

Effect of acid precipitation on leaching of nutritions and aluminium from forest soils

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Abstract—This paper principally deals with the effect of acid precipitation accelerating nutrients, such as potassium, sodium, calcium, magnesium, leached out of forest soils and noxious element - aluminium released from soils on the basis of the result from leaching experiment of forest soils collected from southern and south-western China under artificial rain of different acidity, pH=3.5, 4.0, 4.5, 5.0 and 5.6. It was discussed that the released amount of nutrient elements and aluminium was related to physicochemical properties of soils, leaching volume and the acidity of artificial rain, respectively. The buffering capability generated by the elements releasing from soils against acid precipitation was discussed.

Keywords: soil; forest; acid precipitation.

1 Introduction

Acid precipitation has appeared in some regions of China, especially in the south of Yangtze River. Concentration of SO_2 in air is about $20 \mu\text{g}/\text{m}^3$ in southern and southwestern China, the highest concentration in some cities is over $250 \mu\text{g}/\text{m}^3$ (Zhao, 1991; Ma, 1988), that of SO_4^{2-} in rain is about $100 \mu\text{g}/\text{L}$ in cities, the highest value is over $340 \mu\text{g}/\text{L}$ (Quan, 1988). Annual average pH of rain is about 4.5 or below in some places, such as Chongqing, Guiyang and Guangzhou cities. In addition, the area of acid soils is considerably large in southern and southwestern China. The main acid soils are red earth, yellow earth, lateritic red earth and latosols in the regions, CEC is very low in the acid soils, about 10–20 me/100g, in which exchangeable aluminium is about 1.0–10.0 me/100g. Therefore, acid rain can deplete nutrient elements from these soils and activate a large amount of aluminium.

Acid precipitation is frequently cited as a cause of reduced productivity in terrestrial and aquatic ecosystems (Johnson, 1981). Reduced productivity in terrestrial ecosystems may result from acid rain direct damage to crops and trees and indirect damage through the soil. Some effects of acid precipitation on soils are to change in nutrient availability, increase solubility of aluminium and leach exchangeable base and so on (Liliehholm, 1988).

Accelerated leaching of exchangeable cations in forest soils is thought to play an important role in forest decline, Singh *et al.* (Singh, 1980) found that leaching of Ca and Mg increased at

pH 4.3 in a study on a forest ecosystem. It was found that a reduction in exchangeable cations resulted as soil pH decreased with acid treatments in New Jersey Pine Barrens and that Ca and Mg leaching increased significantly with decreasing treatment solution pH by Schier (Schier, 1984). Wood and Bormann (Wood, 1976) reported that exchangeable K, Na, Ca and Mg were higher at pH 3.5–4.5 than at pH 5.7. These results might show that acid precipitation could accelerate leaching of some nutrient elements in forest soils.

Acid precipitation can not only accelerate leaching of K, Na, Ca and Mg in soils, but also activate Al in soils. Change of soil aluminium leaching may affect change of weathering rate of minerals in soils, change of base saturation, and changes in clay mineralogy. Furthermore, concentration of Al in soil solution is increased and a large amount of Al is transported to lakes and rivers (Johnson, 1981) and increased aluminium concentration in soil solution and water systems may damage the ecosystems (Jackson, 1983; Saigusa, 1980).

The major objectives of this paper are to understand release K, Na, Ca, Mg and Al from the forest soils in southern China under acid precipitation at present and to estimate changes of release the five elements from the soils in the future when acid precipitation become more serious.

2 Material and experiment

2.1 Sampling

All the samples were collected from the forest region in southern and southwestern China. The samples of purplish earth were collected from Ba County and Guangyuan in Sichuan Province, mountain yellow earth from Chongqing in Sichuan Province and Guiyang in Guizhou Province, lateritic red earth from Nanning in Guanxi Autonomy District and red earth from Kunming in Yunnan Province. There were more than 30 samples collected.

The samples were air dried in the laboratory. Then, they were crushed with a wood stick, sieved by mesh screen to remove >2 mm gravel, roots and so on, and mixed homogeneously to be used for experiments.

