연구보문

Ammonia Volatilization from Rice Paddy Soils Fertilized with ^{15}N-Urea Under Elevated CO_2 and Temperature

Sang-Sun Lim[1], Jin-Hyeob Kwak[1], Dong-Suk Lee[1], Sun-Il Lee[1], Hyun-Jung Park[1], Han-Yong Kim[2], Hong-Shik Nam[3], Kyeong-Min Cho[4], and Woo-Jung Choi[1]*

[1]Department of Biosystem & Agricultural Engineering, Institute of Agricultural Science and Technology, Chonnam National University, Yongbongro 77, Gwangju 500-757, Korea

[2]Department of Plant Science, Chonnam National University, Yongbongro 77, Gwangju 500-757, Korea

[3]National Academy of Agricultural Science, Rural Development Administration, Suwon 441-707, Korea.

[4]Watershed Environment Research Section, Yeongsan River Environment Research Center, Gwangju 500-480, Korea.

Abstract: It has widely been observed that the effect of elevating atmospheric CO_2 concentrations on rice productivity depends largely on soil N availabilities. However, the responses of ammonia volatilization from flooded paddy soil that is an important pathway of N loss and thus affecting fertilizer N availability to concomitant increases in atmospheric CO_2 and temperature has rarely been studied. In this paper, we first report the interactive effect of elevated CO_2 and temperature on ammonia volatilization from rice paddy soils applied with urea. Urea labeled with ^{15}N was used to quantitatively estimate the contribution of applied urea-N to total ammonia volatilization. This study was conducted using Temperature Gradient Chambers (TGCs) with two CO_2 levels [ambient CO_2 (AC), 383 ppmv and elevated CO_2 (EC), 645 ppmv] as whole-plot treatment (main treatment) and two temperature levels [ambient temperature (AT), 25.7℃ and elevated temperature (ET), 27.8℃] as split-plot treatments (sub-treatment) with triplicates. Elevated temperature increased ammonia volatilization probably due to a shift of chemical equilibrium toward NH_3 production via enhanced hydrolysis of urea to NH_3 of which rate is dependent on temperature. Meanwhile, elevated CO_2 decreased ammonia volatilization and that could be attributed to increased rhizosphere biomass that assimilates NH_4^+ otherwise being lost via volatilization. Such opposite effects of elevated temperature and CO_2 resulted in the accumulated amount of ammonia volatilization in the order of ACET>ACAT>ECET>ECAT. The pattern of ammonia volatilization from applied urea-^{15}N as affected by treatments was very similar to that of total ammonia volatilization. Our results suggest that elevated CO_2 has the potential to decrease ammonia volatilization from paddy soils applied with urea, but the effect could partially be offset when air temperature rises concomitantly.

Key Words: Ammonia Emission, Global Warming, Paddy Fields, Urea Hydrolysis

INTRODUCTION

Projected increases in atmospheric CO_2 concentration are expecting to enhance photosynthesis (and thus growth) of rice (*Oryza sativa* L.) that is a staple food for more than half of the world's population in at least 95 countries[1-3]. However, to take full advantages of the CO_2 fertilization effect, management of soil N availability has been shown to be very crucial[4-7].

Urea is the most extensively used fertilizer (accounted for 40% of total synthetic fertilizer consumption in the world), and is very susceptible to loss particularly via ammonia volatilization[8]. For example, ammonia volatilization can be as high as 40% of total applied urea-N in paddy fields[9]. Therefore, investigation of the response of ammonia volatilization from paddy

*연락저자:
Tel: +82-62-530-2153 Fax: +82-62-530-2159
E-Mail: wjchoi@chonnam.ac.kr

soils treated with urea to global warming is necessary to understand N loss potential via ammonia volatilization under changing climate conditions. Such information may be useful in developing fertilization strategy to maintain soil N availability in the future.

It is well recognized that temperature is one of the most important driving forces of ammonia volatilization from soils[10-12]. Therefore, it can be simply expected that ammonia volatilization from paddy soils under global warming may increase as compared with the current temperature. However, up to now, there is no study on ammonia volatilization from paddy soils exposed to global warming at a field scale. As increase in temperature is generally coincident with elevation of atmospheric CO_2 concentration[13], it is more worthy of investigating interactive effects of elevated temperature and CO_2 on ammonia volatilization from paddy soils. Regarding the effect of elevated CO_2, it is speculated that elevated CO_2 concentration may decrease ammonia volatilization from paddy soils by biological manners. Increased biomass of roots under elevated CO_2 may reduce the potential of ammonia volatilization by assimilating NH_4^+ produced from urea hydrolysis rapidly otherwise it is likely to be lost via ammonia volatilization[4,14].

