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Effects of Aluminum Toxicity Induced by Acid Deposition on Pine Forest Ecosystem in Longli of Guizhou Province, Southwestern China

ZHANG Jing[1], LYU Zhipeng[2], SHAO Siya[1], LI Fangfang[1], YANG Shengtian[2], SONG Wenlong[2], LI Wei[3], LI Shunjiang[3]

(1. *College of Global Change and Earth System Sciences*, *Beijing Normal University*, *Beijing* 100875, *China*; 2. *School of Geography*, *Beijing Normal University*, *Beijing* 100875, *China*; 3. *School of Environment*, *Beijing Normal University*, *Beijing* 100875, *China*)

Abstract: The effects of acid deposition on pine forest ecosystems in Longli of Guizhou Province, southwestern China are studied using indoor experiments and model simulations. Indoor experiments are designed to explore the aluminum toxicity on pine seedlings, and the long-term soil acidification model (LTSAM) and a terrestrial biogeochemistry model (CENTURY) are used to simulate the influences of acid deposition on pine forest ecosystems. The indoor experiment results of aluminum toxicity show that aluminum ions in solution limit plant growth and acid deposition enhances this effect by facilitating the release of aluminum ions from the soil. Pine seedling biomass and root elongation decrease as the aluminum concentration increases. The results of model simulations show that the soil chemistry varies significantly with different changes in acid deposition. When the acid deposition increases, the pH value in the soil solution decreases and the soil Al^{3+} concentration increases. The increased acid deposition also has negative impacts on the forest ecosystem, i.e., decreases plant biomass, net primary productivity (NPP) and net CO_2 uptake. As a result, the soil organic carbon (SOC) decreases because of the limited supply of decomposition material. Thus acid deposition need be reduced to help protect the forest ecosystems.

Keywords: acid deposition; aluminum toxicity; long-term soil acidification model (LTSAM); terrestrial biogeochemistry model (CENTURY); pine forest

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1 Introduction

Forest degradation has occurred in large areas of Europe and North America since the 1960s, and Ulrich *et al*. (1980) suggested that acid rain might be a direct cause. Under the influence of acid deposition, the Al^{3+} in undissolved materials, such as aluminosilicate and aluminum oxide, may break free and enter the soil solution, thus leading to forest degradation (Ulrich, 1989). The influence of acid deposition on forest ecosystems is becoming increasingly serious (Tomlinson, 1983; Ulrich, 1990; Tang *et al*., 1996; Jiang *et al*., 2002; Zhang *et al*., 2010).

Acid deposition activating aluminum ions may cause an aluminum toxicity effect, which may damage the root tip and lateral root (Kinraide, 1988; Roy *et al*., 1988). Johnson *et al*. (1982) suggested that a low pH value and high Al^{3+} concentration are the main reasons for forest degradation in North America. Many scholars have conducted laboratory test experiments to explore the effects of aluminum toxicity on plants under different acidic conditions. Wagatsuma and Ezoe (1985) grew

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Corresponding author: ZHANG Jing. E-mail: jingzhang@bnu.edu.cn
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seedlings of maize, soybean, cucumber and Japanese radish with a solution containing 6‰ Al^{3+}. The pH of the solution was adjusted to 3.3, 3.6, 4.0, 4.3, 4.6, 5.0, 5.3, 5.6 and 6.0. The experimental results showed that by increasing the pH the Al^{3+} concentration began to decrease until the pH reached 4.0, then decreased remarkably above pH 5.0, and was very low at pH 6.0. Cao *et al.* (1992) cultivated pine seedlings by using Edwards′ nutrient solution (Edwards, 1976) and various aluminum concentrations, and set the pH value of 4.2 with a series of aluminum concentrations (0 mg/L, 15 mg/L, 30 mg/L, 60 mg/L, 120 mg/L and 240 mg/L). The results showed that the growth of pine seedlings began to be restricted when the Al^{3+} concentration reached 15 mg/L; and the fresh weight decreased 8% and 32% for the Al^{3+} concentrations of 15 mg/L and 30 mg/L, respectively. Liu and Liu (1995) chose pH value of 4.0, used different aluminum concentrations (0 mmol/L, 0.05 mmol/L, 0.10 mmol/L, 0.15 mmol/L, 0.20 mmol/L, 0.40 mmol/L, 0.60 mmol/L, 0.80 mmol/L and 1.00 mmol/L), and found that the lowest concentration of aluminum toxicity to be 0.15 mmol/L (4.05 mg/L), and a lower concentration may promote the growth of seedlings. However, the experiment of Liu and Liu (1995) did not reflect the dynamic aluminum toxicity effect with changing pH value.

In the late 20th century, researchers began to use an experimental method to study the impact of acid deposition on soil (Chou *et al.*, 1997; Liao and Jiang, 2002). Because these experiments could not cover large areas and various types of soil, the researchers applied many mathematical models to study acid deposition as well as its influences on forest ecosystems. The models include the Henriksen model (Henriksen, 1979; Wright and Henriksen, 1983), the integrated lake-watershed acidification study (ILWAS) model (Chen *et al.*, 1984; Goldstein *et al.*, 1984; Gherini *et al.*, 1985), the simulation model for acidification′s regional trend (SMART) model (De Vries *et al.*, 1989) and the model of acidification of groundwater in catchment (MAGIC) model (Cosby *et al.*, 1985). Zhao *et al.* (1992) used the MAGIC model to simulate soil acidification under different amounts of acid deposition. The results showed that the amounts of acid deposition in Chongqing and Guizhou cities had exceeded the limit that the ecosystem could withstand.

China became the third largest region in the world with heavy acid deposition after Europe and North America (Zhang and Zhao, 1989). The percentage of acid deposition reached 40% in the 1990s (National Environmental Protection Agency, 1996). The forest in the southwest is the second largest forest in China that occupies approximately 30% of the total forest area of the country (Fang, 2001). The Sichuan Basin and Guizhou Province have been the most impacted with damaged forest areas of 2.756×10^5 ha and 1.405×10^5 ha, respectively (Feng, 1993). Guizhou Province has become one of the regions that suffers from the severest acid deposition, where acid rain has occurred in more than 80% of the cities and the sulfur concentration in 40% of the cities has exceeded grade II of national air quality standards (Guizhou Province Environmental Protection Bureau, 2009), and that makes it in urgent need of quantitative research on acid deposition.

In this study, an indoor experiment was designed to explore the aluminum toxicity effects on individual plants. Accordingly, the dynamic effects were observed and the lowest concentration of aluminum toxicity could therefore be determined more accurately. Based on the experiment results, the long-term soil acidification model (LTSAM) was adopted to simulate the change of the soil pH, and an aluminum toxicity factor was included into the terrestrial biogeochemistry model (CENTURY) model to simulate the dynamics of forest ecosystems on an experimental site in Guizhou Province under different scenarios of acid deposition. Little attention has been paid to the combination of aluminum toxicity experiments and soil acidification model. The results of this study attempted to assess the effect of aluminum toxicity induced by acid deposition on the pine forest ecosystem and evaluate the response of ecosystem to different scenarios of acid deposition in Longli of Guizhou Province, southwestern China.