2.2 Experiment

100g soil sample was put into a leaching column and leached with different acidity of simulating acid rain (Liao, 1991) and pH of the solutions was 3.5, 4.0, 4.5, 5.0, 5.6, respectively. The leachate was collected with a plastic container which was soaked in 1 mol/L HNO_3 solution for 24 hours or more and washed. The leaching volume was equal to 45–55 mm/h rainfall. The leachate was collected every 8 hours, and a part of it was filtered with 0.45 μm membrane to be used for analysis.

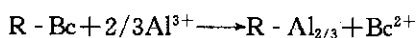
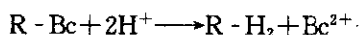
2.3 Analysis

pH of the soil samples was measured by a pH meter (± 0.01 pH unit; soil:water = 1:5) and pH of the leachates was measured immediately by using the same pH meter after it was collected.

The contents of potassium, sodium, calcium, magnesium in the leachates were determined by AAS, and aluminium was determined by ICP.

3 Results and discussion

That hydrogen coming from acid precipitation to a soil is neutralized by the cations released from the soil is the most important short-term buffering process of the soil against acid precipitation. Ion exchange complex reactions, such as



occur in the soil. The exchangeable base cation reservoir is finite size. The long-term buffering capability will depend on the chemical weathering rate of soil minerals. The buffering capability of a soil against acid precipitation is, therefore, dependent on the capability of release basic cations from the soil. The larger the basic cation exchange capacity and the weathering rate are, the higher the buffering capability is.

The total amount of the four elements, K, Na, Ca and Mg, released from the soils collected from southern and southwestern China under artificial rain is listed in Table 1. It can be seen that the total amount of the four elements released from these soils was different under the same acid input. It was highest from purplish earth, and lowest from yellow earth and latosols.

The total amount of the four elements released from the soils is correlated with the acidity input (Table 1). The amount released from yellow earth under the artificial rain of pH 4.0 was 1.25, 1.44 and 1.61 times that under pH 4.5, 5.0 and 5.6 respectively, and under pH 3.5, it was 1.08, 1.35, 1.56 and 1.75 times that under pH 4.0, 4.5, 5.0 and 5.6 respectively. The released amount from purplish earth under the same conditions as yellow earth was 1.47, 1.57 and 1.84, and 1.83, 2.70, 2.88 and 3.38 times, respectively. It can be seen that the leaching amount of the four elements increased with the increasing acidity of the simulated acid rain and was different from one soil to another (Fig. 1).

Table 1 Amount of the nutrient elements released from soils collected from southern and southwestern China

| | | Unit: me/kg | | | | |
|---------------------|-----------|--------------------------------|-----------|-----------|-----------|-----------|
| Soil | | Acidity of artificial rain, pH | | | | |
| Type | pH | 3.5 | 4.0 | 4.5 | 5.0 | 5.6 |
| Yellow earth | | | | | | |
| Range | 3.98—4.47 | 3.99—6.23 | 3.34—5.22 | 3.47—4.20 | 2.20—4.14 | 2.39—3.41 |
| Average | | 4.98 | 4.59 | 3.68 | 3.19 | 2.85 |
| CV, % | | 18.60 | 16.13 | 8.13 | 24.80 | 12.92 |
| Purplish earth | | | | | | |
| Range | 7.58—8.47 | 97.1—107.6 | 53.9—58.9 | 35.2—42.5 | 32.0—39.8 | 28.2—35.4 |
| Average | | 103.44 | 56.38 | 38.26 | 35.95 | 30.61 |
| CV, % | | 3.81 | 3.66 | 7.21 | 7.67 | 9.26 |
| Red earth | 6.67 | 38.8 | 26.8 | 16.9 | 13.2 | 12.2 |
| Lateritic red earth | | | | | | |
| | 5.00 | 9.23 | 7.45 | 4.52 | / | 3.42 |
| Latosols | 4.90 | 4.74 | 3.95 | 3.11 | 2.78 | 2.98 |

CV is variation coefficient. The amount is total amount of K, Na, Ca and Mg released from soil collected from southern and southwestern China

The relationship between the leaching volume and the total amount of potassium, sodium, calcium and magnesium released from red, yellow and purplish earth are given in Fig. 2. It is shown that the total amount of the elements released from these types of soils increased with the leaching volume of rain increased, and it was nearly parabolic at first, but their curvatures were different. The relationship between the amount of the elements released from the soils and leaching volume became linear after the leaching volume 1000 mm when easily soluble salt had been washed out.

