Ammonia Volatilization from Rice Paddy Soils Fertilized with \(^{15}\text{N}\)-Urea Under Elevated CO\(_2\) and Temperature

Sang-Sun Lim\(^1\), Jin-Hyeob Kwak\(^3\), Dong-Suk Lee\(^1\), Sun-II 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.

(Received September 7, 2009, Accepted September 21, 2009)

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 \(^{15}\text{N}\) 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\(^\circ\)C and elevated temperature (ET), 27.8\(^\circ\)C] 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\(_4^+\) 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-\(^{15}\text{N}\) 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 (\textit{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
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\textsuperscript{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\textsubscript{2} concentration\textsuperscript{13}, it is more worthy of investigating interactive effects of elevated temperature and CO\textsubscript{2} on ammonia volatilization from paddy soils. Regarding the effect of elevated CO\textsubscript{2}, it is speculated that elevated CO\textsubscript{2} concentration may decrease ammonia volatilization from paddy soils by biological manners. Increased biomass of roots under elevated CO\textsubscript{2} may reduce the potential of ammonia volatilization by assimilating NH\textsubscript{4}\textsuperscript{+} produced from urea hydrolysis rapidly otherwise it is likely to be lost via ammonia volatilization\textsuperscript{4,14}.

To test such hypotheses, we investigated interactive effects of elevated temperature and CO\textsubscript{2} on ammonia volatilization from paddy fields treated with urea. Urea labeled with \textsuperscript{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\textsubscript{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\textsubscript{2} levels [ambient CO\textsubscript{2} (AC), 383 ppmv and elevated CO\textsubscript{2} (EC), 645 ppmv] as whole-plot treatment (main treatment) and two temperature levels [ambient temperature (AT), 25.8°C and elevated temperature (ET), 27.8°C] as split-plot treatments (sub-treatment) with triplicates. The TGCs were originally designed to simulate atmospheric CO\textsubscript{2} concentration and temperature of A1B scenario of IPCC\textsuperscript{13}.

Pots (depth=40 cm, top area=530.7 cm\textsuperscript{2}) were packed with soils (12 kg on dry basis for each pot) and three seedlings of \textit{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\textsubscript{2} treatment, three pots were located at the position of each temperature level. The three pots at each temperature and CO\textsubscript{2} level were assigned 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\textsubscript{2} × two temperature) × three fertilizations (\textsuperscript{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\textsuperscript{-2}, Fused phosphate 4.5 g P\textsubscript{2}O\textsubscript{5} m\textsuperscript{-2}, KCl 5.7 g K\textsubscript{2}O m\textsuperscript{-2}) at tillering on June 19 (Urea 3.3 g N m\textsuperscript{-2}), and at panicle forming stages on July 23 (Urea 2.2 g N m\textsuperscript{-2}). Urea unlabeled and labeled with \textsuperscript{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>
<thead>
<tr>
<th>Variables\textsuperscript{a}</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size distribution (%): Sand</td>
<td>32.5 (0.7)</td>
</tr>
<tr>
<td>: Silt</td>
<td>46.8 (0.5)</td>
</tr>
<tr>
<td>: Clay</td>
<td>20.7 (0.4)</td>
</tr>
<tr>
<td>Texture: Loam</td>
<td>6.39 (0.23)</td>
</tr>
<tr>
<td>pH\textsubscript{water}</td>
<td>6.39 (0.23)</td>
</tr>
<tr>
<td>Total N (g kg\textsuperscript{-1})</td>
<td>0.90 (0.02)</td>
</tr>
<tr>
<td>NH\textsubscript{4}\textsuperscript{+} (mg N kg\textsuperscript{-1})</td>
<td>10.2 (2.1)</td>
</tr>
<tr>
<td>NO\textsubscript{3}\textsuperscript{-} (mg N kg\textsuperscript{-1})</td>
<td>2.1 (0.5)</td>
</tr>
<tr>
<td>Total C (g kg\textsuperscript{-1})</td>
<td>10.1 (0.2)</td>
</tr>
<tr>
<td>Available P (mg P\textsubscript{2}O\textsubscript{5} kg\textsuperscript{-1})</td>
<td>29.3 (3.6)</td>
</tr>
<tr>
<td>CEC (cmol\textsubscript{+} kg\textsuperscript{-1})</td>
<td>14.2 (0.9)</td>
</tr>
</tbody>
</table>

Values are the means of triplicated measurements with standard errors in the parenthesis.