2 Materials and Methods

2.1 Study area

The experimental catchment, the Yangjichong Reservoir Basin in Longli of Guizhou Province, southwestern China (26°26'30''–26°27'30''N, 107°01'00''–107°02'00''E), was selected as the study area in this study (Fig. 1). The area of the catchment is approximately 12 km^2 and is located approximately 31 km southeast of Guiyang, the capital city of Guizhou Province. The Yangjichong Reservoir has a subtropical humid and mild climate. The average temperature is around 14.7℃ and the annual average precipitation is 1158.5 mm with 70% occurring in spring and summer. Most of the experimental area is on low hills, and the main soil type is yellow soil developed from sand-shale or limestone. The soil pH is between 4.5 and 4.8 and is noticeably acidic. The vegetation of the study area is a broad-leaved and coniferous mixed forest. Most of the vegetation has been planted, and many existing natural vegetation is rare. The tree species include masson pine (*Pinus massoniana*), cedars (*Cunninghamia lanceolata*) and birch (*Betula luminifera*). The masson pine in the study area was planted in 1957 (Guizhou Forest Survey Academy, 2008).

2.2 Aluminum toxicity experiments

To explore the aluminum toxicity effect on individual plants, aluminum toxicity experiments were designed. The pine seeds were first immersed in warm water for 24 h and then sterilized with H_2O_2 (1%). Then, the seeds were planted in substrates composed of the soil samples collected from the pine forest in the study area. After two months, we selected 160 seedlings that have the same growing conditions/status and transplanted them into 16 pots, each of which with 10 seedlings and a nutrient solution with different pH and Al^{3+} concentrations (Table 1). The Al^{3+} concentration was pre-set after chemical calculations to make sure that the aluminum added was soluble. The base nutrient solution was prepared using the Hoagland formula (Hoagland and Arnon, 1950). Because the soil pH of the study area ranged from 4.50 to 4.80, the pH of the nutrient solution was set to be 4.50. In addition, we also set the pH to be equal to 3.00 and 6.00 to compare the aluminum toxicity under different acid conditions. After additional two months,

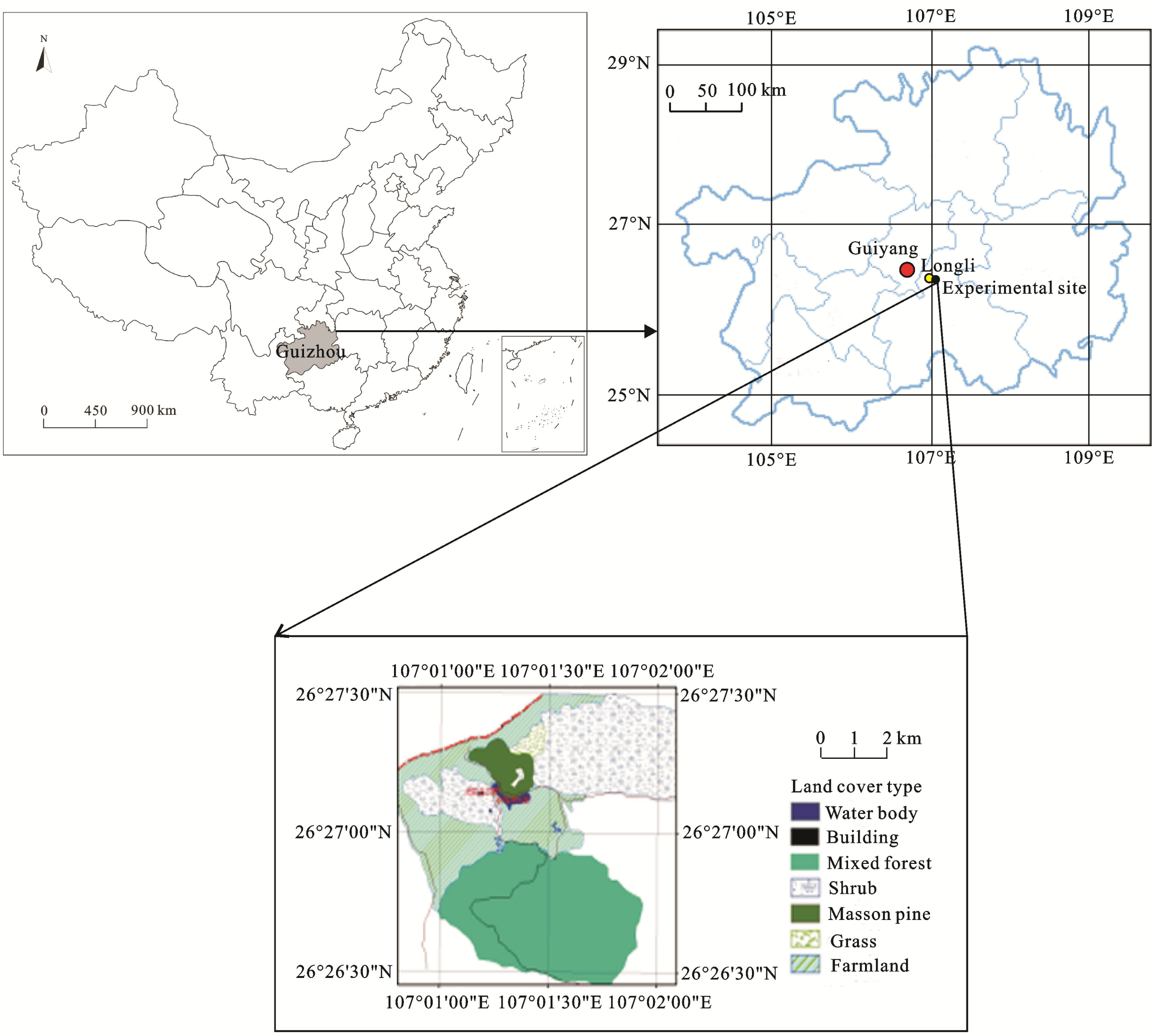

Fig. 1 Location of study area

Table 1 pH value and Al^{3+} concentration set in nutrient solutions

pH	3.00	4.50	6.00
$[Al^{3+}]$ (mg/L)	0.02 (0.00074)	0.02 (0.00074)	0.02 (0.00074)
	0.20 (0.0074)	0.20 (0.0074)	0.20 (0.0074)
	1.00 (0.037)	1.00 (0.037)	1.00 (0.037)
	20.00 (0.74)	10.00 (0.37)	X
	50.00 (1.85)	15.00 (0.56)	X
	0.00	0.00	0.00

Notes: the unit of the value in parentheses is mmol/L; X means that this experiment is not arranged since at pH of 6.00, the maximum soluble $[Al^{3+}]$ is 0.037 mmol/L

we recorded the seedling growth conditions, including root length (with an accuracy of 1 μm), fresh weight, dry weight for the aboveground part, dry weight for the underground part and the nutrient element (including Ca, Mg, K, Al, P and S) concentrations.

The root length was analyzed using the WinRHIZO Pro3.0 root image analysis system (with an accuracy of 1 μm) (Regent Instruments, Canada), and the nutrient element concentration was measured using an inductively coupled plasma spectrometer (ULTIMA, JY, France) with a detection limit of 5 ng/mL and an uncertainty of less than 1%.

2.3 Model description and data collection

2.3.1 Model description

Because many soils contain carbonates in the southern China (Xiong and Li, 1987) and the SO_4^{2-} adsorption/desorption from red or yellow loam in the southern China is an important process, we chose the long-term soil acidification model (LTSAM) which includes the changes in soil pH and ion concentrations, to simulate the effect of acid deposition on the study area. The LTSAM was developed based on the alkalinity conservation and the Ulrich buffering theory (De Vries *et al*., 1989; An and Huang, 1999) and could describe calcareous and non-calcareous soil responses to acidic deposition using moderate input data. The model incorporates the SO_4^{2-} adsorption/desorption processes and includes ten major ions. In addition, the model consists of a set of equilibrium equations, such as mass balance equations, the charge balance equation. Special emphasis is placed on the Ulrich buffering ranges, the alkalinity balance equation and the soil sulfate adsorption.

