Effect of Simulated Acid Rain on Potential Carbon and Nitrogen Mineralization in Forest Soils[*1]

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ABSTRACT

Acid rain is a serious environmental problem worldwide. In this study, a pot experiment using forest soils planted with the seedlings of four woody species was performed with weekly treatments of pH 4.40, 4.00, 3.52, and 3.05 simulated acid rain (SAR) for 42 months compared to a control of pH 5.00 lake water. The cumulative amounts of C and N mineralization in the five treated soils were determined after incubation at 25 °C for 65 d to examine the effects of SAR treatments. For all five treatments, cumulative CO_2-C production ranged from 20.24 to 27.81 mg kg^{-1} dry soil, net production of available N from 17.37 to 48.95 mg kg^{-1} dry soil, and net production of NO_3^--N from 9.09 to 46.23 mg kg^{-1} dry soil. SAR treatments generally enhanced the emission of CO_2-C from the soils; however, SAR with pH 3.05 inhibited the emission. SAR treatments decreased the net production of available N and NO_3-N. The cumulative CH_4 and N_2O productions from the soils increased with increasing amount of simulated acid rain. The cumulative CO_2-C production and the net production of available N of the soil under *Acmena acuminatissima* were significantly higher ($P \leq 0.05$) than those under *Schima superba* and *Cryptocarya concinna*. The mineralization of soil organic C was related to the contents of soil organic C and N, but was not related to soil pH. However, the overall effect of acid rain on the storage of soil organic matter and the cycling of important nutrients depended on the amount of acid deposition and the types of forests.

Key Words: forest soils, mineralization, organic C, organic N, simulated acid rain

INTRODUCTION

Mineralization processes of soil organic C and N are important in regulating the cycling of nutrients in ecosystems and global carbon circulation (Tiessen *et al.*, 1994; Johnson, 1995; Lal, 2001). Many geographic factors and soil properties, such as moisture, temperature, texture, inorganic nutrient supply, and pH, affect the mineralization processes (Weier and Gilliam, 1986; Motavalli *et al.*, 1995; Šimek *et al.*, 2002). Accurate modeling of soil C and N mineralization and their responses to the changes in environment requires a detailed understanding of the factors that control or influence these biogeo- chemical processes. Since the last century, acid deposition, as an important threat to many ecosystems (Karajick, 2001), has been studied worldwide (Seip *et al.*, 1999; Streets *et al.*, 1999; Rodhe *et al.*, 1992; Kato, 1996; Hettelingh *et al.*, 1995; Lacaux *et al.*, 1987; Cogbill and Likens, 1974). Field and laboratory observations show that acid deposition decreases soil pH, increases nutrient loss (Makarov and Kiseleva, 1995) and heavy element activation (Derome and Lindroos, 1998; Michopoulos, 1999), and alters micro- bial community structure (Pennanen *et al.*, 1998; Pennanen, 2001). Despite chronic N deposition that reduces soil respiration (Burton *et al.*, 2004) and suppresses the mineralization of native C (Hagedorn

et al., 2001), the effect of acid deposition on the mineralization of soil organic C and N has not been fully explored.

The mineralization of soil organic matter (SOM) is an essential biological process. Acid deposition might directly affect the mineralization of SOM by changing microbial activity (Zelles *et al.*, 1987; Blagodatskaya and Anderson, 1999), enzyme activity (Haynes and Swift, 1988; Shah *et al.*, 1990), and the composition of the microbial population (Shah *et al.*, 1990; Nodar *et al.*, 1992; Pennanen *et al.*, 1998; Pennanen, 2001; Bååth and Anderson, 2003). Although there are studies on the effect of acid deposition on microbial biomass C, results from those studies are inconsistent. For example, Blagodatskaya and Anderson (1999) found that the extent of microbial biomass C decrease or CO_2 increase corresponded with the amount of initial H^+ ions input. In contrast, Pennanen *et al.* (1998) indicated that treatments of simulated acid rain alone or combined with heavy metals did not affect total microbial biomass. This might be because a bacterial community can adapt to its new environmental conditions, such as more acidic conditions, or the microbial biomass can be re-established with time (Blagodatskaya and Anderson, 1999; Pennanen *et al.*, 1998).

By decreasing soil pH, acid deposition might indirectly influence the content and mineralization of SOM because soil pH has a significant effect on the formation and mineralization of SOM (van Bergen *et al.*, 1998; Nierop and Vertraten, 2003; Motavalli *et al.*, 1995; Ellis *et al.*, 1998). However, results of existing studies with regard to the effect of soil pH on SOM are often conflicting. For example, the mineralization of C increased with soil liming and decreased after acidification (Motavalli *et al.*, 1995; Chandini *et al.*, 1996; Ellis *et al.*, 1998). The negative correlation between soil organic C and soil pH (Spain, 1990) implied that the decrease of soil pH promoted an increase in SOM. However, in cottonwood stands, Lee and Jose (2003) observed a negative correlation between annual soil respiration rates and soil pH. The total microbial biomass estimated by substrate-induced respiration (SIR) and phospholipid fatty acid (PLFA) technique was positively correlated to soil pH (Bååth and Anderson, 2003). This partially supports the hypothesis by Oades (1988) who predicted shorter C turnover times in acidic soils compared with calcareous soils. The fact that there is no definite answer to the effect of soil pH on mineralization of SOM (van Bergen *et al.*, 1998; Motavalli *et al.*, 1995) suggests that factors besides soil pH must be important and should be considered (Oades, 1988; Nierop and Vertraten, 2003).

