

# Effects of simulated acid rain on cation releasing in soils of South China<sup>\*</sup>

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**Abstract**—This paper deals with the release of base cations and  $\text{Al}^{3+}$  at the treatment with simulated acid rain (SAR) in main soil types collected from South China. Results showed that the amounts of base cations increased obviously when the pH value of simulated acid rain was lower than 3.0 or 3.5. Compared with the leaching of  $\text{K}^+$  and  $\text{Na}^+$ , the leaching of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  was affected by the pH value of SAR. Only when the amounts of base cations leached from soils exceeded the cation exchange capacity, the pH value of leaching solutions decreased sharply and the amounts of released  $\text{Al}^{3+}$  increased. The  $\text{H}^+$  buffering mechanisms, which were affected not only by the pH values of SAR, but also by the types and solid components of soils, were proposed for the main soils studied.

**Keywords:** acid deposition; base cations; aluminum; leaching.

## 1 Introduction

The effect of acid deposition on terrestrial and aquatic ecosystem has been considered a global environmental problem. Research results in recent years showed that the pH of precipitation in most damaged areas was not low enough to cause direct injury to forest vegetation and the indirect influence of acidic precipitation on ecosystem was related highly to its influence on the acidity of forest soils (Foster, 1989; Feng, 1993). Acid deposition to soil systems may result in a series of chemical reactions, the first of which is the displacement of base cations from the exchange sites and their subsequent leaching. Further increase in the hydrogen ion concentration may cause the weathering of soil minerals and increase in soluble aluminum concentration. This may have a toxic effect on plant growth by the change of Ca/Al ratios (Cronan, 1995). The primary purpose of this study was to determine the leaching mechanisms of base cations and aluminum ion. The second purpose was to give some evidences for soil sensitivity research classification through the ion leaching properties of main soil types collected from South China, which were treated by simulated acid rain (SAR) with various pH levels.

## 2 Materials and methods

### 2.1 Soil samples

Soil samples were collected from main serious acidic precipitation regions in South China such as Chongqing, Guiyang, Liuzhou, Guangzhou, Shaoguan and Shantou, etc. and from other regions for comparison. The main soil types, which were classified according to Chinese soil taxonomy, and their physico-chemical properties are shown in Table 1.

### 2.2 Leaching experiments

About 80g soil samples passed through an 1 mm sieve were packed into polyvinyl chloride

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cylinder columns of 250 mm in length and 28 mm in i. d. until a desired bulk density, the same as the original soil bulk density, was obtained. The bottom of the column was matted with some glass fiber and a slow-rate filter paper and then plug up with a rubber cork with a small hole.

**Table 1** Some Properties of soils tested

No.	Soil type	Location	pH	OM, g/kg	Clay, g/kg	CEC, cmol/kg			
						Ca <sup>2+</sup>	Mg <sup>2+</sup>	K <sup>+</sup>	Na <sup>+</sup>
1	Red soil	Shaoguan, Guangdong	4.26	43.88	526.44	1.64	0.20	0.18	0.17
2	Latosolic red soil	Guangzhou, Guangdong	4.23	9.86	340.11	1.08	0.18	0.09	0.10
3	Latosol	Qionghai, Hainan	5.06	26.74	220.24	1.24	0.42	0.20	0.05
4	Yellow soil	Chongqing, Sichuan	3.90	10.94	168.13	1.48	0.22	0.08	0.19
5	Purple soil	Chongqing, Sichuan	5.45	0.28	55.48	1.24	0.28	0.52	0.09
6	Rendzina	Guiyang, Guizhou	7.06	44.49	573.35	35.85	9.82	0.86	1.83
7	Red limestone soil	Liuzhou, Guangxi	7.98	22.67	320.84	27.72	2.29	0.81	1.28
8	Coastal solonchak	Shantou, Guangdong	8.55	4.55	24.72	18.00	7.04	0.77	2.03

Leaching solutions of pH 2.5, 3.0, 3.5, 4.5 and 5.6 were prepared from a stock solution of a H<sub>2</sub>SO<sub>4</sub>-HNO<sub>3</sub> mixture (9:1 v/v). A terminated flow method was used to ensure sufficient reaction and equilibrium time between soil solid and solution phases.

The SAR was added to the columns once a day at a rate of 250 mm during a period of 20 days. The leached was collected once per 500 mm effluent. There were 16 soils, 5 treatments and two duplications. The total amount of acidic solution applied was calculated to be equal to 5000 mm precipitation. The pH of effluent was determined immediately by using a glass electrode after the leachate was collected in plastic bottles. Concentrations of Ca, Mg, K and Na were determined by atomic absorption spectrometry. The total Al was determined by aluminum colorimetry.