The CENTURY is one of the terrestrial biogeochemistry models, and it can simulate the relationship among climate, disturbance, vegetation, soil, residue and soil organic matter (Parton *et al*., 1988; 1993; 1995). In this study, the aluminum toxicity factor is added to the CENTURY model to simulate the response of the forest ecosystem to changing acid deposition in the study area. The simulation covers from 2008 to 2110, and five scenarios of acid depositions (–50%, –30%, no change, +50% and +100%) were designed.

2.3.2 Data collection

Data of the amount and the chemical properties of precipitation, together with soil physical and chemical parameters are applied as model input data. Most of the model input data were derived from observed results taken within the study area. Precipitation samples were collected by an automatic sampler during the period of 2007–2008 and then analyzed for their chemical properties using Dionex Ion Chromatography (DX-600, USA). Soil water samples were collected at different soil depths (20 cm, 40 cm and 60 cm), one after every precipitation event. Soil samples were collected at 40 sites in the study area. A total of 40 soil samples and 111 soil water samples were analyzed for their physical and chemical properties and then utilized for the model simulations.

The remaining related parameters are referred from the following literature. The soil-weathering rate was obtained from Duan *et al*. (2000). The selective ion exchange coefficient was calculated using the proportion of ion concentrations in the soil solution and the exchangeable base content in the soil. The $Al(OH)_3$ content in calcareous soils was calculated as 5% of clay (Xiong and Li, 1987). The fraction of sand, silt and clay in the soil was 0.462, 0.323 and 0.215, respectively (Larssen *et al*., 1998). The fraction of the net primary productivity (NPP) allocation was referred from Feng *et al*. (1999). The average monthly precipitation data, the maximum temperature and minimum temperature from 1951 to 2008 were obtained from the China Meteorological Data Sharing Network (http://cdc.cma.gov.cn/), which were derived from the observation sites in Guiyang City.

3 Model Validation

The applicability of the models on the experimental area was tested before the model simulation of the projections. We compared the simulated results with the observed results as well as the results from previous studies in the area.

3.1 Simulation of soil acidification (LTSAM)

The key input parameters for LTSAM include chemical compositions of the precipitation, soil depth, soil bulk density, soil weathering rate, cation exchange capacity (CEC), the maximum absorption capacity and half saturated concentration for absorption of SO_4^{2-}, and base saturation. The soil weathering rate was derived from Duan (2002). All the other physical and chemical properties of the soil were measured in 2007 at the study area. The measurements of acid deposition in 2008 were input into the model and the model was run for one year. Accordingly, the soil chemical data in 2008 were calculated and could be compared with our observations in 2008. And the applicability of the model could therefore be tested.

The results show that the model reflects the changes in the chemical properties of local soil (Fig. 2). All of the calculated ion concentrations (with an accuracy of 0.01 mmol/L) are in the range of actual observations, close to the measured mean values. The calculated pH value of the pine forest soil is in the range of 4.3–4.4. According to the Ulrich buffering theory, the soil is in the transition stage between the positive ion exchange buffering and aluminum buffering.

3.2 Simulation of biomass and production (CENTURY)

The key input parameters for CENTURY include mean monthly maximum temperature, mean monthly minimum temperature and mean monthly precipitation from 1951 to 2008, soil bulk density, soil texture, soil pH and nutritive element content; maturation age, and the allocation ratio for productivity among different organs. The meteorological parameters were obtained from the China Meteorological Data Sharing Network (http://cdc.cma.gov.cn/). The data of soil texture was referred from Larssen *et al*. (1998), and the other soil properties are measured in the study area in 2007. The maturation age and the allocation ratio for productivity among different organs were referred from Feng *et al*. (1999).

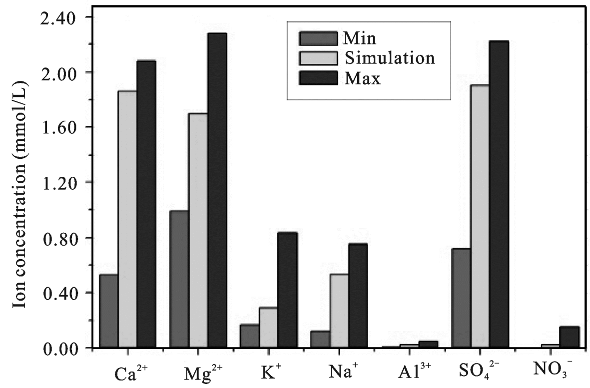

Fig. 2 Comparison of calculated and measured minimum (min) and maximum (max) of ion concentrations

The CENTURY model is initially run for 1000 years to reach a steady state. Then, the model scenario is designed to simulate the planting of the pine trees in 1957 and the growth of trees for 50 years. The total biomass and the biomass of various parts of trees calculated by the model are then compared with the observations in the experimental area (Table 2), which came from the ecological investigation organized by Beijing Normal University in 2007.

Table 2 shows that the simulated results are consistent with the observed results, and the relative error is less than 14%. In the model simulation, the total biomass of the pine trees is 3731.24 g/m^2, and the value agrees with the results from Feng *et al*. (1999), who reported the ranges of biomass being 2992–15 517 g/m^2. Our results were also compared with the study results using the Radiation Use Efficiency model and the Process model (Table 3), and the results of this study were between the

Table 2 Comparison of simulated results and observed results (g/m^2)

	Root	Branch	Leaf	Total
Simulated result	491.51	2782.52	457.21	3731.24
Observed result	482.71	2761.52	403.96	3648.19
Relative error (%)	1.8	0. 7	13.2	2.2

Table 3 Forest net primary productivity (NPP) simulated by different models (g C/(m^2·yr))

Simulated result	Reference	Year of publication
382	This study	
420–529	Sun and Zhu	1999
354–432	Piao and Fang	2001
370–445	Wang	2004
367–439	Zhu	2005
309	Yang	2010
179–824	Observed results[a]	2005

Note: a represents that the observed results came from the data of 690 observation sites during the period of 1989–1993 (Zhu, 2005)

results from Wang (2004) (BioGeochemical Cycles), Piao and Fang (2001), and Zhu (2005) (Carnegie-Ames-Stanford Approach model), lower than the results of Sun and Zhu (1999) (Radiation Use Efficiency model) and higher than the results of Yang *et al*. (2010) (Soil Acidification and Vegetation Growth model).

4 Results and Discussion

To explore the aluminum toxicity effect on individual plants, aluminum toxicity experiments are conducted. In addition, the long-term influences of aluminum toxicity induced by acid deposition on ecosystems are simulated by models in this study. The LTSAM and CENTURY models were run for approximately 100 years from 2008 to 2110. Five acid deposition scenarios were created and applied in our model simulation: 50% acid deposition reduction (–50%), 30% acid deposition reduction (–30%), maintaining the current level of acid deposition, 50% acid deposition increase (+50%) and doubling acid deposition (+100%).

4.1 Effect of aluminum toxicity on pine seedlings in indoor experiment

Among all organs of plants, roots are the primary target of phytotoxic aluminum. Once the root growth is inhibited, nutrients and water uptake are restricted and thus the whole plant is impacted. Aluminum toxicity mainly damages the root tip and lateral root, thickening and blackening the lateral root (Kinraide, 1988; Roy *et al*., 1988). Sivaguru and Horst (1998) found the distal transition zone (DTZ) to be the specific site of aluminum sensitivity, where both cell elongation and cell division are inhibited by aluminum (Doncheva *et al*., 2005). Macklon and Sim (1992) demonstrated that aluminum restricted the absorption of phosphorous by roots. Gunse *et al*. (1997) pointed out that aluminum enhancing the permeability of cell membrane could limit nutrients and water uptake. However, the mechanisms of aluminum-induced inhibition of root growth are still not clearly established and need further study.