The mineralization of SOM might be indirectly affected by acid deposition, which decreases nutrient supply (Cleveland *et al.*, 2002) and increases biologically toxic cations such as Al^{3+} (Berggren and Mulder, 1995; Beets *et al.*, 2002; Schwesig *et al.*, 2003). However, direct tests of this hypothesis have not been found in the literature so far. The objectives of this study were to compare the mineralization of organic C and N in soils treated with simulated acid rain and to identify how simulated acid rain influences the potential mineralization in different forest ecosystems.

MATERIALS AND METHODS

Site description

This study was conducted in the Dinghushan Biosphere Reserve (DHSBR), which lies in central Guangdong Province (23° 10′ N and 112° 34′ E), southern China. The reserve has a monsoon climate and is in a subtropical moist forest zone. The mean annual rainfall of 1 927 mm has a distinct seasonal pattern with 75% of it falling from March to August and only 6% from December to February (Huang and Fan, 1982). The average annual relative humidity is 80%; mean annual temperature is 21.0 °C with the highest average monthly temperature of 28.0 °C in July and the lowest average monthly temperature of 12.6 °C in January.

Two forest sites were selected for this study. One is a monsoon evergreen broadleaf forest at about 250–300 m above sea level (ASL), which occupies about 600 ha and has been protected from human interference for more than 400 years by monks in a local temple (Zhou *et al.*, 1986). The major species of this forest are *Castanopsis chinensis* Hance, *Schima superba* Gardn. et Champ., *Cryptocarya chinensis*

(Hance) Hemsl., *Cryptocarya concinna* Hance, *Acmena acuminatissima* (Bl.) Merr. et Perry, and *Machilus chinensis* (Champ. ex Benth.) Hemsl. in the crown layer, and *Calamus rhabdocladus* Burret, *Ardisia quinquegona* Bl., and *Hemigramma decurrens* (Hook.) Copel. in the understory, with tree heights ranging from 4 to 30 m and diameters from 5 to 163 cm (Wang *et al.*, 1982). The other is a pine forest planted in about 1930 at about 50–200 m ASL, which occupies 600 ha (Wang *et al.*, 1982), and is dominated by *Pinus massoniana* Lamb. The pine stand density ranges from 100 to 1 000 trees ha^{-1} with diameter ranging from 4 to 32 cm, heights from 3 to 11 m, and ages from 12 to 69 years. Understory species include grasses, ferns, vines, and shrubs, totaling 43 species (Brown *et al.*, 1995). The soil types of these two forests are acidic Latosols derived from sandstone. In the monsoon evergreen broadleaf forest, the depth of soil layer is more than 60 cm, but the soil depth under the pine forest is generally less than 30 cm. Some selected soil properties of these two forests are listed in Table I.

TABLE I

Some soil properties (0–10 cm depth) of the two forest sites selected

Property[a]	Monsoon evergreen broadleaf forest	Pine forest
Organic matter (g kg^{-1})	72.4±7.4	36.7±1.4
Total N (g kg^{-1})	2.5±0.2	1.1±0.1
Total C/N ratio	16.81±0.70	19.01±0.80
NO_3^- (mg kg^{-1})	66.14±1.2	59.86±34.3
SO_4^{2-} (mg kg^{-1})	9.28±1.3	7.18±1.2
Exchangeable K^+ (mg kg^{-1})	67.41±0.4	45.11±10.0
Exchangeable Na^+ (mg kg^{-1})	11.94±0.2	15.79±7.1
Exchangeable $1/2Ca^{2+}$ (mg kg^{-1})	434.16±10.2	599.5±82.8
Exchangeable $1/2Mg^{2+}$ (mg kg^{-1})	62.35±0.0	63.15±11.8
Available P (mg kg^{-1})	4.48±0.0	3.74±0.4
Available Fe (mg kg^{-1})	168.08±5.3	92.83±14.1
Activate Al (mg kg^{-1})	1 635±12.3	986.8±89.3
pH (KCl)	3.22±0.0	3.38±0.1

[a] Data for organic matter, total N, and total C/N ratio are obtained from Mo *et al.* (2003).

Pot experiment

In September 2000, soil samples (0–10 cm) were randomly collected from the two forests and mixed. Pots containing approximately 6 kg of the mixed soil samples of the broadleaf soil or the pine soil were planted with two-year-old seedlings of *A. acuminatissima*, *S. superba*, and *C. concinna* from the broadleaf forest or *P. massoniana* from the pine forest, respectively. All the pots were placed in an open area in the DHSBR. After one month, a total of 80 pots with the four species, 20 pots with the same species, were selected and divided into five groups. There were four species and 16 seedlings in each group.