\textsuperscript{a} Particle size distribution with pipette method; Texture as USDA classification; pH\textsubscript{water} with a pH meter at a 1→5 (soil→water) ratio; total N and C using a combustion method; NH\textsubscript{4}\textsuperscript{+} and NO\textsubscript{3}\textsuperscript{-} with Kjeldahl distillation method after extracting with 2 M KCl at 1→5 (soil→extractant) ratio; available P with Bray #1 method; CEC with NH\textsubscript{4}OAc method.
Trapping of volatilized ammonia

A plastic bottle (depth=15 cm, bottom area=59.4 cm²) was inserted into the pot at the depth 5 cm from the surface, and a 25-mL vial containing 10 mL of 2 N H₂SO₄ was placed in the bottle to trap ammonia volatilized from the soil surface. The bottles were capped 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 NH₃ from the soils was determined via the titration of the trap (10 mL of 2 N H₂SO₄ solution) containing NH₄⁺ 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 H₂SO₄ and evaporated to dryness at 65°C in an oven. The atom % ¹⁵N of the powder (ammonium sulfate) was analyzed with a continuous-flow stable isotope ratio mass spectrometer (IsoPrime EA, Micromass, UK) linked to a CN analyzer (NA Series 2, CE Instruments, Italy). Pure N₂ (atom % ¹⁵N = 0.3655 ± 0.0001) gas was employed as a reference.

Calculations and statistical analysis

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 (NH₃-N m⁻² day⁻¹) was calculated. The amounts of volatilized N derived from ¹⁵N-labeled urea fertilizer (NDFF) and that from soil (NDFS) were computed using the following equations:

\[ \text{NDFF} = T \times (A_S/A_P) \quad \text{and} \quad \text{NDFS} = T - \text{NDFF} \]

in which the T and AS are the amount and atom% ¹⁵N excess (relative to the atmospheric N₂ atom % ¹⁵N of 0.3663%) of volatilized total ammonia N, respectively, and AP is atom% ¹⁵N excess (4.6337) of the applied urea.

Analysis of variance (ANOVA) was performed for a 2x2 factorial design with triplications on all experimental 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 CO₂ 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. 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 CO₂ treatments (ACAT and ACET) was significantly (P<0.05) higher than that of elevated CO₂ treatments (ECAT and ECET).

![Fig 1. Temporal changes in the rate of total NH₃ volatilization from pots in each combination treatment (ACAT, ambient CO₂ and ambient temperature; ACET, ambient CO₂ and elevated temperature; ECAT, elevated CO₂ and ambient temperature; ECET, elevated CO₂ 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.](image-url)
The accumulated amount of ammonia volatilized (AVacc) through the experiment period was significantly affected by both temperature ($P<0.001$) and CO2 level ($P<0.001$) in an opposite way without significant interaction of both ($P=0.13$) (Fig. 2). Elevated temperature increased AVacc by 23.0% from 263.7 mg N m$^{-2}$ in ACAT to 324.4 mg N m$^{-2}$ in ACET under ambient CO2, but such effect of temperature became less when CO2 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 AVacc by temperature can be attributable to more rapid production of NH3 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$^\circ$C and from 25 to 45$^\circ$C, respectively.

Comparing within the same temperature level, elevation of CO2 significantly decreased AVacc 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 AVacc by elevated CO2 concentration could have been resulted by rapid microbial/plant assimilation of NH$_4^+$ produced from urea as elevated CO2 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 CO2 treatments than in ambient CO2 treatments by around 50% (unpublished data). Such an opposite effect of elevated CO2 and temperature resulted in AVacc in the order of ACET>ACAT> ECET>ECAT.

The pattern of AVacc from applied urea (NDFF) was very similar to that of total AVacc (Fig. 2). The contribution of NDFF to total AVacc ranged from 31.7 to 41.9% with relatively high percentage under ambient CO2 as compared with elevated CO2 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 AVacc 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 NH3 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 CO2 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

This work was supported by National Research Foundation of Korea Grant funded by the Korean Government (KRF–2006–311–F00039). Institute of Agricultural Science & Technology at Chonnam National University provided assistance with cultivation of rice.
REFERENCES


