

Soil Acidification Stimulates the Emission of Ethylene from Temperate Forest Soils

XU Xingkai*¹ (徐星凯) and Kazuyuki INUBUSHI²

¹*State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry,*

Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029

²*Graduate School of Horticulture, Chiba University, Matsudo, Chiba 271-8510, Japan*

(Received 7 August 2008; revised 13 January 2009)

ABSTRACT

Soil acidification via acid precipitation is recognized to have detrimental impacts on forest ecosystems, which is in part associated with the function of ethylene released from the soil. However, the impacts of acidification on the cycling of ethylene in forest soils have not been fully taken into consideration in global change studies. Forest topsoils (0–5 cm) under four temperate forest stands were sampled to study the effects of a pH change on the emissions of ethylene and carbon dioxide from the soils and concentrations of dissolved organic carbon (DOC) released into the soils. Increasing acidification or alkalization of forest soils could increase concentrations of DOC released into the soils under anoxic and oxic conditions. The ethylene emission from these forest topsoils could significantly increase with a decreasing pH, when the soils were acidified experimentally to a pH < 4.0, and it increased with an increasing concentration of DOC released into the soils, which was different from the carbon dioxide emission from the soils. Hence, the short-term stimulating responses of ethylene emission to a decreasing pH in such forest soils resulted from the increase in the DOC concentration due to acidification rather than carbon mineralization. The results would promote one to study the effects of soil acidification on the cycling of ethylene under different forest stands, particularly under degraded forest stands with heavy acid depositions.

Key words: soil acidification, carbon dioxide, dissolved organic carbon, ethylene emission, volcanic soil

Citation: Xu, X. K., and K. Inubushi, 2009: Soil acidification stimulates the emission of ethylene from temperate forest soils. *Adv. Atmos. Sci.*, **26**(6), 1253–1261, doi: 10.1007/s00376-009-8120-9.

1. Introduction

Ethylene (C₂H₄) production in soil results from a microbial process and is performed by a variety of microbes including fungi and bacteria. The accumulation of C₂H₄ in soil can reach ratios of >10 μL L⁻¹ when conditions promote C₂H₄ production or inhibit C₂H₄ degradation (Smith and Dowdell, 1974; Jackson, 1985), detrimentally affecting plant growth and sensitive soil microorganisms (Frankenberger and Arshad, 1995). Soil acidification due to acid precipitation is recognized to have detrimental impacts on forest growth (Abrahamsen et al., 1994; Zech et al., 1994), which is in part associated with the function of C₂H₄ released from the soil. Unfortunately, the effects of such acidification on C₂H₄ cycling in forest

soils have not been fully taken into consideration in global change studies.

Earlier studies have shown that C₂H₄ can be produced at large rates in forest soils and in soils of low pH (van Cleemput et al., 1983; Sexstone and Mains, 1990). Soil properties such as dissolved organic carbon (DOC) (Xu and Inubushi, 2007; Xu et al., 2008) and metal ions (Arshad and Frankenberger, 1991) can affect the extent of C₂H₄ biosynthesis in soil. Volcanic forest soils generally contain large concentrations of aluminum (Al) and organic carbon (Shoji et al., 1993; Morisada et al., 2002, 2004), and soil acidification can increase Al mobilization and C₂H₄ production in soil due to an increased DOC concentration. Unfortunately, our knowledge is limited about whether decreasing soil pH at what levels can increase C₂H₄

*Corresponding author: XU Xingkai, xingkai_xu@yahoo.com.cn

emission from such forest soils, and the key associated mechanisms are not clear so far.

The pathways of all the known C_2H_4 biosynthesis are considered to require oxygen (Fukuda et al., 1993). However, the mechanism of C_2H_4 production in soil is still unclear, in particular, since C_2H_4 production is generally observed in the anoxic soils (Zechmeister-Boltenstern and Smith, 1998; Zechmeister-Boltenstern and Nikodim, 1999; Xu and Inubushi, 2007). The C_2H_4 accumulation in temperate volcanic forest soils could reach a range from 0.2 to 0.3 and from 1.0 to 3.0 $\mu\text{L L}^{-1}$ in the headspace gases, within 3 days of the oxic and anoxic incubations, respectively, and the addition of glucose increased C_2H_4 accumulation in soil slurry and the same increase was observed during both incubations (Xu and Inubushi, 2007). Both atmospheric nitrogen and acid depositions in central Japan and other Asia districts have become a serious problem due to human's activity, which may affect soil acidification and the evolution of C_2H_4 from forest soils. Thus, the results would promote one to study whether the status of oxygen can affect the function of acidification in stimulating C_2H_4 emission from forest soils derived from volcanic ash.

The objective of this work was to study the responses of C_2H_4 emission to a pH change in temperate volcanic forest soils under oxic and anoxic conditions. Of additional interest were the relationships between the soil C_2H_4 emissions, the increase in DOC concentrations, and carbon mineralization of the soils. Together with our findings about the *in situ* measurements of C_2H_4 production under forest floors (Xu and Inubushi, 2008), the results should promote one to study the C_2H_4 emission from forest soils under acidic stress conditions in the field.