From December 2000 to April 2004, the pots in the same group were treated with 800 mL of local lake water (control, CK, about pH 5.00) and simulated acid rain (SAR) of pH 4.40, 4.00, 3.52, and 3.05 weekly for 42 months. Simulated acid rain was prepared by mixing the lake water with a stock acid solution consisting of H_2SO_4 and HNO_3 (1:1 mole ratio). The accumulative S and N deposition from the 42-month experiment with SAR of pH 4.40, 4.00, 3.52, and 3.05 was equivalent to S deposition of 3.5, 7, 25, and 70 years and N deposition of 7, 21, 60, and 174 years, respectively, of natural precipitation in the area.

Sampling, incubation, and measurements

About 400 g soil samples were collected from each of the pots on April 20, 2004. Soil samples were sieved through a 2-mm sieve immediately after collection to remove coarse roots and stones, and then they were thoroughly mixed. The sieved soil sample was divided into two portions. One was air dried

for measuring the soil properties, and the other was incubated for measuring active carbon, NH_4^+-N, and NO_3^--N.

Moist soil (equivalent to 50 g oven-dried soil) was weighed into a 100-mL polypropylene beaker and adjusted to 60% water holding capacity (WHC), and then the beakers were placed in 1 200-mL PVC containers together with another 100-mL beaker containing 10 mL distilled water to maintain air humidity in the incubation chamber. The PVC containers were sealed with polyethylene film and then placed in a dark room at 25 °C. The headspace of the PVC containers was sampled for CO_2, CH_4, and N_2O at 5, 12, 20, 30, 45, and 65 d using medical gastight syringes. The film of the PVC container and the window of the room were opened and fanned for approximately 2 h at each sampling to prevent anoxia in the container. During the incubation, water content was checked at 12, 30, and 45 d, and distilled water was added if necessary to adjust the beakers to their original weights. After 65 d of incubation, the soil in the beakers was sampled to quantify NH_4^+-N and NO_3^--N. Eight blanks (no soil) were used to estimate background CO_2, CH_4, and N_2O productions.

The active carbon was measured with the colorimetric method after the soil C was oxidized by 0.02 mol L^{-1} alkaline $KMnO_4$ (Weil *et al.*, 2003). The NH_4^+-N and NO_3^--N were extracted with 50 mL 2 mol L^{-1} KCl (soil:extractant = 1:5) by shaking on an end-to-end shaker (160 r min^{-1}) for 1 h, followed by filtration through filter paper. NH_4^+-N was determined using the indophenol blue method, and NO_3^--N was determined using the cadmium reduction method (Liu, 1996). Soil pH was determined in a 1:2.5 soil-to-KCl suspension (1 mol L^{-1}). The available N was defined as the sum of NH_4^+-N and NO_3^--N. Organic C and total N were measured using the wet acid dichromate oxidation and semi-micro Kjeldahl methods, respectively (Liu, 1996). The concentrations of CO_2, CH_4, and N_2O in each syringe were immediately determined after sampling using a gas chromatograph (Agilent HP4890D, USA) with pure N_2 as a carrier gas. The measured CO_2 (μL L^{-1}), CH_4 (μL L^{-1}), and N_2O ($\times 10^{-3}$ μL L^{-1}) concentrations of each sample were used to calculate the amount of evolved CO_2-C (mg kg^{-1} dry soil), CH_4 (μg kg^{-1} dry soil), and N_2O (μg kg^{-1} dry soil) based on the PVC container headspace volume and the soil dry weight in the beaker. The factors to convert μL CO_2-C, N_2O, and CH_4 into μg CO_2-C, N_2O, and CH_4 were 1.80, 1.80, and 0.65, respectively, assuming a mole volume of 22.4 for CO_2, N_2O, and CH_4 at 25 °C under pressure of 1.013 kPa. All concentrations in the soil were expressed on the basis of an oven-dry weight (105 °C).

Statistical analyses

Differences in soil properties and cumulative gas production between treatments and between species were tested with a one-way analysis of variance (ANOVA). When the treatment and species effects were found to be significant ($P \leq 0.05$), the least significant difference (LSD) or Games-Howell multiple range test was used to assess the differences. Correlation analysis was used to determine the relationship between soil properties and cumulative gas production as well as 65 day N production for significance at $P \leq 0.05$. All the analyses were performed using the SPSS software version 11.0.

RESULTS

Soil properties after simulated acid rain treatment

Soil organic C and total N were maximum for the treatment with SAR of pH 4.00 after 42 months of experiment (Table II). The only significant difference in soil total N appeared between the control and pH 4.00 ($P \leq 0.05$), and no significant differences in soil organic C were found for all the treatments. Soil NH_4^+-N of the treatment with SAR of pH 3.05 was significantly higher compared with all other treatments, and NO_3^--N in the control (pH 5.00) was significantly higher than all other treatments ($P \leq 0.05$) (Table II). Available N (NH_4^+-N + NO_3^--N) was significantly higher ($P \leq 0.05$) in the control and the treatment with pH 3.05 SAR than the other treatments (Table II). The percentage of NH_4^+-N in available N was 37.92% in the control, whereas it was more than 54% in the treatments with

SAR. Furthermore, this percentage tended to increase as pH in the treatments decreased (Table II).

