Journal of Environmental Sciences (China) Vol. 3, No. 3, pp. 61–69, 1991 ISSN 1001-0742

Simulating study on the effect of acid precipitation on forest soil weathering

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(Received June 20, 1990)

Abstract — The effect of acid rain on the forest soils in China was discussed on the basis of simulating studies. The soils were collected from five typical areas, including Chongqing in Sichuan Province and Guiyang in Guizhou Province, where there has been heavier acid rain in southwest China, and Huitong in Hunan Province, Zhouzhi in Shaanxi Province, and Xinglong in Hebei Province, all of which were selected as control. Field investigation and sampling were made in the typical forests in all the above five areas. The relationship between pH values in precipitation and rates of soil weathering, the difference between the rates of soil weathering in different areas, and the cause of such a difference, have been worked out. The prediction was also conducted on the supply dynamics of nutrient and toxic elements in various forest ecosystems which were affected by acid deposition in order to understand the long-term effects of acid precipitation on the forest ecosystems studied.

Keywords: acid precipitation; forest ecosystems; soil weathering.

While a soil system is exposed to acid rain, there is being occurred a sequence of reactions, including the exchange of the cations adsorbed on the surface of clay mineral with H^+ in acid deposition, the leaching of elements, the weathering of minerals in soil and so on (Ulrich, 1981). These reactions may lead to the losses of available nutrient elements in the rooting layer of soil, and to the release and activation of some toxic elements. Such chemical reactions can be grouped as follows:

(1) Ion exchange reaction

$$R-Me^{X+}+XH^{+}=XR-H^{+}+Me^{X+},$$

$X=1-3$; R = clay micell; Me = Na, K, Ca, Al

(2) Aluminosilicate weathering reaction

$$\text{Aluminosilicates}+H^{+}=\text{Secondary minerals}+Me^{X+}.$$

(3) Hydrolytic reaction of alumina trihydrate

$$Al_2O_3\cdot 3H_2O+6H^{+}=2Al^{3+}+6H_2O.$$

The above reactions can result in a serious change in the soil environment on which forest

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relies for growth to hinder the normal growth of forest.

Li and Bockheim (1987) have carried out the observation and experiments on the Oak and Jackson forest and soil for two years at Round Lake, Wisconsin, the United States. They measured the deposited matter and the change of chemicals in soil water, conducted the experiments on weathering of minerals in both surface layer and deep layer of soils, and studied the weathering process and geochemical cycle of elements. It was concluded that the exchange of cation and weathering of minerals in soil play more important roles in buffering although forest vegetation can partly neutralize acid precipitation.

General characteristics of curves for weathering kinetics

The weathering reaction of aluminosilicate as a mineral is essentially a hydrolytic reaction. As it is subject to weathering, the mineral draws hydrogen ion from the solution in its surrounding, thus resulting in an increased pH value in the environment of reaction.

During a 64-days simulating experiment of weathering, the concentrations of free ions (Si, Al, Ca, Mg, K, Na) which have been released due to the weathering were measured in every predetermined interval to obtain a curve of weathering as function of time. The curves for weathering kinetics of the soils, which were sampled from Xinglong, Hebei Province; Zhouzhi, Shaanxi Province; Huitong, Hunan Province; Guiyang, Guizhou Province and Chongqing, Sichuan Province, in the environment at various levels of pH have a same feature by fitting in with the following parabolic equation:

$$\log w = a \log t + b,$$

Where w is the integrated amount of weathering of minerals in soil, measured by mg ion/g soil; t is the time of weathering lasted, by days; and a and b are constants.

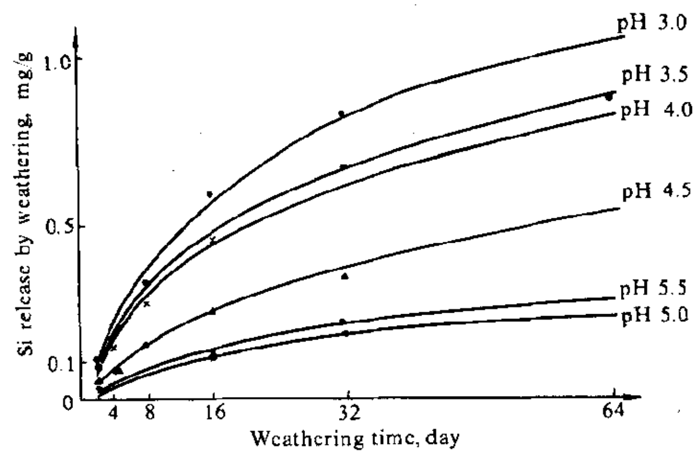

Fig. 1 Curves of the kinetics of Si release by weathering at different pH values in the surrounding of soil from Xinglong, Hebei Province

The curves for weathering of forest soils from Xinglong, and Chongqing are shown in Fig. 1 and Fig. 2, respectively, it reflecting the general states of soils in the north and the south of China. The element Si is taken as an indicator by which the situation of weathering of soil mineral can be well indicated, as other ions exhibit to follow a same rule.