2. Materials and methods

2.1 Soil sampling and chemical analysis

Four temperate forest stands located on gentle (7° – 12°) and steep ($>35^\circ$) slopes were selected within the Chiba University's Environmental Horticulture and Forestry Farm ($36^\circ36'N$, $139^\circ00'E$, altitude 780–810 m). The temperate forest stands included were: (CI) a Japanese cedar forest (*Cryptomeria japonica*, 40 years, 7° – 12° slope), (CII) a pine forest (*Pinus sylvestris* L., 40 years, 7° – 12° slope), and an oak-dominated forest (*Quercus serrata*, >40 years) located on (DI) a gentle (7° – 12°) and (DII) a steep slope ($>35^\circ$) within the above farm. Three 4 m \times 4 m plots under each forest stand were selected according to the distribution of trees and landform, and within each plot one composite soil sample at a depth of 5 cm was taken in October 2003 as described by Xu and Inubushi (2007). All the

samples were kept separately in air-tight plastic bags and rapidly transported to the laboratory.

Field moist soils, classified as Andisols (FAO soil classification), were sieved (2 mm) to remove small stones and roots and stored in the dark, below 5°C for less than two weeks prior to incubation. Ammonium-N and NO_3^- -N in the soils were extracted with a 1 mol L^{-1} KCl solution by shaking for 30 minutes on a reciprocal shaker and then filtered through Advantec No. 6 filter paper (Advantec, Tokyo, Japan). Both NH_4^+ -N and NO_3^- -N concentrations in the filtrates were measured colorimetrically by the nitroprusside and hydrazine-reduction methods, respectively (Kim, 1995). Soil Al concentration was extracted by a 1 mol L^{-1} ammonium oxalate solution and measured by an atomic absorption spectrometry. Maximal water-holding capacity was determined by saturating each soil in glass funnels with water and allowing drainage under cover for 2–3 hours at ambient temperature. Duplicate soil samples were dried at 105°C for 24 hours to determine the moisture content. Soil total C and N contents were measured with a CN analyzer (MT-700 with an Auto Sampler MTA-600, Yanaco, Kyoto, Japan). Fresh soil pH (soil/water, 1:2.5, w/w) was measured with a portable pH meter. Soil water-soluble organic carbon (DOC) was extracted with deionized water at a soil: water ratio of 1:2.5 (w/w) and measured using a TOC-analyzer (Shimadzu TOC-5000, Kyoto, Japan). The main soil characteristics are summarized in Table 1.

2.2 Effect of soil pH on C_2H_4 emission under unsaturated oxic conditions

The influence of soil pH on C_2H_4 emissions from the soils was assayed using sieved forest soils. Soil pH was altered by adding 0.5 mL of various concentrations of hydrochloric acid (HCl , 0–2 mol L^{-1}) or potassium hydroxide (KOH , 0–4 mol L^{-1}) to 10 grams of fresh soil (in triplicate) in 120-mL serum bottles, and the moisture was finally adjusted to about 60% water-filled pore space (WFPS). This treatment resulted in pH values ranging from 2.4 to 7.0. Controls were added with the corresponding volume of deionized water to each soil. In total, there were six different pH levels for each soil. The volume of the soil in each bottle was measured by Xu and Inubushi (2008), and the WFPS was calculated via the equation reported by Franzluebbers (1999). The oxic incubation was done for 8 days at 25°C in the dark. One milliliter of the headspace gases in each bottle was sampled using 1.0-mL air-tight syringes (MS-GAN100) at 0, 24, 48, 72, 96, 120, 164, and 190 hours and immediately injected into a gas chromatograph (Shimadzu GC-14B, Kyoto, Japan) for analysis of C_2H_4 . At the start and end of

Table 1. Main properties of the 0–5 cm soils under different temperate forest stands.

Forest soils	WHC (%)	Topographical slope (°)	Soil pH	WOC ($\mu\text{g C g}^{-1}$)	NH_4^+ ($\mu\text{g N g}^{-1}$)	NO_3^- ($\mu\text{g N g}^{-1}$)	Total C (mg g^{-1})	Total N (mg g^{-1})	C/N ratios	Ammonium oxalate extractable Al (%)
DI	126	7–12	5.3	125	4.0	12.6	124.5	8.3	15.0	4.4
DII	96	> 35	5.8	55	1.7	10.3	110.4	8.1	13.6	3.8
CI	124	7–12	5.7	125	2.2	13.7	127.5	7.6	16.8	4.8
CII	108	7–12	4.9	118	2.4	20.7	150.8	8.6	17.5	5.2

Note: WHC, water holding capacity. WOC, water-soluble organic C. DI, an oak-dominated hardwood forest soil on a grading slope; DII, an oak-dominated hardwood forest soil on a steep slope; CI, a Japanese cedar forest soil; CII, a pine forest soil. The same below.

the 8-day incubation, concentrations of carbon dioxide (CO_2) in all the bottles were measured by injecting one milliliter of the headspace gases into a GC, and the pH values and the DOC concentrations of the soils were measured as above.