TABLE II

Soil carbon, nitrogen, and pH after the 42-month treatment with pH 5.00 lake water (control) and simulated acid rain (SAR) of different pH ($n = 16$) and those under different seedling species ($n = 20$) from the monsoon evergreen broadleaf forest

	pH 5.00 control	pH 4.40 SAR	pH 4.00 SAR	pH 3.52 SAR	pH 3.05 SAR
pH (KCl)	3.31a[a)] (0.08)[b)]	3.28ab (0.17)	3.22bc (0.07)	3.15c (0.04)	2.97d (0.09)
Active C (mg kg^{-1})	935.5a (153.4)	922.2a (160.5)	897.5a (155.0)	913.4a (128.1)	854.5a (116.4)
Organic C (g kg^{-1})	20.4a (7.8)	22.5a (7.7)	23.2a (8.0)	21.5a (7.2)	18.7a (6.3)
NH_4^+-N (mg kg^{-1})	2.86b (1.61)	3.05b (1.78)	3.14b (1.40)	2.96b (1.98)	6.98a (2.75)
NO_3^--N (mg kg^{-1})	4.65a (1.76)	2.446b (1.11)	1.99b (1.74)	1.49b (0.54)	2.03b (1.12)
Available N (mg kg^{-1})	7.52ab (0.57)	5.50c (0.52)	5.13c (0.52)	4.45c (0.57)	9.01a (0.86)
Total N (g kg^{-1})	0.97b (0.41)	1.07ab (0.37)	1.21a (0.35)	1.12ab (0.31)	1.09ab (0.26)
NH_4^+-N in available N (%)	37.92	54.74	64.84	64.58	77.13
Total C/N ratio	21.9a (3.2)	21.6a (4.5)	19.0b (2.4)	19.1b (3.1)	17.1b (3.4)

	Acmena acuminatissima		Schima superba		Cryptocarya concinna
pH (KCl)	3.11b (0.12)		3.26a (0.17)		3.15b (0.13)
Active C (mg kg^{-1})	1 015.4a (81.0)		810.4b (570.1)		1 040.0a (80.4)
Organic C (g kg^{-1})	28.1a (3.3)		16.4b (3.5)		27.5a (2.9)
NH_4^+-N (mg kg^{-1})	3.30a (2.86)		3.01a (1.31)		3.77a (2.71)
NO_3^--N (mg kg^{-1})	2.80a (1.92)		1.55b (0.79)		3.52a (1.90)
Available N (mg kg^{-1})	6.10ab (2.89)		4.56b (1.40)		7.29a (3.52)
Total N (g kg^{-1})	1.37a (0.13)		0.92b (0.28)		1.36a (0.14)
NH_4^+-N in available N (%)	54.10		66.01		51.72
Total C/N ratio	20.62a (2.32)		18.65a (4.76)		20.36a (2.55)

[a)] Values in the same row (within treatments or within species) followed by the same letter(s) are not significantly different at $P \leq 0.05$ (least significant difference test or Games-Howell multiple range test).
[b)] Values in the parenthesis are standard deviation.

Because the soils under the *A. acuminatissima*, *C. concinna*, and *S. superba* seedlings were collected from the monsoon evergreen broadleaf forest before the experiment started, the effect of tree species on the mineralization of soil C and N after the 42-month experiment with acid rain could be compared. The pH of the soil under *S. superba* was significantly ($P \leq 0.05$) higher than that of the soils under *A. acuminatissima* and *C. concinna* (Table II). The concentrations of soil active C, organic C, NO_3^--N, and total N under *S. superba* were significantly lower ($P \leq 0.05$) than those under *A. acuminatissima* and *C. concinna*. The concentration of available N in the *C. concinna* soil was significantly higher ($P \leq 0.05$) than that of the *S. superba* soil. These tree species demonstrated no significant differences for the concentration of NH_4^+-N and total C/N ratio.

Carbon mineralization

For all five treatments, cumulative CO_2-C production at the end of the 65 d incubation ranged from 20.24 to 27.81 mg kg^{-1} dry soil (Fig. 1). Compared to the control with pH 5.00 lake water, treatments with acid rain for 42 months generally enhanced the accumulation of CO_2-C production; however, the cumulative CO_2-C production with SAR of pH 3.05 was inhibited (Fig. 1). The soil treated with pH 3.05 SAR throughout the incubation posed the minimum cumulative CO_2-C production, which was significantly less ($P \leq 0.05$) than those from the soils treated with pH 3.52 and pH 4.00 SAR except for pH 4.00 at day 12. After 12 d of incubation, the cumulative CO_2-C production of the control was significantly less ($P \leq 0.05$) than that from the soil treated with pH 3.52 SAR. After 5 d of incubation, the soil treated with pH 3.52 SAR demonstrated the maximum cumulative CO_2-C production (Fig. 1). The cumulative CO_2-C production was always significantly higher ($P \leq 0.05$) from the soils under *A. acuminatissima* than *C. concinna*. Significant differences ($P \leq 0.05$) were also found in cumulative