To test such hypotheses, we investigated interactive effects of elevated temperature and CO_2 on ammonia volatilization from paddy fields treated with urea. Urea labeled with ^{15}N was used in this study to quantitatively estimate the contribution of applied urea-N to total ammonia volatilization.

MATERIALS AND METHODS

Experimental Settings

This study was conducted using Temperature Gradient Chambers (TGCs) with/without CO_2 fumigation in Chonnam National University during the growth period of rice in 2007. The TGCs (2.4 m in width×24 m in length×2.0 m in height for each TGC) were laid out as split-plot with two CO_2 levels [ambient CO_2 (AC), 383 ppmv and elevated CO_2 (EC), 645 ppmv] as whole-plot treatment (main treatment) and two temperature levels [ambient temperature (AT), 25.8℃ and elevated temperature (ET), 27.8℃] as split-plot treatments (sub-treatment) with triplicates. The TGCs were originally desinged to simulate atmospheric CO_2

concentation and temperature of A1B senario of IPCC[13]. Pots (depth=40 cm, top area=530.7 cm^2) were packed with soils (12 kg on dry basis for each pot) and three seedlings of *Oryza sativa* L. (c.v. Dongjinbyeo) were transplanted on June 4. The selected properties of the soils used are shown in Table 1.

In the TGC for each CO_2 treatment, three pots were located at the position of each temperature level. The three pots at each temperature and CO_2 level were asigned for three times of N fertilization as basal at the transplanting, the first additional at the tillering, and the second additional at the panicle initiation stages. A total 36 pots [four treatments (two CO_2 × two temperature) × three fertilizations (^{15}N fertilization at transplanting, tillering, and panicle forming stages) × three replications] were prepared. Fertilization was performed as follows: at the transplanting on June 4 (Urea 5.5 g N m^{-2}, Fused phosphate 4.5 g P_2O_5 m^{-2}, KCl 5.7 g k$_2$O m^{-2}) at tillering on June 19 (Urea 3.3 g N m^{-2}), and at panicle forming stages on July 23 (Urea 2.2 g N m^{-2}). Urea unlabeled and labeled with ^{15}N (5.0 atom %) was alternately used for each fertilization; i.e. labeled urea was applied as the basal followed by unlabeled urea as additional fertilization to investigate ammonia volatilization of N applied at each fertilization.

Table 1. Selected properties of soils used

Variables[a]		Values
Particle size distribution (%)	Sand	32.5 (0.7)
	Silt	46.8 (0.5)
	Clay	20.7 (0.4)
Texture		Loam
pHwater		6.39 (0.23)
Total N (g kg^{-1})		0.90 (0.02)
NH_4^+ (mg N kg^{-1})		10.2 (2.1)
NO_3^- (mg N kg^{-1})		2.1 (0.5)
Total C (g kg^{-1})		10.1 (0.2)
Available P (mg P_2O_5 kg^{-1})		29.3 (3.6)
CEC (cmol$_c^+$ kg^{-1})		14.2 (0.9)

Values are the means of triplicated measurements with standard errors in the parenthesis.
[a] Particle size distribution with pipette method; Texture as USDA classification; pH$_{water}$ with a pH meter at a 1-to-5 (soil-to-water) ratio; total N and C using a combustion method; NH_4^+ and NO_3^- with Kjeldhal distillation method after extracting with 2 M KCl at 1-to-5 (soil-to-extractant) ratio; available P with Bray #1 method; CEC with NH$_4$OAc method.

Trapping of volatilzed ammonia

A plastic bottle (depth=15 cm, bottom area=59.4 cm^2) was inserted into the pot at the depth 5 cm from the surface, and a 25−mL vial containing 10 mL of 2 N H_2SO_4 was placed in the bottle to trap ammonia votalized from the soil surface. The bottles were caped with lids air tightly, and the traps were replaced with new ones periodically during the experiment on 7, 17, 22, 36, 49, 57, 71, 86, and 100 days after transplanting.

Chemical analyses

The amount of volatilized NH_3 from the soils was determined via the titration of the trap (10 mL of 2 N H_2SO_4 solution) containing NH_4^+ with 1 N NaOH to a pH of 5.4 with the aid of a pH meter. After titration, the solutions were adjusted to pH 3 using 0.1 N H_2SO_4 and evaporated to dryness at 65℃ in an oven[15]. The atom % ^{15}N of the powder (ammonium sulfate) was analyzed with a continuous−flow stable isotope ratio mass spectrometer (IsoPrime EA, Micro−mass, UK) linked to a CN analyzer (NA Series 2, CE Instruments, Italy). Pure N_2 (atom % ^{15}N = 0.3655 ± 0.0001) gas was employed as a reference.