2.3 Effect of soil pH on C_2H_4 evolution under waterlogged anoxic conditions

Fresh sieved soil (5.0 g) (in triplicate) sampled from four forest stands was placed in a 50-mL serum bottle with butyl rubber stoppers, and 12.5 mL of deionized water was added to each. The initial pH values of the soil slurry were adjusted to 0.5, 1.5, 2.5, 3.5, 4.5, 5.5, 6.5, and 7.5, respectively, with a 4 mol L^{-1} HCl and a 4 mol L^{-1} KOH solution. All serum bottles containing the soil slurry were then evacuated (-100 kPa) and flushed with pure N_2 ($+100$ kPa) four times; finally the headspace was vented to atmospheric pressure. The batch incubation was done at 25°C in the dark. On 1, 3, 5, 7, 14, 21, and 28 days after the anoxic incubation, one milliliter of the headspace gases was sampled from each bottle for analysis of C_2H_4 . At the start and end of the incubation (28 days), the CO_2 concentration in each bottle was measured by injecting one milliliter of the headspace gases into a GC, and the pH values and the DOC concentrations of the soils were measured as above.

2.4 Measurement of ethylene and carbon dioxide

Concentrations of C_2H_4 and CO_2 in the headspace gases were measured on a gas chromatograph (Shimadzu GC-14B, Kyoto, Japan) fitted with a flame ionization detector operating at 100°C (thermal conductivity detector at 50°C for CO_2). Ethylene was separated isothermally on a 2-m Porapak Q-packed glass column at 50°C (40°C : CO_2), using N_2 (He: CO_2) as a carrier gas at a flow rate of $20\text{ cm}^3\text{ min}^{-1}$ ($10\text{ cm}^3\text{ min}^{-1}$: CO_2). The detector responses were calibrated using certified gas standards, which contain $101\text{ }\mu\text{L L}^{-1}$ C_2H_4 in N_2 and 1.001% CO_2 in N_2 , respectively.

2.5 Calculation and statistical analysis

All data were calculated on an oven-dried weight basis. Initial rates of C_2H_4 emissions from forest topsoils under both oxic and anoxic conditions were calculated by linear regressions between the headspace C_2H_4 concentration and incubation time (coefficients of determination for linear regressions, $R^2 \geq 0.95$), and expressed in $\text{pmol C}_2\text{H}_4\text{ g}^{-1}$ of dry soil per day. Rates of CO_2 emissions from the soils were calculated from the increase in headspace gas concentrations with incubation time. The increase in concentrations of the DOC released into the soils was calculated from differences in concentrations prior to and after the incubations, and was expressed as $\mu\text{g DOC-C g}^{-1}$ of dry soil per day. Means and standard errors of the three replicates in each treatment were calculated. Significant differences in the means between treatments and forest soils were analyzed by MANOVA using SYSTAT software for Windows (release 12.0). Linear and nonlinear regressions were performed to study the relationships between both C_2H_4 and CO_2 emissions, the increase in the DOC concentration, and the pH values of the soils.

3. Results

3.1 Effect of soil pH on C_2H_4 emission under oxic and anoxic conditions

Within the first week of the anoxic incubation, the smallest C_2H_4 accumulation was observed in all the tested soil slurries at a pH = 3.5, and afterwards it was present in the soil slurry treated with smaller initial pH values (Fig. 1) probably due to the change in pH values of the soil slurry with time (Table 2). Considering that the change in soil slurry pH during the 7-day anoxic incubation was minor, the rates of C_2H_4 emission from the soils were calculated according to the 7-day anoxic incubation and were plotted against initial pH values of the soil slurry ranging from 0.5 to 7.5 (Fig. 2c). In the soils acidified experimentally to a pH <4.0 , the C_2H_4 emission from the

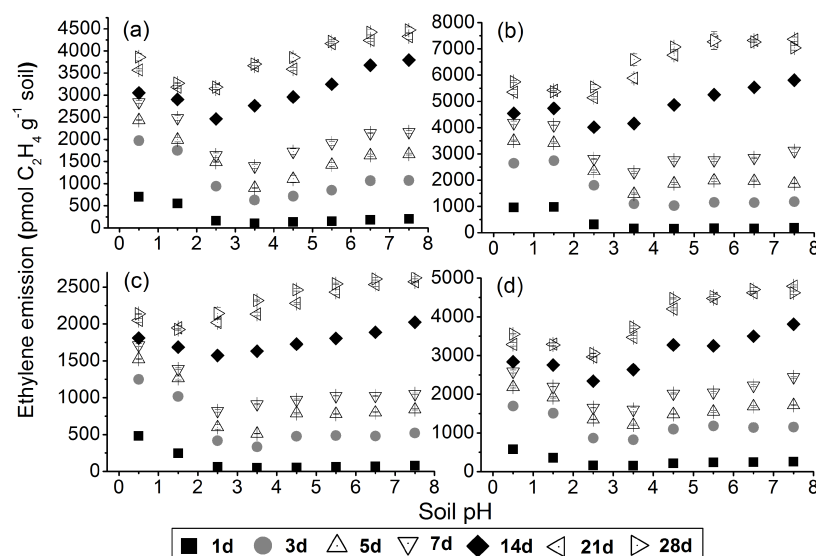


Fig. 1. Effects of soil pH on the dynamics of ethylene emission from soil slurries under waterlogged anoxic conditions. Error bars indicate standard errors of three replicates. (a), an oak-dominated hardwood forest soil on a grading slope; (b), a Japanese cedar forest soil; (c), an oak-dominated hardwood forest soil on a steep slope; (d), a pine forest soil. 1d, 1 day after incubation.