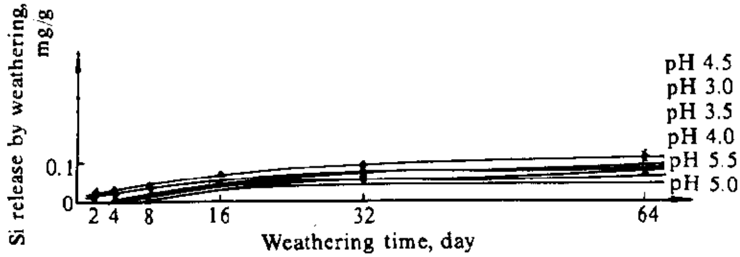

Fig. 2 Curves of the kinetics of Si release by weathering at different pH values in the surrounding of soil from Chongqing, Sichuan Province

The curves for weathering kinetics worked out from this study are consistent with the previous results and theoretical explanations by other researchers on the process of weathering of soil minerals. Within the range of pH as in our experiments, those in an unstable thermodynamic state are the primary minerals of aluminosilicate, including hornblende, pyroxene, olivine, feldspar, sheep silver and so on, as weathering occurs in soil. The effective surface area of these minerals has an effect on the rate of hydrolytic reaction. At its initial stage, the weathering reaction is fast due to that the minerals susceptible to weathering have a rather large effective surface area for reaction. As the reaction proceeds, fine particles are getting disappeared and the total amount of minerals becomes reduced that lead to a decreasing effective surface area for its reaction and thus make the rate of weathering slower.

Difference between the weathering rates of soils from different areas

Under the same conditions of experiment, the soils from the five areas as mentioned above show quite different rates of weathering. A comparison has been made by taking the elements of Si and Mg as indicators (Fig. 3 and 4).

As shown in Fig. 3, at various pH levels, the release of Si due to weathering has a rate by following the order of decreasing rates for soils from Zhouzhi, Xinglong, Guiyang, Huitong, and Chongqing. The rate of Mg release due to weathering is also in the same trend (Fig. 4). The contents of various primary minerals in the soils from the five areas have been determined by Lin *et. al.* (1988) and are shown in Table 1.

Hornblende, plagioclase, sheep silver, and chlorite (including those in the state of their semiweatherin g) among the minerals shown in Table 1 are the minerals prone to weathering. Their proportions by weight in soils from the five areas are also in a decreasing order for the soils, from Zhouzhi, Xinglong, Huitong Guiyand and Chongqing.

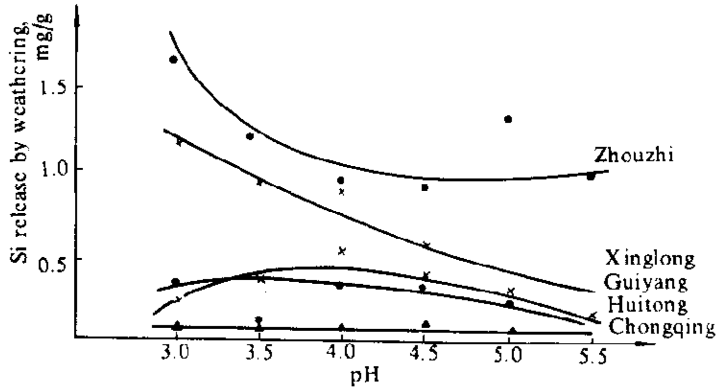

Fig.3 Si release by weathering at different pH vales in the surrounding of soils from different sources in China during a 62-day simulating experiment