Calculations and statistical anslysis

The amount of ammonia volatilization in each pot was calculated based on the area covered with a bottle placed over the ammonia trap vial, after which the ammonia volatilization rate (NH_3−N m^{-2} day^{-1}) was calculated. The amounts of volatilized N derived from ^{15}N−labeled urea fertilizer (NDFF) and that from soil (NDFS) were computed using the following equations16):

$$NDFF = T \times (A_S/A_F) \quad \text{and} \quad NDFS = T - NDFF$$

in which the T and A_S are the amount and atom% ^{15}N excess (relative to the atmospheric N_2 atom % ^{15}N of 0.3663%) of volatilized total ammonia N, respec−tively, and A_F is atom% ^{15}N excess (4.6337) of the applied urea.

Analysis of variance (ANOVA) was performed for a 2×2 factorial design with triplications on all experi−mental variables using the general linear models (GLM) procedure in the SPSS 14.0 package (SPSS Inc., Chicago, IL) to assess the significance of the effects of CO_2 concentration, temperature, and their interaction.

A level of significance at α=0.05 was used for inferring significance of all the statistical analyses.

RESULTS AND DISCUSSION

Temporal changes in ammonia volatilization were the same across all the treatments, showing increasing volatilization right after urea application followed by diminishing volatilization with the elapse of time (Fig. 1). For example, ammonia volatilization rate during the first 7−days after transplanting was between 6.3 and 11.6 mg N m^{-2} day^{-1}; thereafter it decreased to the range from 4.6 to 8.3 mg N m^{-2} day^{-1} during the period between 8 and 15 days after transplanting. Ammonia volatilization rate sharply increased after additional fertilization at panicle forming stage. The relatively high rate of ammonia volatilization was observed for initial N fertilization and this was due to a relatively high N fertilization rate at early growth stage when roots were not established yet as compared with middle or late growth stages[8]. Ammonia volatilization rate between 49 and 57 days right after N fertilization at the tillering stage increased again (Fig. 1) probably due to a higher temperature during the summer season. During this period, ammonia volatilization rate of ambient CO_2 treatments (ACAT and ACET) was significantly ($P<0.05$) higher than that of elevated CO_2 treatments (ECAT and ECET)
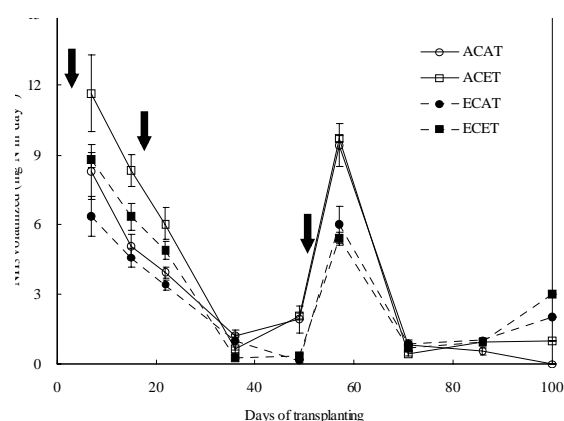

Fig 1. Temporal changes in the rate of total NH_3 volatilization from pots in each combination treatment (ACAT, ambient CO_2 and ambient temperature; ACET, ambient CO_2 and elevated temperature; ECAT, elevated CO_2 and ambient temperature; ECET, elevated CO_2 and elevated temperature). The data are the means of triplications. The vertical bars indicate standard errors of the means and the arrows indicate fertilization time.
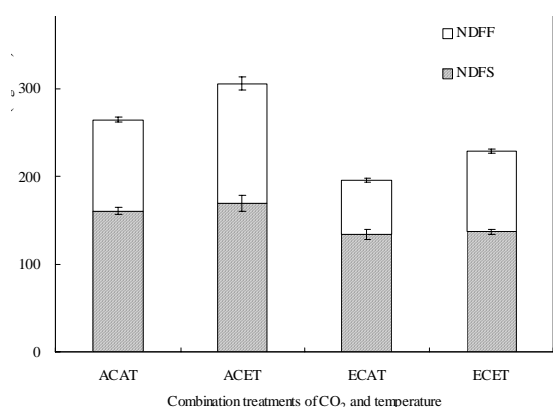
Fig 2. Accumulative amount of NH_3 volatilization from applied fertilizer (NDFF) and from soil (NDFS) over rice cropping seasons in each combination treatment (refer to Fig. 1 caption for the details of the treatments codes). The data are the means of triplications. The vertical bars indicate standard errors of the means and the arrows indicate fertilization time.

and this was attributable to more accumulation of bio-mass including roots under elevated CO_2 conditions[4,14,18].