### 3 Results and discussion

#### 3.1 Effect of acidity of simulated acidic rain on ion leaching

As expected, the stronger the acidity of the input solution, the higher the total concentrations of the four base cation species observed in the leachates. The total amounts of base cations leached from all soil types increased obviously with the decrease of pH of simulated acid rain, especially when pH value of SAR was lower than 3.5 (Table 2).

The total leaching amounts of base cations showed a certain relations with the composition of exchangeable cations. The leaching of K<sup>+</sup> and Na<sup>+</sup> was less affected by the increase of hydrogen ion concentration because the exchange reaction of these two cations needs low energy. Compared with monovalent cation species, the leaching of Ca<sup>2+</sup> and Mg<sup>2+</sup> were restricted largely by hydrogen ion concentrations and increased when the pH of influent was lower than 3.5.

The amounts of cations leached from soil series of ferralsol decreased in the order of red soil, latored soil, latosols, yellow soils, almost in the same sequence as cation exchange capacity. But the amounts of Ca<sup>2+</sup> and Mg<sup>2+</sup> released from yellow soils with pH 2.5 input solution increased rapidly due to the weathering of soil minerals in sand and silt groups which may also cause release of Al<sup>3+</sup> and Si<sup>4+</sup> (Liao, 1989; Qiu, 1997a). The amounts of cations leached from purple soil were affected most evidently by pH of the influent. Compared with pH 5.6 input solution, the amounts

of cations leached were increased by 1.34, 2.32, 4.93 and 9.22 times with pH 4.5, 3.5, 3.0 and 2.5 input solution, respectively. A quantity of weatherable minerals may become the potential supplier of base cations with the continuous infiltration with low pH acid-solution in the purple soil having an original low pH value and low CEC.

Table 2 Amounts of cations leached at different pH simulated acid rain\*

mmol(+) / kg

Sample	Soil type	pH	CEC, mmol/kg		pH of simulated acid rain				
No.					2.5	3.0	3.5	4.5	5.6
1	Red soil	4.26	Ca	16.4	33.90	23.25	13.03	8.21	8.03
			Mg	2.0	3.75	1.51	0.84	0.55	0.74
			K	1.8	0.70	0.36	0.35	0.55	0.74
			Na	1.7	0.94	0.75	0.81	0.80	1.02
2	Latasolic red soil	4.23	Ca	10.8	25.46	18.72	12.66	9.03	8.49
			Mg	1.8	3.01	1.85	0.77	0.51	0.54
			K	0.9	0.37	0.29	0.15	0.15	0.14
			Na	1.0	0.99	0.72	1.04	0.45	0.31
3	Latosol	5.06	Ca	14.8	19.85	17.09	9.35	7.27	9.97
			Mg	4.2	5.51	2.70	2.35	2.02	1.73
			K	2.0	2.48	1.86	1.58	1.59	1.30
			Na	0.5	0.97	1.51	1.08	1.03	0.63
4	Yellow soil	3.90	Ca	12.4	19.85	17.09	9.35	7.27	9.97
			Mg	2.2	3.55	1.46	0.85	0.40	0.23
			K	0.8	0.64	0.44	0.53	0.26	0.22
			Na	1.9	0.81	0.73	0.56	0.54	0.65
5	Purple soil	5.45	Ca	12.4	31.39	11.61	2.38	1.31	1.20
			Mg	2.8	4.07	2.05	0.44	0.14	0.12
			K	5.2	4.37	5.91	5.89	3.08	2.08
			Na	0.9	0.83	2.25	1.53	1.38	1.02
6	Rendzina	7.06	Ca	358.5	36.19	19.49	12.01	9.11	6.56
			Mg	98.2	18.61	11.97	8.08	6.82	6.56
			K	8.6	0.67	0.40	0.40	0.34	0.39
			Na	18.3	1.42	1.30	1.02	1.04	0.51
7	Red limestone soil	7.98	Ca	277.2	34.14	24.58	20.90	15.36	11.73
			Mg	22.9	15.40	9.19	7.51	6.06	5.45
			K	8.1	0.96	0.88	0.65	0.58	0.49
			Na	12.8	2.43	1.78	2.17	2.01	1.76
8	Coastal solonchak	8.55	Ca	180.0	43.92	25.56	12.53	7.46	3.50
			Mg	70.4	6.30	3.20	1.36	1.69	0.83
			K	7.7	1.39	1.00	0.69	0.96	0.69
			Na	20.3	1.13	1.36	1.00	1.06	0.63
Amounts of proton input, mmol/kg					118.60	37.50	11.86	1.19	0.09