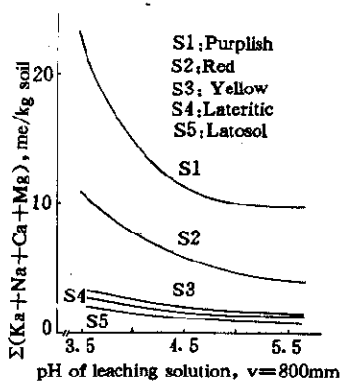


Fig. 1 The amount of the nutrient released from soils collected from southern and southwestern China under artificial rain

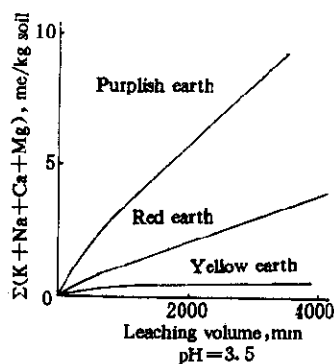


Fig. 2 Relationship between the amount of the elements released from soils and leaching volume

The different amount of the four elements released from soils is related with the physico-chemical properties of the soils. The higher the acidity of a soil is, the smaller the total amount of the elements released from the soil is (Table 1). The reason is that large amount of basic ions had been leached out of acid soils, and the content of the minerals easily weathered is low. The content of the minerals easily weathered is more than 1% in fine sand fraction of purplish earth ($\text{pH} > 7$) and less than 0.5% in yellow earth ($\text{pH} \leq 4.5$; Lin, 1988). Therefore, it is one of the reasons that the amount of the elements released from purplish earth is higher than that from yellow earth. It was proved that acid soils, such as yellow earth, would be easy lacking in nutrition to supply plants under acid precipitation.

The total amount of the four elements released from soils would also be affected by other physical properties. The more there is the large particle fraction in soils, the smaller the amount of the elements released from the soils is under acid precipitation. The particle fraction in size 0.2–2 mm is more than 70% in yellow earth collected from Chongqing (0–35 cm) and in size $< 2 \mu\text{m}$ is less than 3%, but 0.2–2 mm is less than 35% and $< 2 \mu\text{m}$ is more than 12% in yellow earth (0–33 cm) collected from Guiyang (Lin, 1988). And the total amount of the ele-

ments released from the soils is contrary to the content of the size 0.2–2 mm and related with the content of clay. The amount of the elements released from the soil of Guiyang is 1.3–1.9 times that of Chongqing. It was shown that the leaching of sandy soil is easier than viscous soil and that it is a very important part that cations are absorbed by colloidal materials.

Aluminium is one of the most abundant elements and the average is about 7.1% (w/w; Lindsay, 1979) although the content in soils is different from one to another. During the buffering process of soil against acid precipitation, therefore, aluminium plays an important role, especially in acid soils.

The amount of aluminium released from the soils under artificial rain is listed in Table 2. It is shown that the amount released from different soils was different. The amount from red and purplish earth is much less than that from lateritic red earth and latosols under the artificial rain of $\text{pH} \leq 4.5$. The amount released from lateritic red earth or latosols is about 60 times that from purplish earth, about 3 times that from red earth under the artificial rain of $\text{pH}=3.5$. The relationship between the amount of aluminium released from the soils and pH of artificial rain is given in Fig. 3. It was proved that aluminium released from lateritic red earth and purplish earth ($\text{pH} < 5$) increased with the increasing acidity of precipitation, but that from purplish earth ($\text{pH} > 7$) hardly increased.