The experimental results show that the effect of the Al^{3+} concentration on biomass varied significantly among different groups but has the same trend within the group with the same pH (Table 4). The growth of the plant is promoted under low Al^{3+} concentrations and limited under high Al^{3+} concentrations. For the group with the pH of 3.00, the plant biomass obtains the relative maximum value when the Al^{3+} concentration is 0.20 mg/L, and the values of the aboveground biomass and underground biomass are 0.074 g and 0.019 g, respectively. When the Al^{3+} concentration is 50 mg/L, compared with the group with the Al^{3+} concentration of 0.02 mg/L, the inhibition ratios are 27.1% and 22.2%, respectively. For the group with the pH of 4.50, the plant biomass obtains the maximum value when the Al^{3+} concentration is 1.00 mg/L, which is higher than the concentration observed in the group with the low pH value. It indicates that the aluminum toxicity is relieved when the solution pH value increases from 3.00 to 4.50. When the Al^{3+} concentration is 15.00 mg/L, the inhibition ratios of the aboveground and underground biomass are 22.1% and 23.8%, respectively. For the group with the pH of 6.00, the maximum value of the plant biomass appears in the CK group. An important reason is that the aluminum phosphate is undissolved, which inhibits the plant from absorbing phosphorus, and the growth of the plant is suppressed. When the Al^{3+} concentration is 1.00 mg/L, compared with the CK group, the inhibition ratios of the aboveground and underground biomass are 20.6% and 20.8%, respectively. Thus according to our experimental results, the vegetation biomass would decline dramatically if the severe acid deposition proceeds and the pH value continuously decreases in the future.

Table 4 Aboveground and underground biomass of pine seedlings (g)

$[Al^{3+}]$ (mg/L)	pH					
	3.00		4.50		6.00	
	Aboveground	Underground	Aboveground	Underground	Aboveground	Underground
0.02	0.070±0.000	0.018±0.000	0.073±0.004	0.018±0.0033	0.091±0.008	0.022±0.0057
0.20	0.074±0.012	0.019±0.0063	0.082±0.000	0.020±0.0000	0.079±0.022	0.018±0.0056
1.00	0.067±0.005	0.018±0.0010	0.086±0.010	0.021±0.0025	0.077±0.014	0.019±0.0032
10.00	–	–	0.073±0.017	0.017±0.0052	–	–
15.00	–	–	0.067±0.011	0.016±0.0052	–	–
20.00	0.059±0.004	0.017±0.0003	–	–	–	–
50.00	0.051±0.005	0.014±0.0017	–	–	–	–
CK	0.028±0.004	0.014±0.0016	0.074±0.009	0.021±0.0008	0.097±0.015	0.024±0.0004

Note: '–' means that this experiment is not arranged

As to the root elongations of pine seedlings, both groups with the pH of 3.00 and 4.50 exhibit the similar trends (Table 5): low Al^{3+} concentrations promote the root elongation and high Al^{3+} concentrations restrict that. Thus the inhibited ratio was calculated based on the value derived from the experiment with the optimum Al^{3+} concentration for seedling elongation. For the group with the pH of 3.00, the optimum Al^{3+} concentration is 0.20 mg/L. When the Al^{3+} concentration is 50.00 mg/L, the inhibited ratio reaches 40.6%. The reason for this high result is that the root elongation of pine seedlings is strongly inhibited at high Al^{3+} concentrations. For the group with the pH of 4.50, the optimum Al^{3+} concentration is 0.20 mg/L, as well. The inhibition ratio of the elongation is approximately 12.4% when the Al^{3+} concentration is 15.00 mg/L. For the group with the pH of 6.00, the group with the Al^{3+} concentration of 0.02 mg/L has the maximum elongation for the same reason explained above. We also found that in a solution with the same Al^{3+} concentration, the root elongation of the group with the pH of 3.00 is lower than that of the group with the pH of 4.50, which indicates that the inhibitory effect increases with the acidity. This result also shows that acid deposition may enhance the aluminum toxicity.

Figure 3 shows the relationship between the aluminum increment in underground pine seedlings and the aluminum concentration in the nutrient solution (the aluminum increment in aboveground pine seedlings which is not shown here exhibits a similar trend). In this study, the interaction of pH and Al^{3+} in the natural soils was not considered because the concentrations of H^+ and Al^{3+} were arbitrarily set in the indoor experiments. When the Al^{3+} concentration is low, the absorption of the Al^{3+} changes within a relatively narrow range and does not increase with the rise of the Al^{3+} concentration. It shows that the pine tree is aluminum tolerant vegetation and the absorption of the Al^{3+} is passive. After the Al^{3+} concentration reaches 10.00 mg/L, the absorption

Table 5 Root elongations of pine seedlings (cm)

$[Al^{3+}]$ (mg/L)	pH		
	3.00	4.50	6.00
0.02	181.81±38.83	198.25±65.23	198.45±76.37
0.20	200.54±85.46	203.91±63.57	194.86±38.06
1.00	180.12±57.33	198.87±45.83	186.37±44.65
10.00	–	179.07±64.78	–
15.00	–	178.63±55.67	–
20.00	156.99±13.16	–	–
50.00	119.18±35.62	–	–
CK	90.95±30.10	182.79±34.53	198.18±64.55

Note: '– ' means that this experiment is not arranged

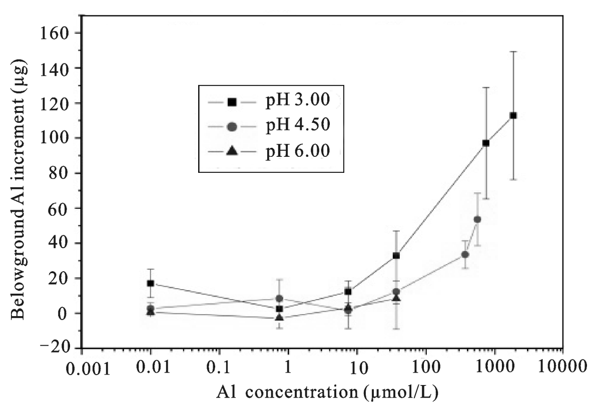

Fig. 3 Relationship between aluminum (Al) increment in underground pine seedlings and aluminum concentrations in solutions

rate of Al^{3+} begins to increase quickly and the pine seedling with the pH of 3.00 absorbs clearly more Al^{3+} than the solutions with higher pH value. It indicates that the acid environment can promote the absorption of Al^{3+} and enhance the aluminum toxicity effect.

According to the results of the experiment, for the group with the pH of 4.50 (approximate to the observed soil water pH), the threshold value of Al^{3+} concentration for aluminum toxicity to come into effect is approximately 1.00 mg/L for the biomass of pine seedlings and 0.20 mg/L for the root elongations, respectively. Since the root elongations observed in the experiment with Al^{3+} concentration of 1.00 mg/L differed not much from those observed from the experiment with the optimum Al^{3+} concentration, the Al^{3+} concentration of 1.00 mg/L was chosen in this study as the threshold value for aluminum toxicity. This value was applied to design the aluminum toxicity factor, which was then added into the CENTURY model to simulate the dynamics of forest ecosystems in the study area.