\*: Amounts of infiltration were all equivalent to 5000 mm precipitation

In general, the amounts of cations leached from calcareous soils and coastal solonchak, which usually contained  $\text{CaCO}_3$  nodules or soluble salts, were much higher than those from above soils. When pH of the input solution was higher than 4.5, dissolution or neutralization resulted in that the amounts of cations leached were much higher than those of  $\text{H}^+$  input. With the further increased of acidity, cation exchange reaction became the dominant resources of leaching base cations. Under these conditions, the diffusion process of cations would be the limit factor that determined the rate of equilibration between soil solid phase and input solution. This may also be seen from the result that the leaching amounts increased out of proportion to the increase of  $\text{H}^+$  input when pH value of influent was lower than 3.5.

In initial stage of infiltration, the leaching losses of base cations were much higher than those

in later stage where a constant and equilibrated leaching state was achieved gradually (Fig.1). This phenomenon was attributed to the so-called salt effect (Liu, 1990). But when the pH value of input solution was lower than 3.5, the amounts of cations leached from purple soil, coastal solonchak and yellow soil that contained a quantity of sand and silt increased obviously in late stage of infiltration due to the weathering of weatherable soil minerals.

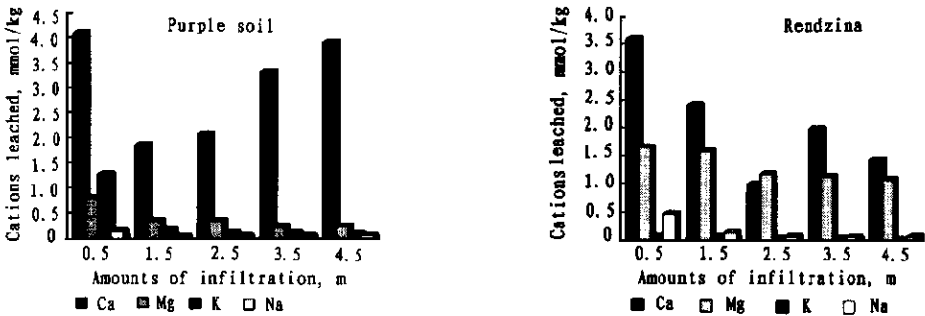


Fig.1 Releasing dynamics of cations leached from rendzina (pH of leaching solution = 3.0) purple soil (pH of leaching solution = 2.5)

3.2 pH changes of soil leachates

The pH of leachates from calcareous soils and coastal solonchak was constantly over 7.0 all the way under the pH 2.5 treatment (Table 3). In the process of leaching, the pH of leachates from soil series of ferralsol had an abruptive change point where the amounts of base cations leached were almost equivalent to the cation exchange capacity of soils. It demonstrated that the cation exchange was the first-order proton buffering reaction and the buffering capacity decreased rapidly after the exchangeable base cations were leached.

Table 3 Dynamics changes of pH value of soil leachates

Soil type	pH of SAR	Amounts of infiltration, mm									
		500	1000	1500	2000	2500	3000	3500	4000	4500	5000
Red soil	pH=2.5	7.08	7.02	6.89	4.06	3.99	3.37	3.19	3.22	3.22	3.42
	pH=3.5	7.09	7.22	7.57	7.34	7.30	7.29	7.62	7.37	7.46	7.53
Latasolic red soil	pH=2.5	7.60	7.12	4.89	3.16	2.90	2.77	2.88	2.92	2.78	2.85
	pH=3.5	7.78	7.26	7.45	7.03	7.23	7.33	7.44	7.14	6.77	6.91
Latosol	pH=2.5	7.14	6.05	6.45	5.63	5.65	4.25	4.22	4.12	4.07	4.14
	pH=3.5	6.67	7.97	7.20	7.04	6.80	7.15	6.57	6.95	7.00	7.31
Yellow soil	pH=2.5	7.30	7.09	7.14	7.16	6.78	4.40	4.26	4.05	3.89	3.95
	pH=3.5	6.82	7.18	7.56	7.24	7.65	6.85	7.06	6.82	6.77	6.75
Purple soil	pH=2.5	7.38	7.04	7.02	6.52	6.22	6.72	5.66	5.83	5.77	5.59
	pH=3.5	6.86	7.03	7.11	7.10	7.11	6.97	7.03	5.97	6.72	6.63
Rendzina	pH=2.5	8.08	7.35	8.19	7.64	8.22	7.62	7.53	7.55	7.39	7.69
	pH=3.5	8.12	7.36	7.92	7.40	7.70	7.70	7.37	7.73	7.64	7.76

The pH of leachates from purple soil was over 5.6 through the whole period of the experiment, whereas the amounts of cations leached were much higher than CEC under the pH 2.5 treatment due to the existence of a great quantity of weatherable minerals compared with other zonal soils (Liu, 1993).