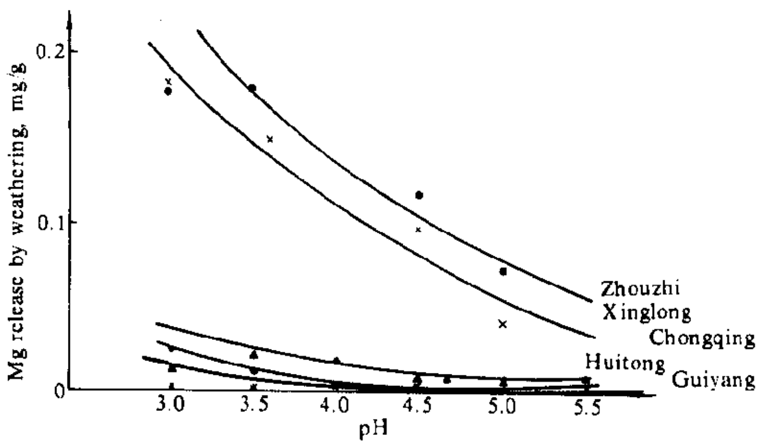

Fig.4 Mg release by weathering at different pH values in the surrounding of soils from different sources in China during a 62-day simulating experiment

The results indicate that the rate of soil weathering is highly related to the composition of minerals in soil, and especially to the kinds and proportions of the minerals susceptible to weathering in soils. Both states of New York and Wisconsin, the United States, have been suffered from the damages by acid precipitation. However, the forests in the State of New York have declined obviously while those in Wisconsin have being less affected. The reason for this is in that the state of New York has relatively elder soils in which there remain not much of primary

Table 1 Contents of minerals in the fine particles of forest soils from different sources in China, weight %

Sources of soil	Alkali - feldspar	Plagi - oclase	Quartz	Sheep silver, chlorite	Calc-spar	Hornb - lende	Zircon sand	Rutilite anatase brookite	Magn - etite	Semi - weat - hered minerals	Weath - erable minerais*
Zhouzhi, Shaanxi	0.0	8.3	8.1	48.0	0.0	0.0	0.0	0.0	0.0	35.5	91.8
Xinglong, Hebei	0.0	37.6	19.8	12.0	0.0	3.8	0.0	0.0	16.1	10.7	64.1
Huitong, Hunan	0.0	4.9	24.1	17.6	0.0	0.0	0.0	0.0	0.0	33.3	75.8
Guiyang, Guizhou	10.0	0.0	30.0	10.0	0.0	0.0	0.0	0.0	0.0	50.0	60.0
Chongqing, Sichuan	22.5	0.0	61.2	9.2	0.0	0.0	0.6	0.6	0.0	53.3	15.1

*Weatherable minerals include: plagioclase, sheep silver, chlorite, hornblende and semi-weathered minerals.

minerals easily being weathered, but the soils in Wisconsin are younger ones which formed during the last glacial age and contain more minerals prone to weathering that offer stronger capability of buffering (Bockheim, 1987). The present study suggests that the same phenomena of acid rain impact under the control of soil arc also present in China. The soils in Shaanxi and Hebei contain a large proportion of the minerals prone to weathering. And acid rain occurs in these areas, the minerals absorb a large amount of H^+ and their hydrolytic reactions take place that act as buffering. The predominant minerals in the soils sampled from Chongqing are quartz and alkalifeldspar difficult to be weathered and contain only 15.1% of minerals prone to weathering that result in a very low capability of buffering acid deposition.

Effect of pH on the rate of weathering

The main process of the weathering of soil minerals is hydrolytic reaction so that the concentration of hydrogen ion in the surrounding of reaction is an important factor to control the kinetics of weathering. As the concentration of hydrogen ion increases, the hydrolysis of aluminosilicate accelerates. This mechanism is very important to evaluate the effect of acid rain on soil system. The results show that the mechanism is followed.

From Fig. 1 it can be seen that when the value of pH is reduced there is an increased rate of the release of Si due to the weathering of soils from Xinglong. The weathering reactions of soils from Zhouzhi, Huitong, Chongqing and Guiyang are also in the similar cases (Table 2).

The selection of Si as an indicator for determining the rate of mineral weathering is because

Table 2 Total amount of Si released by weathering at different pH values in the surrounding of forest soils from different sources in China during a 62-days simulating experiment, ppm

Sources of soil	Total amount of Si released pH 3.0	3.5	4.0	4.5	5.0	5.5
Xinglong, Hebei	1.18	0.89	0.89	0.58	0.32	0.31
Zhouzhi, Shaanxi	1.67	0.95	0.97	0.91	1.34	1.00
Huitong, Hunan	0.34	0.14	0.35	0.33	0.21	0.18
Guiyang, Guizhou	0.23	0.39	0.54	0.40	0.25	0.18
Chongqing, Sichuan	0.10	0.09	0.09	0.11	0.07	0.07

the hydrolytic reaction of aluminosilicate would speed up with pH value lowering and the solubility of amorphous Si compounds decreases with the reduction of pH value. Therefore, when an increase in free Si appears due to the lowering of pH value in the surrounding, a contribution from the dissolution of amorphous secondary Si compounds in soil can be neglected.