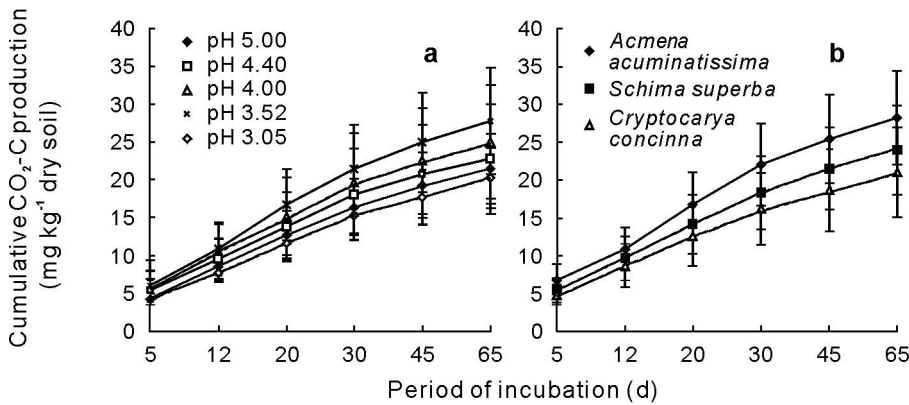CO_2-C production between *A. acuminatissima* and *S. superba* in the first 5 d and after 20 d.

Fig. 1   Effects of simulated acid rain with different pH compared to the control with pH 5.00 lake water ($n = 16$) (a) and wood species ($n = 20$) (b) on cumulative CO_2-C production during soil incubation at 25 °C. Data are mean ± standard deviation.

Cumulative CH_4 production from the soil of the control was always significantly less than that from the soil treated with pH 3.05 SAR ($P \leq 0.05$). After 20 d, cumulative CH_4 production from the soils treated with pH 4.40 and pH 4.00 SAR became lesser than that from the soil treated with pH 3.05 SAR ($P \leq 0.05$). The maximum cumulative CH_4 was found in the control, and the minimum cumulative CH_4 was found in the soil treated with pH 3.05 SAR (Fig. 2a). This pattern persisted throughout the incubation. The cumulative CH_4 production tented to increase with the increasing amount of acid rain. Cumulative CH_4 production from the soil under *S. superba* was always significantly higher ($P \leq 0.05$) than those from the soils under *A. acuminatissima* and *C. concinna*. Cumulative CH_4 of all soils except those treated with pH 3.05 SAR from 30 to 65 d was below zero (Fig. 2b).
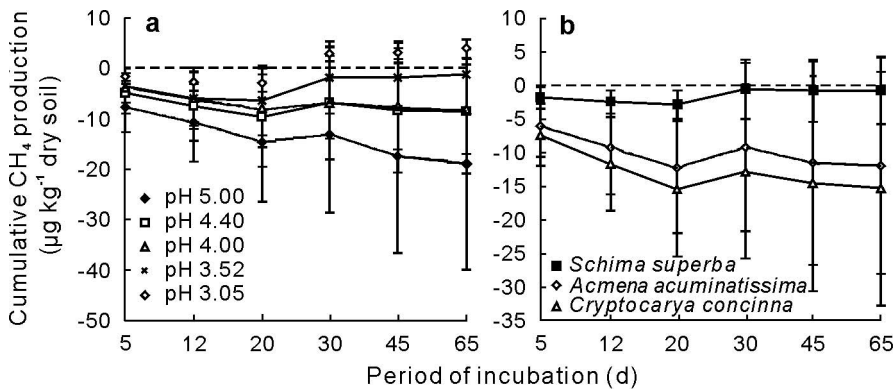

Fig. 2   Effects of simulated acid rain with different pH compared to the control with pH 5.00 lake water ($n = 16$) (a) and wood species ($n = 20$) (b) on cumulative CH_4 production during soil incubation at 25 °C. Data are mean ± standard deviation.

Nitrogen mineralization

In the soils treated with SAR, the net production of available N ranged from 17.37 to 48.95 mg kg^{-1} and the net production of NO_3^--N ranged from 9.09 to 46.23 mg kg^{-1} with a tendency to decrease with the decrease in SAR pH (Fig. 3a). In the soils treated with pH 3.05 SAR, both net productions of available N and of NO_3^--N were significantly lower ($P \leq 0.05$) than those in the soil of the control as well as the soils treated with pH 4.40, pH 4.00, and pH 3.52 SAR (Fig. 3a). The percentage of net NH_4^+-N production in the net available N production ranged from 4.67% to 54.07% and tended to increase with

