soil), ferralsols (red soil, latasolic red soil and latosol). $CaCO_3$ equilibrium or cation exchange reactions with a fast equilibrium rate were the main buffering H^+ reactions in vertisols and calcareous soils which had a high pH value, rich clay content and exchange cations. Usually these reactions with great buffering capacity were easy to balance. This feature can also be demonstrated by the Q_1/Q (input acid of first day/accumulated input acid), of which most was higher than 0.5 and some even up to 0.73. The Q value of coastal solonchak was only less than that of above soils, but the Q_1/Q value (0.77) reflected that the buffering reaction in this soil, mainly by the neutralization of alkaline salts, was also easy to balance. Whereas the Q values of ferralsols were very low, especially of sandy yellow soil which were sampled in a region where a serious injury to ecosystem caused by acidic deposition had lasted for a long time (Feng, 1993). In these soils, the hydrolysis of oxides was one of the main buffering reaction and was difficult to reach equilibrium due to a slow reaction rate with most of Q_1/Q ratios below 0.5.

3.2 Effect of solid components on acid buffering capacity

In alkaline soils ($pH > 7.0$), the acid buffering capacity of Group B (without organic matter) was slightly lower than that of Group A as shown in Table 2. This may have been caused by the sites becoming available for H^+ buffering that otherwise were blocked by an organic matter coating and by the decrease of soil total acidic materials.

Fig.1 shows that the acid buffering capacity of Group D was all lower than that of Group B. The higher the content of activated oxides, the more obvious the differences between Q_B and Q_D. These results agreed well with those reported previously (Ulrich, 1986), where oxides in soils were found to take part in the H^+ buffering reaction by hydrolysis after the pH was lower than 4.2. This confirmed that the hydrolysis of oxides was really the important H^+ buffering reaction under low pH condition.

Table 2 Soil acid buffering capacity of Group A, B and C

No.	Soil type	Location	Group A			Group B		Group C	
			Q, ml	Q/ΔpH	Q_1/Q	Q, ml	Q_1/Q	Q, ml	Q_1/Q
1	Chao soil	Panyu	3.89	1.98	0.43	4.49	0.29	1.69	0.52
2	Latasolic red soil	Shantou	1.09	0.32	0.54	1.42	0.35	0.85	0.61
3	Solonchak	Shantou	9.20	1.67	0.77	7.92	0.69	6.28	0.83
4	Rendzina	Guiyang	13.96	3.55	0.54	12.09	0.28	3.53	0.82
5	Yellow soil	Chongqing	0.79	0.96	0.63	1.90	0.35	1.62	0.56
6	Yellow soil	Chongqing	1.05	0.97	0.50	2.03	0.34	1.33	0.53
7	Yellow limestone soil	Guiyang	16.64	4.06	0.42	7.04	0.32	3.38	0.71
8	Yellow limestone soil	Guiyang	15.60	3.46	0.54	10.11	0.41	3.07	0.44
9	Red limestone soil	Liuzhou	16.09	3.25	0.43	16.50	0.38	3.86	0.43
10	Latasolic red soil	Guangzhou	2.06	1.86	0.27	2.91	0.22	1.92	0.36
11	Red soil	Shaoguan	2.43	2.07	0.41	4.16	0.21	2.53	0.38
12	Latosol	Qionghai	3.71	1.89	0.27	7.00	0.19	2.09	0.56
13	Latosol	Lianjiang	3.12	2.01	0.40	5.78	0.20	2.02	0.39
14	Latosol	Lingao	7.65	3.28	0.41	9.94	0.23	3.44	0.44
15	Udic vertisol	Baise	55.92	11.03	0.73	45.77	0.73	9.09	0.87
16	Paddy soil	Qujing	8.85	2.04	0.50	9.19	0.29	2.30	0.42