Table 2 Amount of aluminium released from soils

| Site and layer | Acidity of artificial rain, pH | | | | |
|---------------------|--------------------------------|-------|------|------|------|
| | 3.5 | 4.0 | 4.5 | 5.0 | 5.6 |
| Purplish earth | | | | | |
| A | 0.51 | 0.40 | 0.40 | 0.49 | 0.48 |
| B1 | 0.48 | 0.68 | 0.89 | 1.28 | 1.11 |
| B2 | 0.56 | 0.67 | 1.45 | 1.83 | 2.17 |
| Purplish earth | | | | | |
| A | 0.36 | / | 0.48 | 0.48 | 0.80 |
| B | 0.71 | 0.83 | 0.83 | 0.95 | 1.85 |
| C | 0.56 | 0.56 | 1.95 | 1.85 | 1.50 |
| Lateritic red earth | | | | | |
| A | 28.19 | 20.74 | 1.67 | / | 1.22 |
| B | 29.69 | 28.30 | 6.12 | 0.42 | 0.51 |
| C | 31.52 | 28.19 | 6.69 | 0.59 | 0.32 |
| Red earth | | | | | |
| A | 8.26 | 0.66 | 0.28 | 0.34 | 0.36 |
| B | 16.62 | 0.81 | 0.44 | 0.30 | 0.44 |
| Latosols | | | | | |
| A | 29.02 | 23.41 | 3.45 | 1.72 | 2.17 |
| B1 | 29.86 | 32.52 | 5.45 | 1.39 | 0.96 |
| B2 | 24.68 | 25.13 | 5.13 | 1.11 | 1.61 |

The relationship between the amount of aluminium released from soils and the leaching volume of the artificial rain is given in Fig. 4. It is shown that the relationship is nearly linear in lateritic red earth, purplish earth and latosols, but it was parabolic in red earth, and that it was parabolic at first in yellow earth and then it became linear. It was proved that the characteristic of aluminium release was nearly constant in lateritic red earth, purplish earth and latosols under acid precipitation, and exponentially increased with rain in red earth.

During the buffering of soil against acid precipitation, the capability of soil release cations is not only related with the acidity of acid precipitation, but also it is related with the acidity of soils. The relationship to the total amount of the five cations, pH of simulating acid rain and pH of the soils is given in Fig. 5. It is shown that the capability of soil release cations was increased with increasing pH of soils and that the capability of release cations from acid soils in southern and southwestern China was considerably low. The relationship between the total amount of the five cations and pH of soils is nearly linear, that is

$$M = a + b \times \text{pH}(s) \quad (R > 0.9, n = 14).$$

Where M is the total amount of the five cations released from soils under simulating acid rain, pH (s) is the pH of soils.

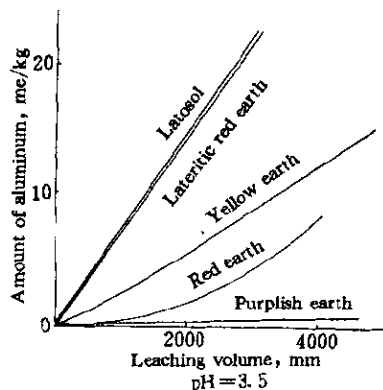


Fig. 4 Relationship between releasing amount of aluminium and leaching volume

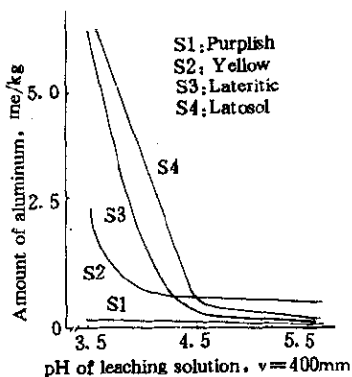


Fig. 3 Releasing of aluminium under artificial rain from soils

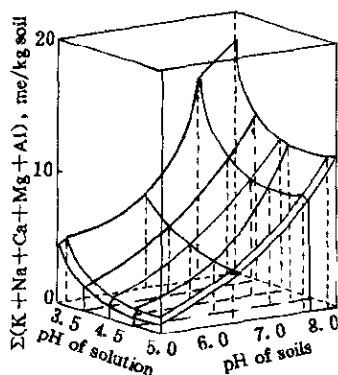


Fig. 5 The relationship to the amount of the five cations released from soils, pH of soils and artificial rain