4.2 Effect of acid deposition on soil in model simulation

The simulated results show that the soil pH value decreases when the total acid deposition increases (Fig. 4a). The reason is that a large number of H^+ is imported to the soil and destroys the initial buffering condition. Then, the soil quickly adapts to the new deposition condition and corrects the buffering curve, thus avoiding the sharp decrease of the soil pH value. Because the buffering of the soil in the study area is in the stage between positive ion exchange buffering and aluminum buffering and the Al^{3+} is not sufficient to buffer the imported H^+ from acid deposition, the pH value decreases slowly. Then, the soil enters the aluminum buffering stage and the chemistry reaction in the soil is enough to buffer the imported H^+, thus the pH value stays constant during this period. As shown in Fig. 4a, under the scenario in which the acid deposition is doubled, the soil completes the transition from positive ion exchange buffering to aluminum buffering in 2110. The pH value stay steady

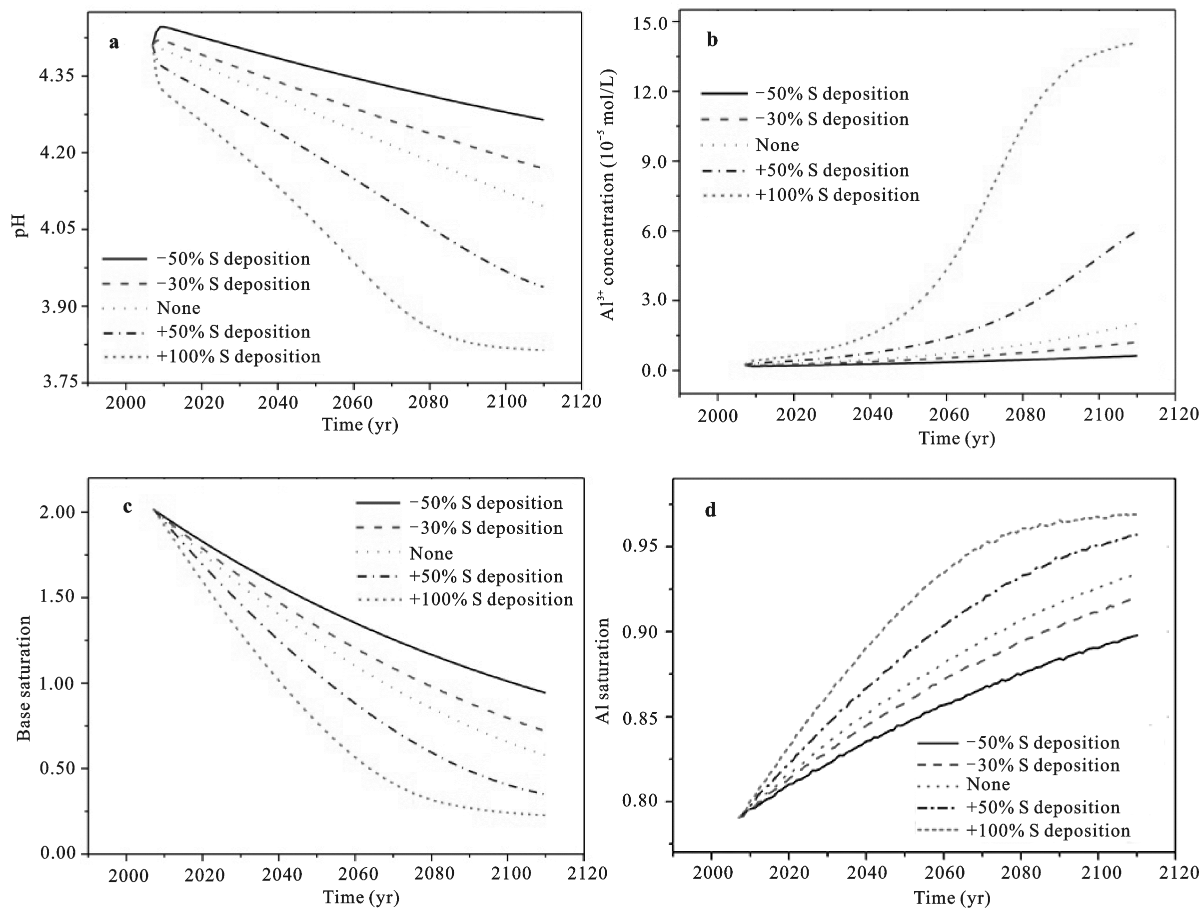

Fig. 4 Trend of soil chemical properties under different acid deposition scenarios. a, soil pH; b, Al^{3+} concentration; c, base saturation; d, aluminum (Al) saturation. ′S′ represents the deposition of sulfuric acid

at 3.81 in the aluminum buffering stage, and this is consistent with the Ulrich buffering theory (Ulrich, 1989). The soil will enter the ferrum buffering stage if the aluminum oxide and aluminum hydroxide are depleted.

Figure 4a also shows that, under the scenario with current deposition, the soil pH decreases slowly and has no significant change in the short period. Under the scenarios with the increased deposition, the changing rate of the soil pH increases with the deposition quantity. The decrease of the soil pH may affect the ion content and chemistry reaction in the soil and damage the ecosystem function. Under the scenarios with decreased deposition, the decreasing rate of the soil pH is lower than that under the scenario with current deposition. Under the scenarios with the –30% and –50% acid depositions, the soil pH is relatively stable at 4.17 and 4.26, respectively after the simulation has been completed.

As shown in Fig. 4b, when the acid deposition increases, the Al^{3+} concentration does not increase immediately. The reason is that the increment of Al^{3+} concentration depends on the H^+ import and the dissolution equilibrium constant of aluminum hydroxide. However, the Al^{3+} in the soil solution may accumulate with the increase of acid deposition over the long-term, which may damage the plant more seriously.

In Fig. 4b, the increasing rate of Al^{3+} concentration was higher under the scenarios that have relatively higher acid deposition, and the increasing speed accelerates with time. In the beginning of the simulation, the Al^{3+} concentration is very low, thus the exchange quantity with positive ions is small and the amount of Al^{3+} remaining in the soil is very little. Then, the quantity of Al^{3+} accumulated in the soil increases, and the Al^{3+} absorbed by soil particles increases as well. The comparison between the two scenarios with increased acid deposition (+100% and +50% depositions) shows that, in the early stage, the changing trend of Al^{3+} concentration accumulated in the soil is similar. Under the scenario with deposition doubled, the Al^{3+} concentration remain steady around 0.14 mmol/L in the end of the simulation because the exchange reaction and dissolution reaction in soil can meet the needs to buffer the imported H^+. Under the scenarios with –30% and –50% deposition, the increasing rate of Al^{3+} concentration is slowed down and the Al^{3+} concentrations of the soil are 12.2 μmol/L and 6.28 μmol/L, respectively, when the simulation is completed. The soil may stay in the transitional stage for a long time and the dominating buffering process is positive ion exchange. In this way, the appearance of an aluminum toxicity effect is inhibited, which is a benefit for the long-term development of the ecosystem.

The positive ions absorbed by the soil can be divided into two types: base cations, such as Ca^{2+}, Mg^{2+}, Na^+, K^+ and NH_4^+; and other ions, such as H^+ and Al^{3+}. The exchange capacity is the total absorbed quantity. Base saturation is the percentage that base ions take up of all the positive ions exchanged and it is the main expression of soil acidification. The base saturation decreases when the soil acidification is aggravated, and the plant may be damaged by the increased Al^{3+} concentration. Aluminum saturation is the percentage that exchangeable Al^{3+} takes up of CEC, and it is used as an index to represent the aluminum toxicity effect (Brenes and Pearson, 1973; Pavan *et al*., 1982; Abruna *et al*., 1983).

In this study, five scenarios of different acid deposition are simulated to observe the changes of base saturation and aluminum saturation. From Fig. 4c, it can be found that the higher the deposition quantity, the higher the decreasing speed of base saturation. The increased acid deposition leads to the acceleration of the activated speed of aluminum oxide and aluminum hydroxides and increases the Al^{3+} concentration in the soil solution. The Al^{3+} exchange to the positive ions is absorbed by the soil colloid and then remains in the soil system, which leads to the decreasing of the exchangeable positive ions and the increasing of the percentage of occupied Al^{3+}. This will be toxic to the plants and result in less nutrient uptake by plants and ultimately forest ecosystem deterioration.