The accumulated amount of ammoina volatilized (AV_{acc}) through the experiment period was significantly affected by both temperature ($P<0.001$) and CO_2 level ($P<0.001$) in an opposite way without significant interaction of both ($P=0.13$) (Fig. 2). Elevated temperature increased AV_{acc} by 23.0% from 263.7 mg N m^{-2} in ACAT to 324.4 mg N m^{-2} in ACET under ambient CO_2, but such effect of temperature became less when CO_2 concentration was co-elevated along with temperature (by 13.5% from 195.8 mg N m^{-2} in ECAT to 222.3 mg N m^{-2} in ECET). The increases in AV_{acc} by temperature can be attributable to more rapid production of NH_3 via urea hydrolysis, a shift of chemical equilibrium (between $NH_4^+ \leftrightarrow NH_3$), and increase in NH_3 diffusion rate[17]. In a laboratory study, He et al.[10] reported that the potential maximum ammonia volatilization predicted by the Langmuir kinetic model increased by 2.0- and 3.4-fold with increases in temperature from 5 to 25℃ and from 25 to 45℃, respectively.

Comparing within the same temperature level, elevation of CO_2 significantly decreased AV_{acc} by 25.8% from 263.7 mg N m^{-2} (ACAT) to 195.8 mg N m^{-2} (ECAT) under ambient temperature and by 31.5% from 324.4 mg N m^{-2} (ACET) to 222.3 mg N m^{-2} (ECET) under elevated temperature. Such a decrease in AV_{acc} by elevated CO_2 concentration could have

been resulted by rapid microbial/plant assimilation of NH_4^+ produced from urea as elevated CO_2 generally causes more accumulation of biomass including roots and also increases root exudate that is the substrate for microbial activity[4,14,18]. In our pot experiment, dry matter of roots was higher in elevated CO_2 treatments than in ambient CO_2 treatments by around 50% (unpublished data). Such an opposite effect of elevated CO_2 and temperature resulted in AV_{acc} in the order of ACET>ACAT> ECET>ECAT.

The pattern of AV_{acc} from applied urea (NDFF) was very similar to that of total AV_{acc} (Fig. 2). The contribution of NDFF to total AV_{acc} ranged from 31.7 to 41.9% with relatively high percentage under ambient CO_2 as compared with elevated CO_2 concentration. This range is within the values (from 20 to 50%) reported by Matsushima et al.[8] who investigated ammonia volatilization from upland soils amended with livestock manure compost and urea. In our study, NDFF of AV_{acc} was equivalent to be less 1.0% of total amount of applied urea-N (11 g N m^{-2}). This value is considerably small as compared with other studies; e.g. 6 to 40% in upland soils[19], 8 to 16% in calcareous soils[20], and 40% in paddy soils[9]. The substantially low ammonia volatilization of applied urea was probably attributable to the experimental method as closed chamber method adopted in our study is likely to result in a low ammonia volatilization by preventing the wind-driving mass flow of NH_3 gas[21]. Matsushima et al.[8] also reported that less than 1.0% of applied urea was volatilized from upland soils by using the closed chamber method.

Our results show that elevation of temperature can increase N loss via ammonia volatilization but co-elevation of CO_2 concentration with temperature may reduce N loss from paddy soils applied with urea. However, the effect of such decrease in ammonia volatilization under the projected global warming on total N efficiency needs to be further studied.

ACKNOWLEDGEMENT

REFERENCES

1. Kim, H. Y., Lieffering, M., Kobayashi, K., Okadas, M., and Miura, S. (2003) Seasonal changes in the effects of elevated CO_2 on rice at three levels of nitrogen supply: a free air CO_2 enrichment (FACE) experiment. *Global Change Biol*. 9, 826−837.

2. Bannayan, M., Kobayashi, K., Kim, H. Y., Lieffering, M., Okada, M., and Miura, S. (2005) Modeling the interactive effects of atmospheric CO_2 and N on rice growth and yield. *Field Crop Res*. 93, 237−251.

3. Krishnan, P., Swain, D. K., Bhaskar, B. C., Nayak, S. K., and Dash, R. N. (2007) Impact of elevated CO_2 and temperature on rice yield and methods of adaptation as evaluated by crop simulation studies. *Agr. Ecosyst. Environ*. 122, 233−242.