The pH of leachate from all soil types treated by pH over 3.5 input solution remained relatively constant and higher than 7.0 for the amounts of cations leached were lower than CEC throughout the experiment. The pH of leachate from soils treated with pH 3.0 input solution remained at a relatively high pH level ( $\text{pH} > 6.5$ ) although the amounts of proton input in 5000mm effluent were equivalent to those treated with pH 2.5 input solution in 1500mm effluent and also the total leaching losses of cations were higher than CEC (Table 4 and Table 2). This phenomenon reflected that a secondary buffering system depended on the reaction time and related with soil solid components existed in soils besides the apparent buffering system such as cation exchange reactions *etc.* (Li, 1988; Liao, 1991; Hornung, 1995; Qiu, 1997b). Further, it reflected that there were some differences between the situation in vitro and in vivo due to the short time scale of simulated experiment.

Table 4 Ion balance of red soils leached by different pH SAR

pH of simulated acid rain	Accumulated amounts of ions, mmol/kg	Amounts of infiltration, mm									
		500	1000	1500	2000	2500	3000	3500	4000	4500	5000
pH=2.5	Amounts of $\text{H}^+$ input	11.86	23.72	35.58	47.44	59.30	71.16	83.02	94.88	106.70	118.60
	Base cations leached	7.16	12.32	17.05	19.98	23.08	27.01	29.56	32.49	35.54	39.31
	$\text{Al}^{3+}$ leached	—	—	—	2.01	3.47	4.10	6.09	8.40	10.25	12.15
	pH value of effluent	7.08	7.02	6.89	4.06	3.99	3.37	3.19	3.22	3.22	3.42
pH=3.0	Amounts of $\text{H}^+$ input	3.75	7.50	11.25	15.00	18.75	22.50	26.25	30.00	33.75	37.50
	Base cations leached	5.80	8.46	11.45	14.11	15.14	17.05	19.59	21.96	23.53	25.88
	$\text{Al}^{3+}$ leached	—	—	—	—	0.06	0.11	0.11	0.11	0.11	0.21
	pH value of effluent	7.09	7.22	7.57	7.34	7.30	7.29	7.62	7.37	7.46	7.53
pH=3.5	Amounts of $\text{H}^+$ input	1.19	2.37	3.56	4.74	5.93	7.12	8.30	9.49	10.67	11.96
	Base cations leached	4.21	5.93	7.44	8.38	9.29	10.66	11.86	12.93	13.99	15.04
	$\text{Al}^{3+}$ leached	—	—	—	—	0.10	0.16	0.16	0.31	0.31	0.38
	pH value of effluent	7.08	7.22	7.32	7.01	7.33	7.44	7.51	7.19	7.41	7.41

3.3 Release of aluminum

The amounts of aluminum leached from ferralsols were usually high under the treatment of pH 2.5 input solution as shown in Fig.2. Especially when the proton input was much higher than CEC, the amounts of aluminum released increased rapidly, whereas the amounts of  $\text{Al}^{3+}$  leached from purple soil staged at a low level equivalent to those from alkaline calcareous soils and coastal solonchak.

From the amounts of  $\text{Al}^{3+}$  released, two various regions could be divided according to the pH values of leachates. Al concentration in leached increased rapidly with pH lower than 4.5 while it decreased abruptly with pH higher than 4.5. Compared with the figure of hydrolysis of aluminum ion (Lindsay, 1979), it can be concluded that the forms and solubility

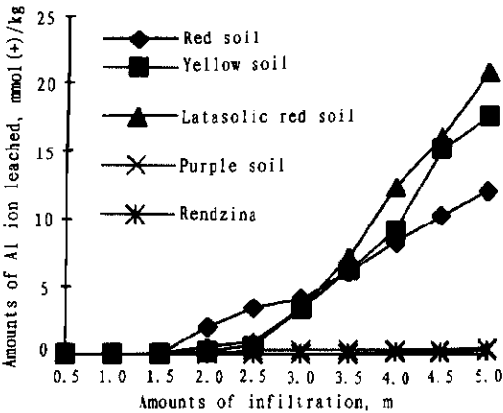


Fig.2 Relations of  $\text{Al}^{3+}$  released varying with amounts of infiltration (pH=2.5)