When the deposition is doubled (+100% increase of deposition), the base saturation decreases rapidly (Fig. 4c) and the aluminum saturation increases rapidly (Fig. 4d) until a constant (0.95) is reached. It indicates that the Al^{3+} in the soil has reached a dynamic balance among the aluminum oxide and aluminum hydroxide dissolution, the soil colloid absorption exchange and the underground stream output. This balance shows that the soil has entered the aluminum buffering stage.

4.3 Effect of acid deposition on pine forest ecosystem

Acid deposition solubilizes aluminum into a phytotoxic form, which is a major growth-limiting factor for roots in acid soils. Such a reduction of roots growth typically decreases the nutrients and water taken up by plants and results in poor growth by disturbing plant metabolism, which will ultimately cause the forest ecosystem to deteriorate. The model simulation of this study is designed to quantify this influence under different acid deposition scenarios.

Though varying under different scenarios, vegetation biomass changes show the same trend that more deposition leads to less biomass according to the simulation by CENTURY model (Fig. 5). The most serious impact occurs on leaf biomass, and under the scenarios with increased acid deposition, the leaf biomass decreases significantly because the growth of new leaf is slower than the falling of existing leaf. The impact of acid deposition on plant roots may decrease the nutrition absorption speed, thus the nutrition transported to the leaf of plant and the leaf rebuilding are limited. Branches also suffer from acid deposition. The change trend of tree biomass is similar to that of branch biomass because the branch biomass occupies a large percentage of the tree biomass.

The change trend of the vegetation NPP is similar to that of the vegetation biomass (Fig. 6a). A decrease in root biomass reduces the absorption of nutrients and a decrease in leaf biomass reduces plant photosynthesis. Both reduction leads to a decrease in vegetation NPP. Under the scenarios with increased acid deposition, the damage is more serious and the speed of the NPP decrease is higher than that under the scenario with unchanged acid deposition. On the contrary, lower acid deposition may relieve the aluminum toxicity; the plant

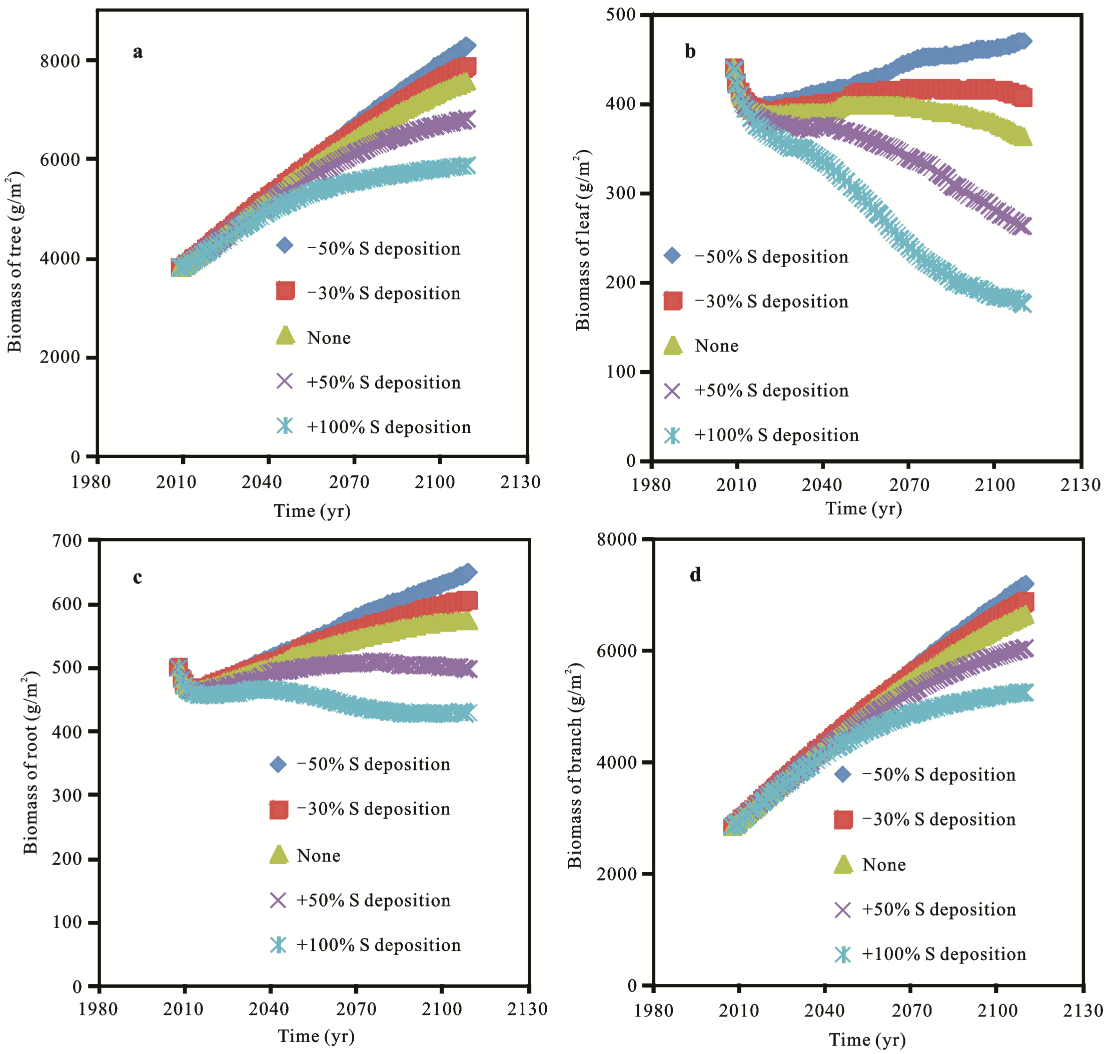

Fig. 5 Biomass of vegetation in different organs. a, biomass of tree; b, biomass of leaf; c, biomass of root; d, biomass of branch. 'S' represents the deposition of sulfuric acid