4. Kim, H. Y., Lieffering, M., Miura, S., Kobayashi, K., and Okada, M. (2001) Growth and nitrogen uptake of CO_2−enriched rice under field conditions. *New Phytol*. 150, 223−229.

5. Kim, H. Y., Lieffering, M., Kobayashi, K., Okada, M., Mitchell, M. W., and Gumpertz, M. (2003) Effects of free−air CO_2 enrichment and nitrogen supply on the yield of temperate paddy rice crops. *Field Crop Res*. 83, 261−270.

6. Weerakoon, W. M. W., Ingram, K. T., Moss, D. N. (2005) Atmospheric CO_2 concentration effects on N partitioning and fertilizer N recovery in field grown rice (*Oryza sativa* L.). *Agr. Ecosyst. Environ*. 108, 342−349.

7. Yang, L., Wang, Y., Kobayashi, K., Zhu, J., Huang, J., Yang, H., Wang, Y., Dong, G., Liu, G., Han, Y., Shan, Y., Hu, J., and Zhou, J. (2008) Seasonal changes in the effects of free−air CO_2 enrichment (FACE) on growth, morphology and physiology of rice root at three levels of nitrogen fertilization. Global Change Biol. 14, 1844−1853.

8. Matsushima, M., Lim, S. S., Kwak, J. H., Park, H. J., Lee, S. I., Lee, D. S., and Choi, W. J. (2009) Interactive effects of synthetic nitrogen fertilizer and composted manure on ammonia volatilization from soils. *Plant Soil* (DOI 10.1007/s11104−009−9967−3).

9. Cai, G. X., Freney, J. R., Humphreys, E., Demand, O. T., Samson, M., and Simpson, J. R. (1987) Use of surface film to reduce ammonia volatilization from flooded rice fields. *Aust. J. Agric. Res*. 39: 177−196.

10. He, Z. L., Alva, A. K., Calvert, D. V., and Banks, D. J. (1999) Ammonia volatilization from different fertilizer sources and effects of temperature and soil pH. *Soil Sci*. 164, 750−758.

11. Choi, W. J., Chang, S. X., Kwak, J. H., Jung, J. W., Lim, S. S., Yoon, K. S., and Choi, S. M (2007) Nitrogen transformations and ammonia volatilization losses from ^{15}N−urea as affected by the co−application of composted pig manure. Can. *J. Soil Sci*. 87, 485−493.

12. Liu, G. D., Li, Y. C., and Alva, A. K. (2007) Temperature quotients of ammonia emission of different nitrogen sources applied to four agricultural soils. *Soil Sci. Soc. Am*. J. 71, 1482−1489.

13. IPCC (2007) Climate Change 2007: Synthesis report. IPCC, Geneva, Switzerland.

14. De Costa, W. A. J. M., Weerakoon, W. M. W., Herath, H. M. L. K., Amaratunga, K. S. P., and Abeywardena, R. M. I. (2006) Physiology of yield determination of rice under elevated carbon dioxide at high temperature in a subhumid tropical climate. *Field Crop Res*. 96, 336−347.

15. Feast, N. A. and Dennis, P. F. (1996) A comparison of methods for nitrogen isotope analysis of groundwater. *Chem. Geol*. 129, 167−171

16. Hauck, R. D. and Bremner, J. M. (1976) Use of tracers for soil fertilizer nitrogen research. *Adv. Agron*. 28, 219−266

17. Avnimelech, Y. and Laher, M. (1977) Ammonia volatilization from soils: Equilibrium considerations. *Soil Sci. Soc. Am. J*. 41, 1080−1084.

18. Freeman, C., Fenner, N., Ostle, N. J., Kang, H., Dowrick, D. J., Reynolds, B., Lock, M. A., Sleep, D., Hughes, S., and Hudson, J. (2004) Export of dissolved organic carbon from peatlands under elevated carbon dioxide levels. *Nature* 430, 195−198.

19. Nathan, M. V. and Malzer, G. L. (1994) Dynamics of ammonia volatilization from turkey manure and urea applied to soil. *Soil Sci. Soc. Am. J.* 58, 985−990.

20. Fenn, L. B. and Escarzaga, R. (1976) Ammonia volatilization from surface applications of ammonium compounds on calcareous soils: V. Soil water content and methods of nitrogen application. *Soil Sci. Soc. Am*. J. 40, 537−541.

21. Bouwman, A. F., Boumans, L. J. M., and Batjes, N. H. (2002) Estimation of global NH_3 volatilization loss from synthetic fertilizers and animal manure applied to arable lands and grasslands. *Global Biogeochem. Cy*. 16, 1024.