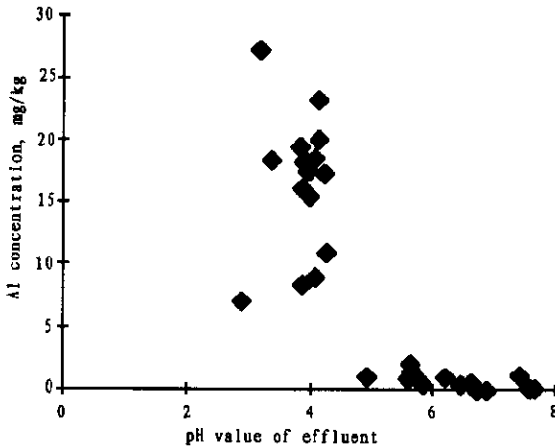


Fig.3 Relations between Al concentration and pH value of effluent

of cations was restricted by the processes of dissolution and translocation of cations and so that the amounts of cations leached were controlled by precipitation (Ervio, 1991). This can be demonstrated by the results that the leaching amounts of monovalent cations with high ability of dissolution and translocation were not obviously affected by the pH values of SAR.

of aluminum ion were controlled by the hydrolysis reaction of leachate or soil solution. The abrupt change of pH value ranging from 4.0 to 4.5 was the pH range at which the proton buffering system of soils changed into the scope of the aluminum buffering system (Fig.3; Liao, 1989).

### 3.4 Discussion

Amounts of cations leached were higher than proton input at a high pH of influent, while it was lower than proton input at a low pH of influent (Fig.4). However, total amounts of cations leached from soils were different. When the pH of influent was higher than 3.5, the release

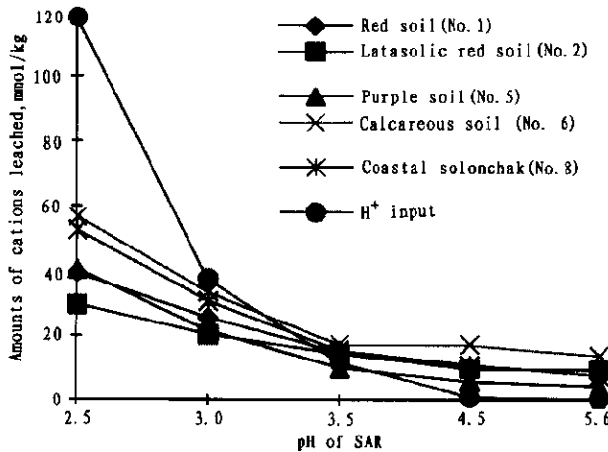


Fig.4 Comparison of amounts of cations leached and proton input (amounts of infiltration = 5000mm)

When the pH of influent was equal to 3.5, the pH of effluent kept constant at about 7.0 due to the rapid buffering reaction of base cations released by the cation exchange buffering system of soils. The total amounts of base cations released preserved an equivalent relation with H<sup>+</sup> input.

With the pH of influent lower than 3.5, several reactions may consume the proton input besides the cation exchange reaction. Most important is the absorption of anions that in ferralsols, widely distributed soils in South China having high contents of Fe and Al oxides. In addition, the weathering reaction of silicate is also an important proton buffering system that needs further study. This is also the important cause of the differences on research results of soil sensitivity

between the situation in vitro and the results deduced by CEC (Hornung, 1995). Certainly the balance-errors between  $H^+$  input and ions leached were also attributed to experimental error of  $H^+$  in solution and soil chemical reactions that act as sinks for applied  $H^+$ , as well as to pH-dependent variation on the negatively charged surfaces of oxides (Liu, 1990).

The amounts of base cations leached from calcareous soils and coastal solonchak were lower than the cation exchange capacity and the amounts of  $Al^{3+}$  released being lower than 0.40 mmol/kg throughout the treatment with SAR of each pH value from 2.5 to 5.6. The  $H^+$  buffering processes of these soils were still in the range of cation exchange and carbonate-silicate dissolution. When the amounts of base cations leached from soil series of ferralsols exceeded the cation exchange capacity, the pH of leaching solutions decreased sharply and the amounts of  $Al^{3+}$  released increased. Al dissolution was regarded as one of the main  $H^+$  buffering reactions in these soils (Blake, 1993; Cronan, 1995). In purple soil, the amounts of leached based cations were far beyond the CEC when the pH value of SAR was lower than 3.0, but the amounts of  $Al^{3+}$  released increased scarcely and the pH of leaching solutions was kept stable because there existed a lot of weatherable primary and secondary minerals with high Sa ( $SiO_2/Al_2O_3$ ) value (Qiu, 1997a). This implies that the  $H^+$  buffering of purple soil was still in the scope of the weathering of silicate.

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