the decrease in SAR pH (Table III). The net production of available N accounted for 5.84%–1.62% of soil total N, and the net production of NO_3^--N for 5.56%–0.72% (Fig. 3a). These percentages decreased with the decrease in SAR pH. The net production of available N in the *A. acuminatissima* soil was significantly higher than those in the *S. superba* ($P \leq 0.001$) soil and *C. concinna* ($P \leq 0.01$) soil (Fig. 3b). Less NO_3^--N was released from the *S. superba* soil than the *A. acuminatissima* ($P \leq 0.01$) and *C. concinna* ($P \leq 0.05$) soils. The percentage of NH_4^+-N in net available N production in the soils under *A. acuminatissima*, *S. superba*, and *C. concinna* are shown in Table III.
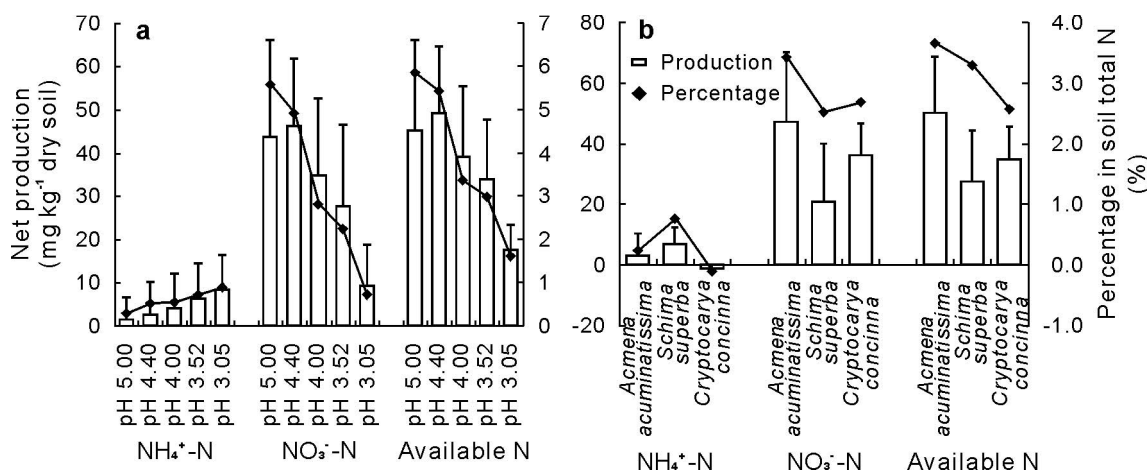

Fig. 3 Effects of simulated acid rain with different pH compared to the control with pH 5.00 lake water ($n = 16$) (a) and wood species ($n = 20$) (b) on net productions of NH_4^+-N, NO_3^--N, and available N and their percentages in soil total N after soil incubation at 25 °C. Data are mean ± standard deviation.

TABLE III

Percentages of net NH_4^+-N production in net available N production in the soils of the control with pH 5.00 lake water and the different pH simulated acid rain (SAR) treatments ($n = 16$) after incubation at 25 °C and that under different seedling species ($n = 20$) from the monsoon evergreen broadleaf forest

Treatment					Species		
Control (pH 5.00)	pH 4.40 SAR	pH 4.00 SAR	pH 3.52 SAR	pH 3.05 SAR	*Acmena acuminatissima*	*Schima superb*	*Cryptocarya concinna*
6.78	4.67	13.89	28.14	54.07	11.10	39.11	−4.90

Cumulative N_2O production from the soil of the control was significantly ($P \leq 0.05$) less than that from the soils treated with pH 3.52 and pH 3.05 SAR ($P \leq 0.05$) in the first 5 d, and thereafter higher than that from all the soils treated with SAR. The cumulative N_2O production from the soils treated with pH 4.40 and pH 4.00 SAR was also significantly ($P \leq 0.05$) less than that from the soil treated with pH 3.52 SAR before 20 d, and thereafter less than that from the soils treated with pH 3.52 and pH 3.05 SAR ($P \leq 0.05$) (Fig. 4a). The cumulative N_2O production tended to increase with the decrease in SAR pH. There was no significant difference in soil N_2O production among the species (Fig. 4b).

Relationships of soil properties with the parameters of C and N mineralization

Both cumulative CO_2-C and CH_4 productions were not significantly correlated with soil pH after acid rain treatment (Table IV). The cumulative CO_2-C production was significantly positively correlated with soil organic C ($P \leq 0.01$) and total N ($P \leq 0.05$), but significantly negatively correlated with the available N content ($P \leq 0.01$). The net available N production was positively related to soil pH, active C, organic C, NO_3^--N, and total C/N ratio, and negatively related to the NH_4^+-N content, but not to total N and available N in soil. The soil NO_3^--N was significantly and negatively correlated with the