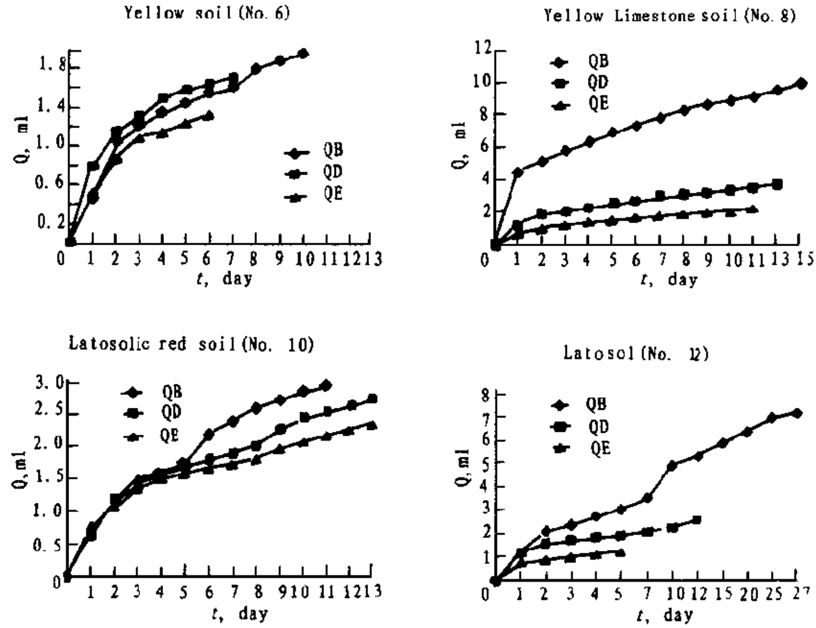

Fig. 1 Comparison of the accumulative volume of sulfate acid input in Group B, D, and E

The results that Q_E was slightly lower than Q_D showed that crystalline oxides had a positive effect on acid buffering capacity, while the effect was restricted by the rate of activation reactions.

The differences between Q_D and Q_E decreased with the activated degree of oxides. However, compared with Q_A, the Q_C of some soils with a low content of activated oxides increased slightly. This might be caused by the complexity of binding of soil solid components and in some way by the activation of inorganic and organic colloid during the chemical extraction processes.

3.3 Multiple stepwise regression analysis of factors affecting acid buffering capacity

A total of 80 soil samples, including Groups A, B, C, D and E, which representing a wide range of soil types and soil characteristics in South China were used in mathematical treatment. A data base was constructed that combined 14 independent variables, namely pH, organic matter, clay content, Fe_0, Al_0, Mn_0, Fe_d, Al_d, Mn_d, CEC and the contents of four clay minerals (montmorillite, kaolinite, 1.4 nm minerals and illite) and one dependent variable, namely accumulated volume of acid input. Multivariate stepwise regression analysis was then used to determine which combinations of the 14 independent variables produced the best prediction of the acid buffering capacity.

After significant level check ($\alpha < 0.05$) and F value check, the factors with zero regression coefficient were reject and other factors were compared according to the absolute value of standard partial sum of square of regression (V value). The results showed that factors that had a significant effect on soil acid buffering capacity were content of montmorillite, soil original pH value, Al_0, Mn_0 and CEC in decreasing order. By further stepwise analysis of other parameters, only kaolinite, illite, clay content, organic matter, Mn_d were selected in descending sequence as affective factors that had not significant partial regression.

The regression equation obtained only include 5 parameters that had significant partial regression coefficients and was expressed as follows:

$$Y = 0.41x_1 - 1.89x_2 + 1.07x_3 - 4.36x_4 + 0.31x_5 - 14.67,$$

where x_1 is the content of montmorillite, x_2 is the original pH value, x_3 is the content of activated Al oxide, x_4 is the content of activated Mn oxide and x_5 is CEC.