Table 2. Variations of pH values in the soil slurries after 28 days of the anoxic incubation.

Initial soil pH	Final soil pH			
	DI	DII	CI	CII
0.5	2.82 (0.00)	3.06 (0.01)	2.64 (0.01)	2.87 (0.01)
1.5	3.07 (0.03)	3.21 (0.01)	2.84 (0.04)	3.07 (0.01)
2.5	3.77 (0.06)	4.44 (0.20)	4.02 (0.10)	3.58 (0.01)
3.5	4.52 (0.05)	5.08 (0.01)	4.73 (0.03)	4.53 (0.01)
4.5	5.25 (0.15)	5.89 (0.04)	5.58 (0.11)	5.50 (0.01)
5.5	5.74 (0.10)	6.16 (0.06)	5.89 (0.01)	5.70 (0.02)
6.5	6.01 (0.02)	6.34 (0.02)	6.01 (0.02)	5.89 (0.04)
7.5	6.07 (0.02)	6.48 (0.02)	6.16 (0.04)	6.04 (0.02)

Note: Values are the means of three replicates, and standard errors are shown in parentheses.

soil significantly increased with a decreasing soil pH (significance level, $P < 0.05$) (Fig. 2c and Table 3). However, when the soils were adjusted to a $\text{pH} > 4.0$, the C_2H_4 emission rate between the pH-treated and non-treated soils showed a minor difference during the anoxic incubation (Fig. 2c). Considering that the pH values measured after the 8-day oxic incubation differed from the initial soil pH by generally less than 0.2-pH, the means calculated for both pH measurements were considered values of the soil pH used in this study. The C_2H_4 emission rate in each soil under oxic conditions could significantly increase with decreasing soil pH ($R^2 = 0.86$, $P < 0.0001$), however it was not seen in the soils regulated to a $\text{pH} > 4.0$ (Fig. 2a). The Japanese cedar forest soil gave the largest response of C_2H_4 accumulation to decreasing

pH during the oxic and anoxic incubations among all tested forest soils ($P < 0.05$) (Figs. 2a, c and Table 3). Hence, C_2H_4 emission from such forest soils, particularly under the oxic conditions, substantially increased with an increasing acidification ($P < 0.05$) (Figs. 2a, c), when the soils were acidified to a $\text{pH} < 4.0$.

3.2 Effect of soil pH on DOC concentrations under oxic and anoxic conditions

The increase in concentrations of DOC released into the soils during both oxic and anoxic incubations was well plotted against the soil pH, using an inverted parabola with a peak at the bottom ($R^2 = 0.56$, $P < 0.001$ and $R^2 = 0.65$, $P < 0.0001$, respectively) (Figs. 3a, b). When the soil pH was adjusted to 4.5–5.0, there was the smallest increase in DOC concen-

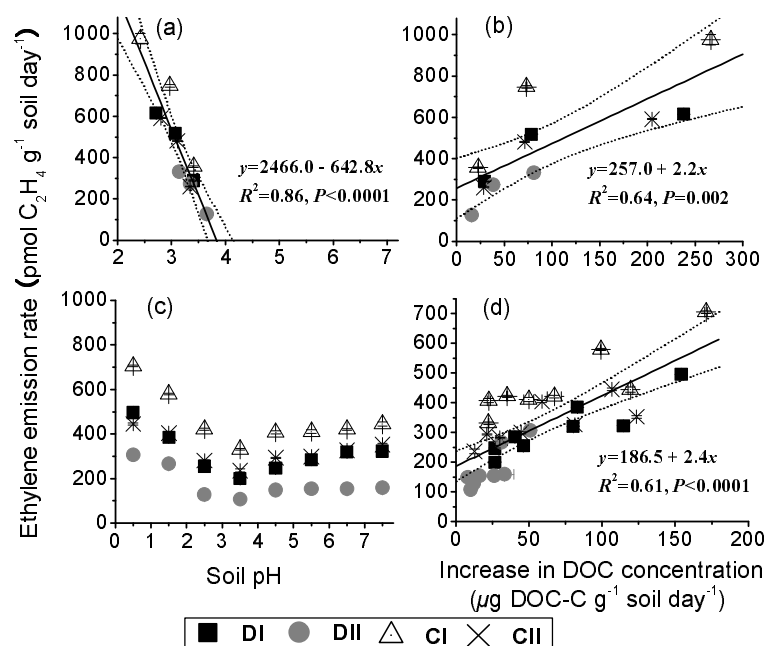


Fig. 2. Relationships between ethylene emissions from forest soils, soil pH, and the increase in water-soluble organic C (DOC) concentrations of forest soils under oxic and anoxic conditions. a–b: during the 8-day oxic incubation with 60% WFPS; c–d: within 7 days of the waterlogged anoxic incubation. Error bars indicate standard errors of three replicates. Solid lines represent linear regressions of the ethylene emission rates, y , respectively, against (the soil pH or the increase in DOC concentrations), x , and dotted lines represent the upper and lower 95% confidence limits. Coefficients of determination of regressions (R^2) and P values are shown.