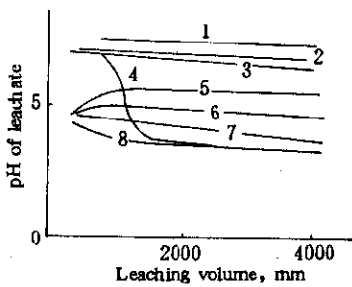


Fig. 6 Relationship between the acidity of the leachate and leaching volume

- 1, purplish earth, pH 3.5—5.6 artificial rain
 2, red earth, pH 4.5—5.6 artificial rain
 3 and 4, red earth, pH 4.0—3.5 artificial rain
 5—8, yellow earth, pH 5.6, 4.5, 4.0 and 3.5 artificial rain

capability of release cations from purplish earth was stronger than from yellow earth and red earth and that red earth could be easily acidified under the precipitation of high acidity.

Table 3 Amount of exchangeable cations and base saturation

| Soil type and layer | Ex. K | Ex. Na | Ex. Ca | Ex. Mg | BS |
|---------------------|-------|--------|--------|--------|-------|
| Yellow earth | | | | | |
| A | 1.41 | 0.13 | 3.25 | 0.46 | 8.31 |
| B1 | 0.90 | 0.21 | 2.62 | 0.33 | 7.47 |
| B2 | 1.03 | 0.24 | 5.32 | 0.82 | 11.54 |
| Red earth | | | | | |
| A | 3.08 | 0.19 | 6.53 | 1.18 | 13.46 |
| B | 2.04 | 0.22 | 3.99 | 0.52 | 7.52 |
| Latosols | | | | | |
| A | 1.81 | 0.24 | 2.77 | 0.40 | 4.12 |
| B1 | 1.55 | 0.52 | 2.92 | 0.24 | 4.50 |
| B2 | 1.24 | 0.43 | 3.08 | 0.40 | 5.01 |
| Purplish earth | | | | | |
| A | 2.69 | 0.66 | 381.60 | 3.01 | / |
| B | 2.21 | 0.68 | 390.90 | 2.75 | / |
| C | 2.47 | 0.65 | 378.50 | 2.49 | / |

Unit: amount of exchangeable cations, mmol/kg; base saturation, % Notes: Ex is exchangeable

The buffering capability of soil against acid precipitation is principally dependent on the capability of soil release cations. The capability of soil release cations is related to the content of exchangeable cations and the weathering rate of minerals in soil. Exchangeable cations play a very important role in the process of soil buffering acid precipitation, but the role is a short-term buffering mechanism. The mechanism is dependent on the amount of exchangeable cations, principally on exchangeable Ca, Mg, K and Na. The amount of exchangeable K, Na, Ca and Mg and base saturation are given in Table 3. It is seen that the amount of exchangeable base cations in purplish earth was very high, but the amount was considerable low in latosols. It was proved

that the short-term buffering capability of purplish earth was much larger than those of yellow earth and latosols.

4 Conclusion

It could be considered that, based on the result of simulating acid rain leaching the soils collected from southern and southwestern China, the capability of soil release K, Na, Mg and Al was different from one soil to another under the conditions of acid precipitation. The release amount of K, Na, Ca and Mg increased with increasing exchangeable base cations and pH of soil, and was related with the component of grain size in soils. Amount of Al decreased with the increasing soil pH. In the areas, release capability of K, Na, Ca and Mg from purplish earth was much larger than from yellow, red and lateritic red earth and latosols, and release capability of Al from lateritic red earth and latosols was much higher than from purplish and red earth.

Under the condition of artificial acid rain, the amount of release K, Na, Ca and Mg from acid soils in southern and southwestern China, such as yellow earth, lateritic red earth and latosols, increased small with the decreasing the solution pH, but that from purplish earth ($\text{pH} > 7$) increased greatly. In contrary, the amount of release Al from acidic soils increased greatly with the decreasing solution pH, and that from alkaline earth hardly increased with the pH. It might be shown that released aluminium from acidic soils could damage plant growing when acid precipitation becomes more serious in the areas.

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