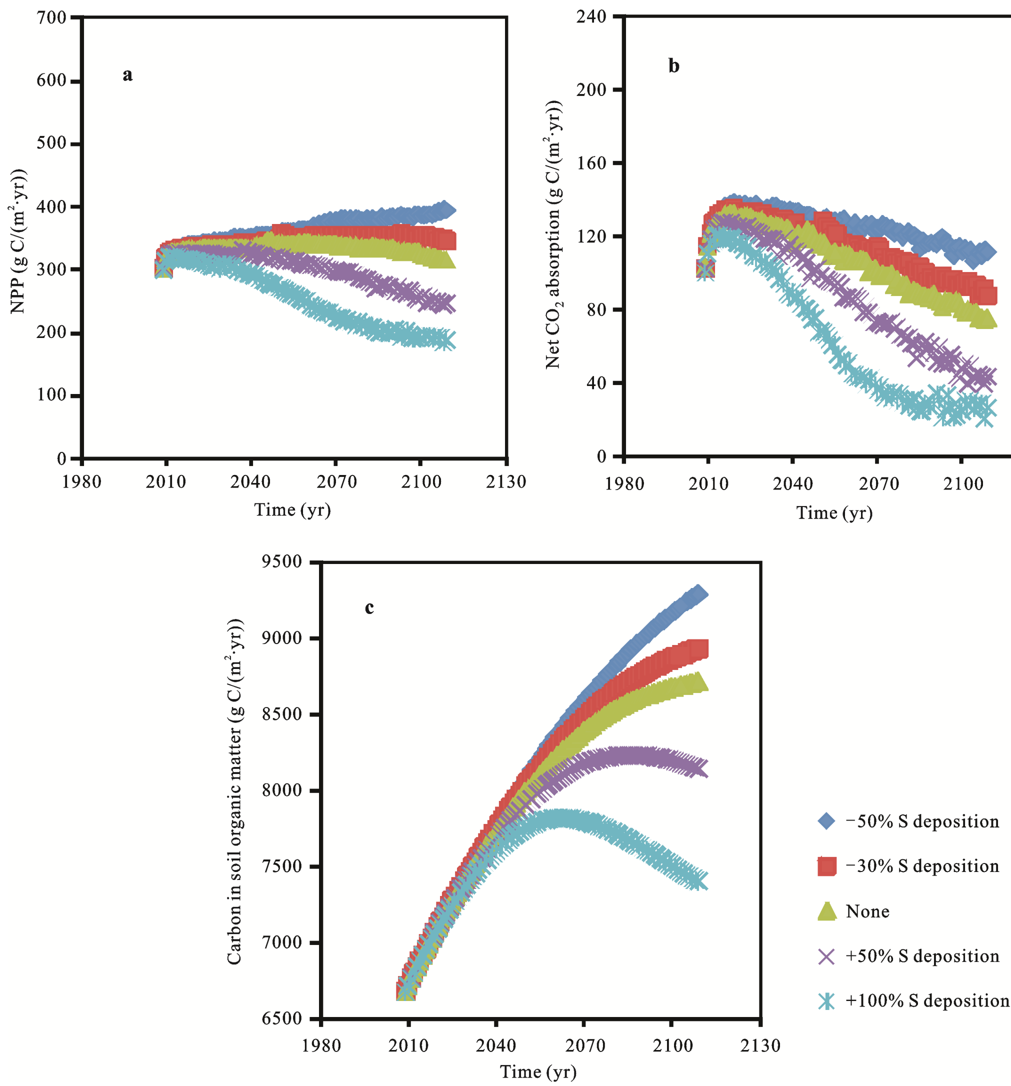

Fig. 6 Trend of some processes of carbon cycle in pine forest ecosystem. a, net primary productivity (NPP); b, net CO_2 absorption; c, carbon in soil organic matter. 'S' represents the deposition of sulfuric acid

biomass increases slightly and the vegetation NPP remains the same. The net CO_2 absorption of an ecosystem is the vegetation NPP minus the respiration CO_2 of soil microorganisms. The vegetation NPP is closely related to the CO_2 absorption, thus the net CO_2 absorption exhibits the same trend as the vegetation NPP (Fig. 6b).

Under different acid deposition scenarios, the soil organic carbon content shows a slightly different trend (Fig. 6c). The soil organic carbon increases under the scenarios with decreased acid deposition, compared with that in the scenario with unchanged acid deposition; While under the scenarios with increased acid deposition, the impact of acid deposition is significant, in particular for the scenario with doubled acid deposition. The soil organic carbon increases slowly in the beginning and then decreases drastically. The acid deposition decreases the vegetation biomass and NPP, thus the organic matter transported to the soil decreases, which leads to the decrease of the soil organic carbon content.

5 Conclusions

In this study, we designed an indoor experiment to explore how the aluminum toxicity affects the individual plants. Based on the experimental results, the LTSAM was used to simulate the impact of acid deposition on soil chemistry in Longli of Guizhou Province, southwestern China. Then the LTSAM and CENTURY model were coupled to simulate the influence of aluminum toxicity on forest ecosystems under acid deposition.

The indoor aluminum toxicity experiment shows that aluminum may restrict plant growth and the acidic conditions may aggravate this effect. This restriction is observed in the decrease of pine seedling biomass and root elongation. For the pine seedling group with the pH of 3.00, when the Al^{3+} concentration is 50.00 mg/L, compared with the group with the Al^{3+} concentration of 0.02 mg/L, the inhibition ratio of aboveground and underground biomass is 27.1% and 22.2%, respectively. Under the same condition, the inhibited ratio of root elongation is as high as 40.6%. When the Al^{3+} concentration is 10.00 mg/L, the pine seedling with the pH of 3.00 absorbs more Al^{3+} than the other two solutions with higher pH values, indicating that the acidic environment can promote the absorption of Al^{3+} and enhance the aluminum toxicity effect.

The simulated results indicate that the degree the soil acidification enhances under the scenarios of increased acid deposition: the pH value decreases, the soil Al^{3+} concentration increases, and the nutrient ions in soil solution decrease because of the large amount of H^+ imported into the soil system. The increased acid deposition also has a negative impact on the forest ecosystem. It reduces the absorption of nutrients and the photosynthesis rates of leaves, which causes the vegetation biomass and NPP to decrease. And this in turn results in a decrease in the supply of soil decomposition material as well as the soil organic matter.

References

Abruna F, Rodriquez J, Silva S, 1983. Crop response to soil acidity factors in Ultisols and Oxisols in Puerto Rico.VI. Grain-sorghum. *Journal of Agriculture of the University of Puerto Rico*, 67(1): 28–38.

An J L, Huang M Y, 1999. Long-term soil acidification model (LTSAM) development and application for analyzing soil responses to acidic deposition. *Water*, *Air* & *Soil Pollution*, 110: 255–272. doi: 10.1023/A:1005084803350

Brenes E, Pearson R W, 1973. Root responses of three Gramineae species to soil acidity in an Oxisol and an Ultisol. *Soil Science*, 116(4): 295–302.

Cao Hongfa, Gao Jixi, Shu Jianmin, 1992. Study on the response of Pinus Massoniana seedling to aluminum. *Acta Ecologica Sinica*, 12(3): 209–246. (in Chinese)

Chen C W, Gherini S A, Peters N E *et al*., 1984. Hydrologic analyses of acidic and alkaline lakes. *Water Resources Research*, 20(12): 1875–1882.

Chou Rongliang, Dong Hanying, Lv Yuena *et al*., 1997. Soil sensitivity to acid deposition in South China VII. Cation leaching and buffering mechanism. *Environmental Science*, 18(5): 23–27. (in Chinese)

Cosby B J, Wright R F, Hornberger G M *et al*., 1985. Modelling the effects of acid deposition: estimation of long-term water quality responses in a small forested catchment. *Water Resources Research*, 21(11): 1591–1602.

De Vries W, Posch M, Kämäri J, 1989. Simulation of the long-term soil response to acid deposition in various buffer ranges. *Water*, *Air*, & *Soil Pollution*, 48: 349.

Doncheva S, Amenós M, Poschenrieder C *et al*., 2005. Root cell patterning: a primary target for aluminum toxicity in maize. *Journal of Experimental Botany*, 56(414): 1213–1220. doi: 10.1093/jxb/eri115

Duan Lei, 2002. *Study on Mapping Critical Loads of Acid Deposition in China*. Beijing: Tsinghua University. (in Chinese)

Duan Lei, Hao Jiming, Jenkins A *et al*., 2000. Mapping critical loads of acid deposition for soils in China. *Tsinghua Science and Technology*, 5(3): 270–278. (in Chinese)

Edwards J H, 1976. Aluminum toxicity symptoms in peach seedlings. *Journal of the American Society for Horticultural Science*, 101: 139–142.