Table 3. Regression models of the C_2H_4 emission from forest soils (y) acidified experimentally to a pH < 4.0 on the initial soil pH (x) within the first week of the anoxic incubation.

Forest soils	Regression equations	R^2	P
DI	$y = (537.6 \pm 25.4) - (101.8 \pm 11.1)x$	0.98	0.01
DII	$y = (349.7 \pm 36.1) - (73.6 \pm 15.7)x$	0.92	0.04
CI	$y = (765.1 \pm 20.2) - (127.9 \pm 8.8)x$	0.99	<0.01
CII	$y = (491.2 \pm 25.6) - (74.6 \pm 11.2)x$	0.96	0.02

Note: Coefficients of regression models are shown as the means \pm standard errors of three replicates.

trations during both incubations. Beyond this critical pH, concentrations of DOC released into the soils were increased by a decreasing or an increasing pH during both oxic and anoxic incubations ($P < 0.05$), particularly during the oxic incubation (Figs. 3a, b).

3.3 Effect of soil pH on CO_2 emissions under oxic and anoxic conditions

The soil CO_2 emission during the oxic incubation was well plotted against the soil pH, using an inverted parabola with a peak at the bottom ($R^2 = 0.34$, $P < 0.05$) (Fig. 4a), which paralleled the increase in DOC concentrations versus the soil pH (Fig. 3a). How-

ever, the soil CO_2 emission during the anoxic incubation increased linearly as the initial pH value of the soil slurry increased ($R^2 = 0.62$, $P < 0.0001$) (Fig. 4c).

3.4 Relationships between C_2H_4 and CO_2 emissions from soils and the increase in DOC concentrations

During both oxic and anoxic incubations, about 60% of the variance in the rates of C_2H_4 emission from the soils could be accounted for by the increase in DOC concentrations; the slopes of the linear regressions of the rates on the increase in DOC concentrations were

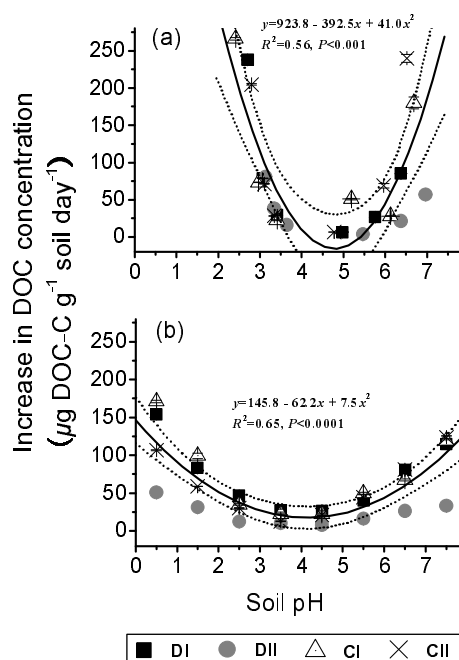


Fig. 3. Effects of soil pH on the increase in water-soluble organic C (DOC) concentrations of forest soils under (a) oxic and (b) anoxic conditions. Error bars indicate standard errors of three replicates. Solid lines represent non-linear regressions of the increase in DOC concentrations, y , against the soil pH, x , and dotted lines represent the upper and lower 95% confidence limits. Coefficients of determination of regressions (R^2) and P values are shown.

the same during both incubations (Figs. 2b, d). The results suggest that the DOC-dependent C_2H_4 emission can be present in the acidified forest soils and is not affected by the status of oxygen. During the oxic incubation, the CO_2 emission from all the tested soils was well plotted against the increase in DOC concentrations, using a parabola with a peak at the top ($R^2 = 0.33$, $P < 0.05$) (Fig. 4b). However, under the anoxic conditions, no obvious relationships were observed between the soil CO_2 emission and the increase in DOC concentrations (Fig. 4d).

4. Discussion

The change in soil pH via acid deposition has been recognized to have vital impacts on forest ecosystems (Abrahamsen et al., 1994). By comparing DOC concentrations and fluxes at three spruce stands receiving different rates of acid deposition, Zech et al. (1994) reported that anthropogenic soil acidification results in an increasing DOC output of the mineral soil. Under experimental conditions, a decreasing soil pH resulted in an increasing concentration of DOC released into the soils, which was much stronger during the oxic

incubation (Fig. 3a) than during the anoxic incubation ($P < 0.05$) (Fig. 3b). The smallest increase in the DOC concentration was observed at a pH=4.5–5.0 (Figs. 3a, b), which was close to the native soil pH (Table 1). Probably, increasing acidification of these topsoils under temperate forest stands would increase concentrations of DOC released into the underlying soil in the field.