Comparisons were also made for Mg and Ca both of which are the main structuring elements in primary aluminosilicate. As shown in Fig. 4 and 5, during a 62-days weathering reaction, the total releases of both Mg and Ca increase also with the lowering of pH value in the surrounding of weathering.

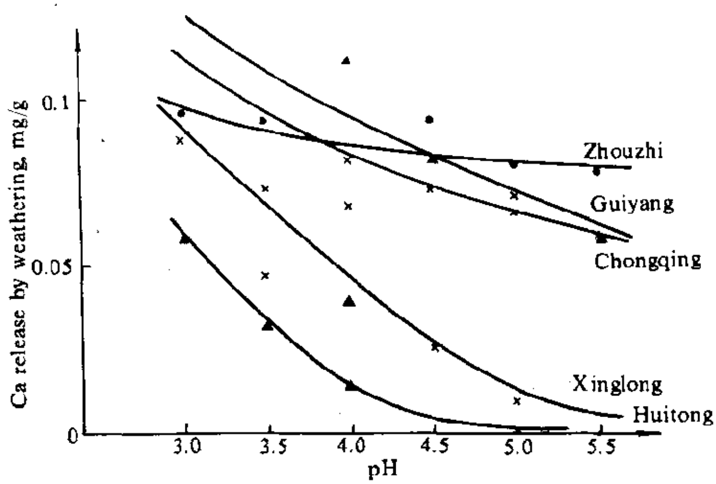

Fig. 5 Ca release by weathering at different pH values in the surrounding of soils from different sources in China during a 62-days simulating experiment

Discussion on the release of Al

In the process of weathering, aluminum ion may be released from two sources: the hydrolysis of primary aluminosilicates and the dissolution of secondary alumina trihydrate. The reaction of alumina trihydrate is expressed by the following equation:

$$Al_2O_3 \cdot 3H_2O + 6H^+ = 2Al^{3+} + 6H_2O.$$

The equation suggests that as pH value is lowered (i.e., the concentration of H_+ is increased), the dissolution of alumina trihydrate becomes larger.

The phenomenon of the increase in Al release with the lowering of pH value in the surrounding of weathering exhibits clearly as shown in Fig. 6.

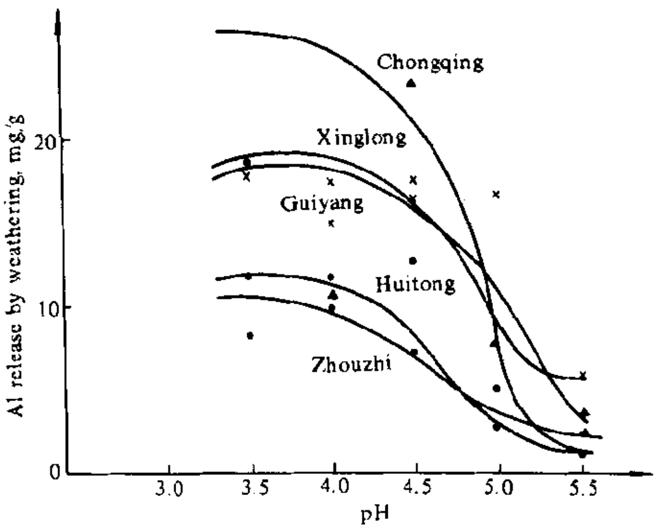

Fig. 6 Al release by weathering at different pH values in the surrounding of soils from different sources in China during a 62-days simulating experiment

When Fig. 3 is compared with Fig. 6, an interesting difference can be seen between them. The decreasing order of Si release due to weathering, by ranking the sources of soil, as shown in Fig. 3 is: Zhouzhi, Xinglong, Guiyang, Huitong and Chongqing. However, the decreasing order of Al release due to weathering, by ranking the sources of soil, as shown in Fig. 6 is: Chongqing, Guiyang, Xinglong, Huitong and Zhouzhi. The results from analyses for minerals in the soils from various sources show that the soil from Chongqing, Sichuan does not have apparently much primary minerals susceptible to weathering which are available to weathering. This is true as if it is reflected by very small amount of Si released. Thus it can be considered that a large amount of Al ion present in the soil is not from the primary aluminosilicates but from the secondary Al compounds such as alumina trihydrate. Alumina trihydrate is a common secondary mineral which is generated in the process of stronger weathering and leaching and is present widely in red earth and yellow earth in the south of China. When these soils are subject to an impact of acid rain, Al is easier released from Al^{3+}. Al in such a state of free ion is easily uptaken by plant and thus produces a greater phytotoxicity.