Fang Jingyun, 2001. Dynamic forest biomass carbon pool in China and their significance. *Acta Botanica Sinica*, 43(9): 967–973. (in Chinese)

Feng Zongwei, 1993. *The Influence of Acid Rain on Ecosystem*: *Study of Acid Rain in Southwest China*. Beijing: China Science and Technology Press, 177. (in Chinese)

Feng Zongwei, Wang Xiaoke, Wu Gang, 1999. *The Biomass and Productivity of Chinese Forest Ecosystem*. Beijing: Science Press, 398. (in Chinese)

Gherini S A, Mok L, Hudson R J M *et al*., 1985. The ILWAS model: formulation and application. *Water*, *Air*, & *Soil Pollution*, 26: 425–459. doi: 10.1007/978-94-009-5498-4_7

Goldstein R A, Gherini S A, Chen C W *et al*., 1984. Integrated acidification study (ILWAS): a mechanistic ecosystem analysis and discussion. *Philosophical Transactions of the Royal Society of London. Series B*, *Biological*, 305: 409–425.

Guizhou Forest Survey Academy, 2008. Forest Management Plan in Longli, Guizhou (2008–2017). Guiyang: Guizhou Forest Survey Academy. (in Chinese)

Guizhou Province Environmental Protection Bureau, 2009. Guizhou Environmental Status Bulletin in 2008. Guiyang: Guizhou Province Environmental Protection Bureau. (in Chinese)

Gunse B P, Schenieder C, Barcelo J, 1997. Water transport properties of roots and root cortical cells in proton and Al-stressed maize varieties. *Plant Physiology*, 113(2): 595–602.

Henriksen A, 1979. A simple approach for identifying and measuring acidification of freshwater. *Nature*, 278: 542–545. doi: 10.1038/278542a0

Hoagland D R, Arnon D I, 1950. The water-culture method for growing plants without soil. *California Agricultural Experiment Station*, *Circular*, 347: 1–32.

Jiang Wenhua, Zhang Sheng, Chen Gangcai *et al*., 2002. Effect of acid deposition on soil and vegetation of forest ecosystem in

Nanshan of Chongqing. *Research of Environmental Sciences*, 15(6): 8–11. (in Chinese)

Johnson A H, Turner J, Kelley J M, 1982. Effects of acid rain on forest nutrient status. *Water Resources Research*, 18(3): 449–461.

Kinraide T B, 1988. Proton extrusion by wheat roots exhibiting severe aluminum toxicity symptom. *Plant Physiology*, 88(2): 418–423.

Larssen T, Xiong J L, Vogt R D *et al*., 1998. Studies of soils, soil water and stream water at a small catchment near Guiyang, China. *Water*, *Air* & *Soil Pollution*, 101: 137–162. doi: 10.1023/A:1004985209931

Liao Bohan, Jiang Qing, 2002. Acid deposition and acidification of forest soils in southern China. *Agro-environmental Protection*, 21(2): 110–114. (in Chinese)

Liu Ruoan, Liu Houtian, 1995. Effect of acidity and aluminum on the growth of PinusMassoniana seedlings. *Acta Botanica Sinica*, 37(2): 154–158. (in Chinese)

Macklon A E S, Sim A, 1992. Modifying effects of non-toxic levels of aluminum on the uptake and transports of phosphate in ryegrass. *Journal of Experimental Botany*, 43(7): 915–923. doi: 10.1093/jxb/43.7.915

National Environment Protection Agency, 1996. *Acid Deposition and Its Influence Control Technology*. Nanjing: Hohai University Press, 19. (in Chinese)

Parton W J, Ojima D S, Schimel D S, 1995. Models to evaluate soil organic matter storage and dynamics. In: Carter M T *et al*. (eds.). *Structure and Organic Matter Storage in Agricultural Soil. Advances in Soil Science*. New York: Lewis Publishers, 421–448.

Parton W J, Scurlock J M O, Ojima D S *et al*., 1993. Observation and modeling of biomass and soil organic matter dynamics of the grassland biome worldwide. *Global Biogeochemistry Cycles*, 7(4): 785–809. doi: 10.1029/93GB02042

Parton W J, Stewart J W B, Cole C V, 1988. Dynamics of C, N, P and S in grassland soil: a model. *Biogeochemistry*, 5(1): 109–131.

Pavan M A, Bingham F T, Pratt P F, 1982. Toxicity of aluminum to coffee in Ultisols and Oxisols amended with $CaCO_3$, $MgCO_3$, and $CaSO_4/2H_2O$. *Soil Science Society of America Journal*, 46(6): 1201–1207.

Piao Shilong, Fang Jingyun, Guo Qinghua, 2001. Application of CASA Model to the estimation of Chinese terrestrial net primary productivity. *Chinese Journal of Plant Ecology*, 25(5): 603–608. (in Chinese)

Roy A K, Sharma A, Talukder G, 1988. Some aspects of aluminum toxicity in plants. *Botanical Review*, 54: 145–177.

Sivaguru M, Horst W J, 1998. The distal part of the transition zone is the most aluminum sensitive apical root zone of maize. *Plant Physiology*, 116(1): 155–163.

Sun Rui, Zhu Qijiang, 1999. Net primary productivity of terrestrial vegetation—a review on related researches. *Chinese Journal of Applied Ecology*, 10(6): 757–760. (in Chinese)

Tang Dagang, Wang Wei, Pang Yanbo, 1996. Contribution of NO_X to acid rain in Minnan area. *Research of Environmental Sciences*, 9(5): 38–40. (in Chinese)

Tomlinson G H, 1983. Air pollution and forest decline. *Environmental Science and Technology*, 17(6): 246–256.

Ulrich B, 1989. Effects of acidic precipitation on forest ecosystems in Europe. In: Adriano *et al*. (eds.). *Acidic Precipitation*, *Biological and Ecological Effects*. New York: Springer, 189–272.

Ulrich B, 1990. Waldsterben: forest decline in West Germany. *Environmental Science and Technology*, 24(4): 436–441.

Ulrich B, Mayer R, Khanna P K, 1980. Chemical changes due to acid precipitation in a Loess-derived soil in Central Europe. *Soil Science*, 130(4): 193–199.

Wagatsuma T, Ezoe Y, 1985. Effect of pH on ionic species of aluminum in medium and on aluminum toxicity under solution culture. *Soil Science and Plant Nutrition*, 31(4): 547–561. doi: 10.1080/00380768.1985.10557463

Wang Junbang, 2004. *Chinese Terrestrial Net Ecosystem Productive Model Applied Remote Sensing Data*. Hangzhou: Zhejiang University, 91. (in Chinese)

Wright R F, Henriksen A, 1983. Restoration of Norwegian lakes by reduction in sulphur deposition. *Nature*, 305: 422–424.

Xiong Yi, Li Qingkui, 1987. *China Soil*. Beijing: Science Press, 19–40. (in Chinese)

Yang Shengtian, Sheng Haoran, Song Wenlong *et al*., 2010. The structure of the soil acidification spatial information module and its application at an experiment station in Longli of Guizhou Province. *Acta Scientiae Circumstantiae*, 30(1): 24–33. (in Chinese)

Zhang Guanghua, Zhao Dianwu, 1989. *Acid Rain*. Beijing: China Environmental Science Press. (in Chinese)

Zhang Junping, Zhang Xinmin, Zeng Chunjun *et al*., 2010. Studying advances of effects of acid rain on acidifying of ecosystem. *Journal of Agro-Environment Science*, 29(z1): 245–249. (in Chinese)

Zhao Dianwu, Zhang Xiaoshan, Xiong Jiling, 1992. Determination of critical load for acid deposition using MAGIC model. *China Environmental Science*, 12(2): 93–97. (in Chinese)

Zhu Wenquan, 2005. *Estimation of Net Primary Productivity of Chinese Terrestrial Vegetation Based on Remote Sensing and Its Relationship on Climate Change*. Beijing: Beijing Normal University, 163. (in Chinese)