There were no differences in C_2H_4 emissions from soil slurry after 21 and 28 days of the anoxic incubation, for a wide range of soil pH from 0.5 to 7.5 (Fig. 1). The inhibition of the C_2H_4 emission from the forest soil after 3 weeks of the anoxic incubation was also reported by Xu and Inubushi (2007). Hence, after several weeks of the waterlogged anoxic incubation, the soil C_2H_4 emission can be inhibited, perhaps due to the reduction in soil E_h (redox potential). In the soil slurry experimentally acidified to a pH ≤ 1.5 , the C_2H_4 emission after 3 days of the anoxic incubation reached c. 50% of the total emissions throughout the 28-day anoxic incubation, which was different from less than 20% in the soil slurry initially adjusted to a pH=7.5 (Fig. 1). When the soils were acidified to a pH < 4.0 , the soil C_2H_4 emission during the 7-day anoxic incubation significantly increased as the soil pH decreased ($P < 0.05$) (Fig. 2c). However, at the pH above 4.0, no differences of the C_2H_4 emission were observed between the pH-treated and non-treated soils (Fig. 2c). Hence, a decreasing soil pH would stimulate the C_2H_4 emission at a fast speed under waterlogged anoxic conditions.

The C_2H_4 accumulation in the anoxic soil slurry results from C_2H_4 production due to the inhibition of C_2H_4 consumption (Frankenberger and Arshad, 1995), which can be associated with the DOC concentrations in the soil (Xu and Inubushi, 2007). There was a parallel between the rate of C_2H_4 emission and the increase in DOC concentrations of the anoxic soil slurries adjusted to pH values ranging from 0.5 to 7.5 (Figs. 2c and 3b). The soil C_2H_4 accumulation during the anoxic incubation increased linearly with an increasing DOC concentration in the soil slurry ($R^2 = 0.61$, $P < 0.0001$) (Fig. 2d). The minimum C_2H_4 emission was observed in the anoxic soils acidified experimentally to a pH=3.5 (Fig. 2c), which was in good accordance with the smallest increase in concentrations of DOC released into the soils (Fig. 3b). In contrast to the soil C_2H_4 emission, CO_2 accumulation in the anoxic soil slurry increased with increasing initial pH values from 0.5 to 7.5 (Fig. 4c), and did not present an obvious relationship to the increase in DOC concentrations (Fig. 4d). Hence, the responses of C_2H_4 emission to a decreasing pH resulted from the increase in DOC concentrations rather than C miner-

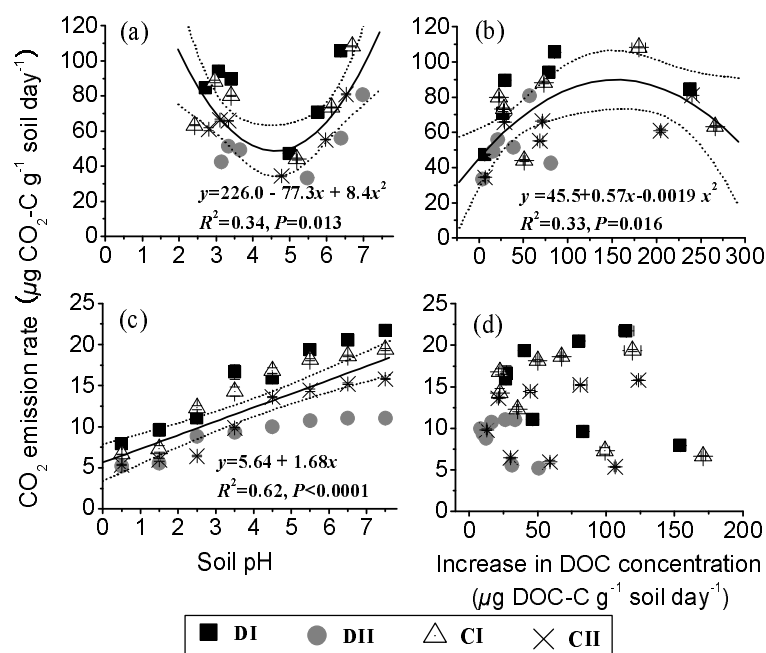


Fig. 4. Relationships between CO_2 emissions from forest soils, soil pH, and the increase in DOC concentrations of forest soils under oxic and anoxic conditions. a–b: during the 8-day oxic incubation with 60% WFPS; c–d: within 7 days of the waterlogged anoxic incubation. Error bars indicate $1 \times$ standard errors of three replicates. Solid lines represent linear and nonlinear regressions of the CO_2 emission rates, y , respectively, against (the soil pH or the increase in DOC concentrations), x , and dotted lines represent the upper and lower 95% confidence limits. Coefficients of determination of regressions (R^2) and P values are shown.

alization under waterlogged anoxic conditions.