Estimation on the effects of acid rain on the soils in five areas

While it is subject to an erosion by acid rain, soil has leaching and weathering occurred in it. The effect of leaching allows the free ions of solubility to be transferred from an upper layer of soil to a lower layer of soil or even finally to the system of underground water and thus to move out of the localization. Such an effect will lead to the losses of many nutrient elements in soil. Weathering has an opposite effect which allows the primary or secondary minerals in soil to release more free ions, including the nutrient elements such as Ca^{2+}, Mg^{2+}, K^- and Na^+, and the toxic elements such as Al^{3+} and Mn^{2+}. For this reason, when an evaluation is conducted for the effect of acid rain on soil, an attention must be paid to the effect of weathering while leaching is being taken into account.

If the production of Ca^{2+}, Mg^{2+} and K^+ due to weathering is regarded as a positive factor in favour of forest growth and the production of Al^{3+} is regarded as a negative factor which is unfavourable to forest growth, the two factors can be constructed as a ratio which in turn is taken as an index to measure the ecological effect of weathering on forest:

$$E = \frac{R\ (\mathrm{Ca+Mg+K})}{R\ (\mathrm{Al})}$$

where E is an index of the ecological effect of weathering on forest, R (Ca+Mg+K) is the rate of the releases of Ca^{2+}, Mg^{2+} and K^+ due to weathering, and R(Al) is the rate of Al^{3+} release by weathering.

The values of E for the five areas studied have been calculated and shown in Table 3. From Table 3, it can be found that when the pH value in the surrounding of soil is in the range of 3.5–5.0, the decreasing order of E values by ranking the sources of soil is : Zhouzhi, Xinglong, Huitong, Guiyang, and Chongqing. This result indicates that when an acid rain in the range of pH 3.5 to 5.0 occurs in China, the loess area in China represented by Zhouzhi will have the largest resistance to the acid rain namely that under the action of acid rain it can produce more nutrient ions, such as Ca^{2+}, Mg^{2+} and K^+, and less toxic ions, such as Al^{3+}. In the same case, the mountainous brown soil represented by that in Xinglong, will have also a certain resistance to the acid rain. However, with an E value less than that for loess, the yellow earth such as that in Chongqing, or in Guiyang, exhibits a pernicious response to the acid rain. When the pH value in the surrounding of soil is less than 4.5, the weathering of soils in Chongqing, and Guiyang, will produce Al in an amount of 60 –160 times the content of Ca^{2+}, Mg^{2+}, K^+ and Na^+. If the release of Al^{3+} by weathering in 50 times the release of Ca^{2+}, Mg^{2+}, K^+, Na^+ by weathering (i. e., $E=0.02$) is taken as a threshold value of risk, the soils in Zhouzhi, and in Xinglong, will have no risk; the soil in Huitong, will have a risk only if the acid rain has a pH value less than 3.5; and the soils in Chongqing and Guiyang, will exhibit risks at a pH valuc lower than 4.5.

Table 3 Index (E) of the ecological effects of acid rain at different pH values on forest in selected areas in China, based on a 62-days simulating experiment

Sources of Soil	E			
	pH			
	3.5	4.0	4.5	5.0
Zhouzhi, Shaanxi	0.16	0.13	0.17	0.20
Xinglong, Hebei	0.053	0.055	0.020	0.028
Huitong, Hunan	0.016	0.045		
Guiyang, Guizhou	0.006	0.016	0.008	0.75
Chongqing, sichuan	0.005	0.016	0.007	0.040

This study focuses only on the effects of acid rain on the weathering of minerals in soils without relating to the function of exchangeable ions in soils. Therefore, it is not so exact to take this to judge all responses of soil to acid rain. However, the authors of this paper believe that, as for the long-term effect of acid rain, the weathering would be an important indicator to judge the capability of soil to provide cations sustainably. For this reason, the conclusion drawn from our study in this paper can be yet regarded as having the importance to judge the responses of soil to acid rain in China.

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