cumulative N_2O production ($P \leq 0.01$) as well as the emission of N_2O in the first five days ($P \leq 0.05$). The soil pH was significantly and negatively correlated with cumulative N_2O production ($P \leq 0.01$) and not with the emission of N_2O in the first 5 days (Table IV).
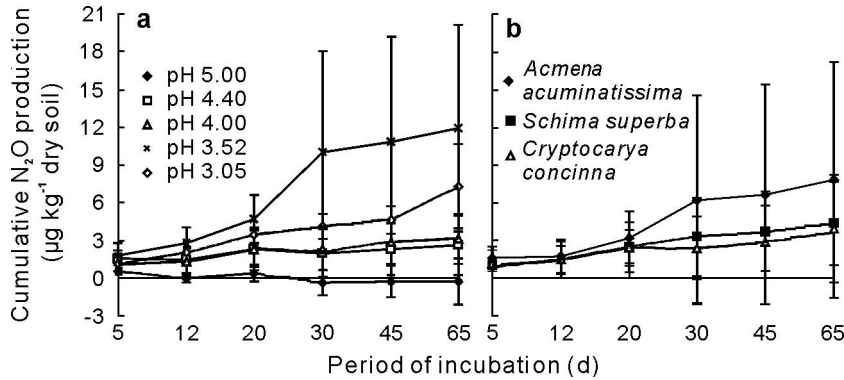

Fig. 4 Effects of simulated acid rain with different pH compared to the control with pH 5.00 lake water ($n = 16$) (a) and wood species ($n = 20$) (b) on cumulative N_2O production during soil incubation at 25 °C. Data are mean ± standard deviation.

TABLE IV

Correlation coefficients between the soil properties after acid rain treatment and the characteristic parameters of organic C and N mineralization during soil incubation

Mineralization parameter	Soil property after acid rain treatment							
	pH (KCl)	Active C	Organic C	NH_4^+-N	NO_3^--N	Available N	Total N	Total C/N ratio
N_2O production in the first 5 d	−0.14	0.22	0.27*	−0.05	−0.28*	−0.23	0.25	0.01
Cumulative CO_2-C production	−0.05	0.19	0.38**	−0.31**	−0.26*	−0.42**	0.29*	0.22
Cumulative CH_4 production	−0.18	−0.60**	−0.55**	0.43**	−0.59**	0.03	−0.44**	−0.20
Cumulative N_2O production	−0.40**	0.09	0.17	0.19	−0.40**	−0.09	0.23	−0.10
Net NO_3^--N production	0.32**	0.46**	0.49**	−0.42**	0.38**	−0.13	0.31**	0.37**
Net available N production	0.32**	0.31**	0.36**	−0.38**	0.30**	−0.15	0.18	0.38**

*, **Significant at $P \leq 0.05$ and $P \leq 0.01$, respectively.

DISCUSSION

Soil properties and mineralization of C and N

The results of this study suggested that acid rain (deposition) had a strong effect on the mineralization of soil C and N. The original soil pH did not explain the differences in cumulative CO_2-C and CH_4 productions among the treatments; that is, that original pH of the soil played a minimum role in mineralization. The changes of soil pH with the treatments of SAR of decreasing pH (Table II) were not consistent with the cumulative productions of CO_2-C (Fig. 1a) and CH_4 (Fig. 2a) at day 65. Neither was significantly correlated with soil pH (Table IV).

The relationships between the 65-d cumulative CO_2-C production and the soil properties (Table IV) implied that the release of soil CO_2 could be promoted by soil organic C ($P \leq 0.01$) and total N ($P \leq 0.05$), but it could be inhibited by the available N content ($P \leq 0.01$). Additionally, C and N status, but not soil pH, influenced the bacterial activities (methanotrophy) in oxidizing CH_4 in these acidic soils. These indicated that acid rain could influence the mineralization of organic C in acid soils by changing factors such as soil organic C and N status, rather than reducing soil pH alone. This finding is consistent with the observations by Bradford *et al.* (2001), who concluded that a single addition of HNO_3 or H_2SO_4 at equivalent H^+ concentrations had different impacts on CO_2 production and net CH_4 oxidation of soil cores. Possible explanations for our observation are as follows. Firstly, the soils used in

this study had a very low pH (Table I), and a small change of pH caused by acid rain had a minimum effect on the microbial community in the soil (Bååth and Anderson, 2003). Secondly, the microbial community might have adapted to the chronic acid rain conditions during the 42-month experiment (Blagodatskaya and Anderson, 1999; Pennanen et al., 1998). Finally, the chronic acid rain condition had a strong effect on the soil chemical properties, such as nutrient supply (Liu et al., 2004).

In contrast to C mineralization, the net available N production was positively related to soil pH, active C, organic C, NO_3^--N, and total C/N ratio, and negatively related to the NH_4^+-N content, but not to total N and available N in soil (Table IV), implying that the influence of acid deposition upon the mineralization of organic N was related to soil pH value, although the way in which soil pH alters the rates of organic N mineralization has not been well documented (Curtin et al., 1998). However, the decrease in the total C/N ratio with the treatments of SAR showed that soil total N was correspondingly enriched, which implicated the occurrence of microbial N assimilation followed by the incorporation of N in SOM (Sjöberg and Persson, 1998). No significant correlation between the net production of available N and soil total N implicated that the substantial quantities of N were incorporated into the stable organic pool that was not readily susceptible to microbial remineralization (Kaye et al., 2002). The increase of stable organic N pool did not increase the net available N production during the short-term incubation (Updegraff et al., 1995). It seemed that the decrease of organic N quality associated with the pH decline caused by acid rain directly influenced the organic N mineralization.