The activity of C_2H_4 consumption in the same soils acidified experimentally to a $\text{pH} < 4.0$ was negligible, whereas it was increased by an increasing soil pH and reached the maximum at a $\text{pH} = 6.0\text{--}6.5$ (Xu and Inubushi, 2009a). Hence, C_2H_4 emission rates were observed only in the aerobically incubated soils acidified experimentally to a $\text{pH} < 4.0$ (Fig. 2a), which was positively correlated to the increase in DOC concentrations of the soil ($R^2 = 0.64$, $P = 0.002$) (Fig. 2b). The slopes of the regressions of the rates on the soil pH during the oxic incubation (Fig. 2a) were much larger than those during the anoxic incubation (Table 3) ($P < 0.05$), when the soils were acidified experimentally to a $\text{pH} < 4.0$. This difference resulted from the large concentration of DOC released into the soils (Fig. 3) and the high activity of soil respiration (Fig. 4) under the oxic conditions. Together with the results obtained during the anoxic incubation, it is suggested that acidifying soil to a $\text{pH} < 4.0$ can stimulate C_2H_4 emission under forest stands in the field, and this functioning of the soil is variable with the kinds of forest stands.

The minimum C_2H_4 emission from the soils acidified experimentally to a $\text{pH} = 3.5$ was due in part to the occurrence of Al forms and their phytotoxicity. Volcanic forest soils contained large ammonium oxalate extractable Al concentrations (Table 2). When the soils were acidified to a $\text{pH} < 4.0$, monomeric Al as $\text{Al}(\text{H}_2\text{O})_6^{3+}$ is probably a major Al species in the soil solution. The partial neutralization of a simple acidic Al solution may produce aluminum tridecamer (Al_{13}) (Hiradate and Yamaguchi, 2003), which is more responsible for the phytotoxicity of acid soils than monomeric Al (Shann and Bertsch, 1993; Comin et al., 1999; Hiradate and Yamaguchi, 2003). In the chemical solution without the addition of organic ligands, Al_{13} formed at a $\text{pH} = 3.9\text{--}4.6$, but the formation of Al_{13} was inhibited by the presence of organic ligands, including humic acids (HA), which depended on the solution's pH and the COOH/Al ratio (Yamaguchi et al., 2003; Hiradate and Yamaguchi, 2003). Hence, at an extremely low pH, the increase in concentrations of DOC released into such volcanic soils (Figs. 3a, b) can reduce the formation of Al_{13} and promote the formation of precipitates of octahedral Al-HA complexes includ-

ing monomeric and polymeric Al (Hiradate and Yamaguchi, 2003). Considering the pH-dependent concentrations of DOC released into the soils, the smallest C₂H₄ emission from the tested volcanic forest soils acidified to a pH=3.5 under the anoxic and oxic conditions was probably attributable from the phytotoxic effect of Al species on soil microorganisms. However, the CO₂ emission from the anoxic soil slurry increased linearly as the initial soil pH increased ($R^2 = 0.62$, $P < 0.0001$) (Fig. 4b), which was different from the pH-dependent CO₂ emission from the oxic soils (Fig. 4a). Hence, it is interesting to study the relationships between the behavior of Al species and C₂H₄ emission from the acidified volcanic forest soils, especially under anoxic conditions.

The use of chloride acid may overestimate the sensitivity of soil microorganisms to pH change compared to the other acids. It is not clear at the present whether there are the same stimulating responses of the soil C₂H₄ emission to different acids. Since acid deposition is comprised primarily of nitric and sulfuric acids, the results presented here cannot confirm the functioning of soil acidification in stimulating C₂H₄ emission in the field. Extrapolations are limited since laboratory studies of short-term pulsed acidification may not adequately incorporate the functions of low levels of acid inputs over long periods in the field. According to annual reports about acid depositions at Nakanoji in the Gunma prefecture, Japan, which is the nearest to the tested forest sites, the mean pH values in precipitation from 1999 to 2003 ranged from 3.9 to 4.8, and the annual wet acid depositions as sulfuric, nitric, and chloride acids were 2.2–3.4, 2.5–3.3, and 1.1–1.2 g m⁻², respectively. Probably, soil acidification under these forest stands would become serious in the future. Hence, further research should be done to study the effects of soil acidification on C₂H₄ production and consumption in the soil under different forest stands, and how the processes interact with the soil atmospheric methane oxidation (Xu and Inubushi, 2008, 2009b; Xu et al., 2008).

5. Conclusions

Increasing acidification or alkalization of forest soils increased the concentrations of DOC released into the soils under anoxic and oxic conditions. The C₂H₄ emission from forest soils, particularly under the oxic conditions significantly increased with a decreasing pH, when the soils were acidified experimentally to a pH < 4.0. The soil C₂H₄ emission under the anoxic and oxic conditions significantly increased with an increasing DOC concentration, which was different from the CO₂ emission from the soils. Hence, the short-

term responses of C₂H₄ emission to a decreasing soil pH resulted from the increase in DOC concentrations released into the soils due to acidification rather than carbon mineralization. The results would promote one to study the effects of soil acidification on C₂H₄ cycling in the soil beneath different forest stands and its interaction with the soil atmospheric methane consumption.

Acknowledgements. This work was funded jointly by the National Natural Science Foundation of China (Grant Nos. 40875085, 20777071, and 20477044), by the Hundred Talents Project from the Chinese Academy of Sciences, and by the Japan Society for the Promotion of Sciences. The authors thank two anonymous reviewers for their specific comments. Also the authors thank Dr. Watanabe Mirai for collecting the atmospheric wet depositions literature.