The contributions of factors to acid buffering capacity of soils were different from each other and the buffering mechanisms were also different. The existence of montmorillite usually implies the high, sol pH value and a certain amount of $CaCO_3$, and then an intensive soil apparent buffering system. Soil pH is a complex expression of ion equilibrium among soil inorganic colloid, organic colloid and soil solution *etc*. The higher the soil original pH value, the bigger the buffering capacity of soils to acid deposition. CEC represented the cation exchange capacity of soils and exchange reaction was also the primary reaction of H^+ buffering in all soils (Zhou, 1992; Mitchell, 1994; Starr, 1996). Al_0 and Mn_0 also took part in the buffering reaction under low pH condition (Cronan, 1995; Qiu, 1997b) while Fe_0 was not the significant factor because it played a buffering role only when pH was lower than 3.0 (Ulrich, 1986).

3.4 Sensitivity classification of soils studied

Since the soil sensitivity was largely related to the acid buffering capacity, the sensitivity classification system should be established on the basis of soil acid buffering capacity studies. Two classification systems set up according to the buffering intensity ($Q/\Delta pH$) and acid buffering capacity (Q) respectively, where only one soil sample was classified into two sensitive types

(Table 3 and Table 4), showed the same tendency. But it was difficult to see the close or distant relationships between soils classified inflexibly only by single index and to judge which system was more rational. Therefore, five soil properties that had a remarkable effect on acid buffering capacity combined with the Q and $Q/\Delta pH$ value were chosen for multiple fuzzy cluster analysis.

Table 3 Soil sensitivity classification system according to $Q/\Delta pH$

Index ($Q/\Delta pH$)	Soil types (sample No.)	Acid sensitive type
>10 ml	No. 15	Not sensitive
3—5 ml	No. 4, No. 7, No. 8, No. 9, No. 14	Slightly-sensitive
1—3 ml	No. 11, No. 16, No. 13, No. 1, No. 12, No. 10, No. 3	Sensitive
0—1 ml	No. 5, No. 5, No. 2	Very sensitive

Table 4 Soil sensitivity classification system according to Q (accumulated volume of acid input)

Index (Q)	Soil types (sample No.)	Acid sensitive type
>20 ml	No. 15	Not sensitive
10—20 ml	No. 7, No. 9, No. 8, No. 4	Slightly-sensitive
2—10 ml	No. 3, No. 16, No. 14, No. 1, No. 12, No. 13, No. 11, No. 10	Sensitive
0—2 ml	No. 2, No. 6, No. 5	Very sensitive

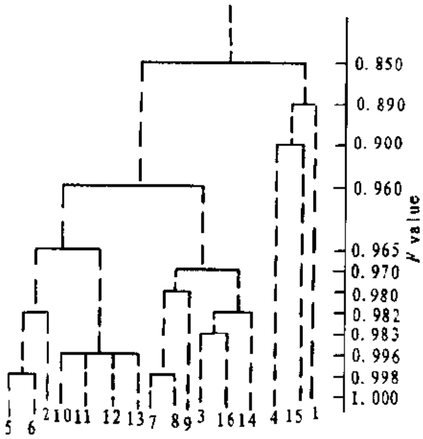

Fig. 2 Cluster dynamics figure of soils studied

The intercept matrix R_λ was built up on the basis of fuzzy similar matrix where the choice of intercept level (F) was based on the crowded degree of fuzzy similarity coefficient. After that, a cluster dynamics figure which can visually reflect the similarity of soils is drawn (Fig. 2). On the basis of Fig. 2, the soils studied can be classified into four types with a intercept level (F) of 0.960 and 0.965 respectively (Table 5).

Table 5 Soil sensitivity classification system according to fuzzy cluster analysis

Grade	Soil types (sample No.)	Acid sensitive type
I	No. 4, No. 15, No. 1	Not sensitive
II	No. 7, No. 8, No. 9, No. 3, No. 16, No. 14	Slightly-sensitive
III	No. 10, No. 11, No. 12, No. 13	Sensitive
IV	No. 5, No. 6, No. 2	Very sensitive

The fuzzy cluster can better reflect the similarity of soils because the indices chosen for analysis included the main affective factors on soil acid buffering capacity. Also this classification system in which most forralsols fall in sensitive or very sensitive types was in accordance with the acidifying tendency of soils in vivo. No. 5 and No. 6 in which a serious ecosystem damage has occurred were grouped into very sensitive types.

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