The percentage of net NH_4^+-N production in the net available N production ranged from 4.67% to 54.07% (Table III), so the net production of NO_3^--N in the net available N production ranged from 45.93% to 93.2%, which suggests that most of NH_4^+-N from mineralization was eventually transformed into NO_3^--N by nitrification. Acid deposition reduced the net production of NO_3^--N (Fig. 3). One possible explanation is that the decrease in the supply of NH_4^+-N affected nitrification (Montagnini and Buschbcher, 1989; Robertson, 1984). Acid deposition reduced the supply of NH_4^+-N (the net available N production) from mineralization (Fig. 3). Because the net NO_3^--N production was significantly ($P \leq 0.01$) and positively correlated with soil pH (Table IV), another possible explanation is that the decrease in soil pH inhibited the growth of nitrifying bacteria (Keeney, 1980). Although nitrification occurs in soil with low pH (Martikainen and Boer, 1993), the rate is generally very low when the soil pH is lower than 6.0 (Alexander, 1977). This explained why NH_4^+-N became the major form of the available N in the soils after being treated with SAR (Table II).

The treatments of simulated acid rain with decreasing pH increased the cumulative N_2O production (Fig. 4a). This was consistent with the results of several other studies (Šimek and Cooper, 2002). The emission of N_2O was mainly from a biological process, such as nitrification and denitrification (Robertson and Tiedje, 1987). Šimek et al. (2002) suggested that denitrification was the major cause of N_2O production. However, in acidic soils, the emission of N_2O was mainly from the nitrification of NH_4^+-N (Martikainen and Boer, 1993; Martikainen et al., 1993). In this study, we were not sure how N_2O was produced. The change of the net NO_3^--N production with the SAR treatments (Fig 3a) was opposite to the cumulative N_2O production (Fig. 4a), and the net NO_3^--N production was not significantly correlated with the cumulative N_2O production ($R^2 = -0.07$, $P \leq 0.56$). This implied that the emission of N_2O did not result from nitrification. However, the soil NO_3^--N was significantly and negatively correlated with the cumulative N_2O production ($P \leq 0.01$) as well as the emission rate of N_2O in the first five days ($P \leq 0.05$) (Table IV). This suggested that the emission of N_2O did not result from denitrification either. The soil pH was significantly and negatively correlated with cumulative N_2O production ($P \leq 0.01$,) but not with the emission rate of N_2O in the first 5 days (Table IV), and this meant that there was no direct relationship between soil pH and N_2O emission (Šimek and Cooper, 2002). The correlation analysis also showed that the soil properties did not have any role in controlling the emission of N_2O. The factors that induced the differences in the emission of N_2O seemed to be very complicated and require further investigation.

No significant correlation of cumulative CO_2-C production with the net production of available N

(Table VI) indicated that the mineralized C in the soil was not covalently bound to the mineralized N in the soil. The controlling factors affected these two processes in different manners. Hart *et al.* (1994) reported that gross rates of N transformation could closely vary with the release of CO_2 during long-term incubations, but the net N mineralization rates are poorly correlated with the gross N transformation rates. The fact that the estimates of the N mineralization are net rate, whereas the estimates of the C mineralization are gross rate, could be used to explain the poor relationship between the mineralization of N and C (Giardina *et al.*, 2001; Xue *et al.*, 2003). Therefore, the determination of gross N mineralization rate with acid deposition is required to gain insight into the relationship between C mineralization and N mineralization.

Tree species and mineralization of C and N

The mineralization rates of soil C in the pine-dominated soils exceeded those in the aspen-dominated soils, but the net N mineralization rates were not related to the species (Giardina *et al.*, 2001). The results of this study suggested that both cumulative CO_2-C production (Fig. 1b) and net available N production (Fig. 3b) of the soils under *A. acuminatissima* were significantly higher ($P \leq 0.05$) than those under *S. superba* and *C. concinna*. The difference might not necessarily reflect the litter quality of these species because the litter quality was not always a good indicator of the species differences in the mineralization of soil C and N (Giardina *et al.*, 2001). Also, the species differences in soil properties (Table II) were not completely consistent with the species differences in cumulative CO_2-C production (Fig. 1b) and net available N production (Fig. 3b). For example, there was no difference in soil total C/N ratio among species, whereas the active C, organic C, and total N in the soils under *A. acuminatissima* and *C. concinna* were significantly higher than those under *S. superba* (Table II). However, the influence of species on the composition of soil microbial communities could explain those differences. Giardina *et al.* (2001) showed that, although quality of aspen litter was higher than that of pine litter, the pine soil released more CO_2-C than the aspen soil because the pine soil C supported microbial communities with a higher ratio of active fungi to active bacteria. Therefore, the composition of soil microbial communities needs to be explored to gain insight into the relationship between species and soil mineralization.

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