REFERENCES

- Abrahamsen, G., A. O. Stuanes, and B. Tveite, 1994: *Long Term Experiments with Acid Rain in Norwegian Forest Ecosystems*. Springer, New York, 342pp.
- Arshad, M. A., and W. T. Frankenberger, 1991: Effects of soil properties and trace elements on ethylene production in soils. *Soil Science*, **151**, 377–386.
- Comin, J. J., J. Barloy, G. Bopurrié, and F. Trolard, 1999: Different effects of monomeric and polymeric aluminum on the root growth and on the biomass production of root and shoot of corn in solution culture. *European Journal of Agronomy*, **11**, 115–122.
- Frankenberger, W. T., and M. Arshad, 1995: *Phyt hormones in Soils—Microbial Production and Function*. Marcel Dekker, New York, 520pp.
- Franzluebbers, A. J., 1999: Microbial activity in response to water-filled pore space of variably eroded southern Piedmont soils. *Applied Soil Ecology*, **11**, 91–101.
- Fukuda, H., T. Ogawa, and S. Tanase, 1993: Ethylene production by microorganisms. *Advances in Microbial Physiology*, **35**, 275–306.
- Hiradate, S., and N. U. Yamaguchi, 2003: Chemical species of Al reacting with soil humic acids. *Journal of Inorganic Biochemistry*, **97**, 26–31.
- Jackson, M. B., 1985: Ethylene and responses of plants to soil waterlogging and submergence. *Annual Review of Plant Physiology and Plant Molecular Biology*, **36**, 145–174.
- Kim, H. T., 1995: *Soil Sampling, Preparation and Analysis*. Marcel Dekker, New York, 432pp.
- Morisada, K., A. Iwaya, and K. One, 2002: Temporal changes in organic carbon of soils developed on volcanic andesitic deposits in Japan. *Forest Ecology and Management*, **171**, 113–120.
- Morisada, K., K. Ono, and H. Kanomata, 2004: Organic carbon stock in forest soils in Japan. *Geoderma*, **119**, 21–32.
- Sextstone, A., and C. N. Mains, 1990: Production of

- methane and ethylene in organic horizons of spruce forest soils. *Soil Biology and Biochemistry*, **22**, 135–139.
- Shann, J. R., and M. Bertsch, 1993: Different cultivar response to polynuclear hydroxo-aluminum complexes. *Soil Science Society of America Journal*, **57**, 116–120.
- Shoji, S., M. Nanzyo, and R. A. Dahlgren, 1993: *Volcanic Ash Soils: Genesis, Properties, and Utilization*. Elsevier, Amsterdam.
- Smith, K. A., and R. J. Dowdell, 1974: Field studies of soil atmosphere: 1. Relationships between ethylene, oxygen, soil moisture content, and temperature. *Journal of Soil Science*, **25**, 217–230.
- van Cleemput, O., A. S. ElSebaay, and L. Baert, 1983: Evolution of gaseous hydrocarbons from soil: Effect of moisture content and nitrate level. *Soil Biology and Biochemistry*, **15**, 519–524.
- Xu, X. K., and K. Inubushi, 2007: Production and consumption of ethylene in temperate volcanic forest surface soils. *European Journal of Soil Science*, **58**, 668–679.
- Xu, X. K., and K. Inubushi, 2008: Measurement of ethylene and methane production in a temperate forest soil using inhibition of acetylene and carbon monoxide. *Chinese Science Bulletin*, **53**, 1087–1093.
- Xu, X. K., and K. Inubushi, 2009a: Responses of ethylene and methane consumption to temperate and pH in temperate volcanic forest soils. *European Journal of Soil Science*, **60**, 489–498.
- Xu, X. K., and K. Inubushi, 2009b: Ethylene oxidation, atmospheric methane consumption, and ammonium oxidation in temperate volcanic forest soils. *Biology and Fertility of Soils*, **45**, 265–271.
- Xu, X. K., B. Yuan, and J. Wei, 2008: Vertical distribution and interaction of ethylene and methane in temperate volcanic forest soils. *Geoderma*, **145**, 231–237.
- Yamaguchi, N. U., S. Horadate, M. Mizoguchi, and T. Miyazaki, 2003: Formation and disappearance of Al Tridecamer in the presence of low molecular weight organic ligands. *Soil Science and Plant Nutrition*, **49**, 551–556.
- Zech, W., G. Guggenberger, and H. R. Schulten, 1994: Budgets and chemistry of dissolved organic carbon in forest soils- effects of anthropogenic soil acidification. *Science of the Total Environment*, **152**, 49–62.
- Zechmeister-Boltenstern, S., and K. A. Smith, 1998: Ethylene production and decomposition in soils. *Biology and Fertility of Soils*, **26**, 354–361.
- Zechmeister-Boltenstern, S., and L. Nikodim, 1999: Effect of water tension on ethylene production and consumption in montane and lowland soils in Austria. *European Journal of Soil Science*, **50**, 425–432.