Kinetic Responses of Soil Carbon Dioxide Emission to Increasing Urea Application Rate

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Abstract

BACKGROUND: Application of urea may increase CO2 emission from soils due to both CO2 generation from urea hydrolysis and fertilizer-induced decomposition of soil organic carbon (SOC). The objective of this study was to investigate the effects of increasing urea application on CO2 emission from soil and mineralization kinetics of indigenous SOC.

METHODS AND RESULTS: Emission of CO2 from a soil amended with four different rates (0, 175, 350, and 700 mg N/kg soil) of urea was investigated in a laboratory incubation experiment for 110 days. Cumulative CO2 emission (Ccum) was linearly increased with urea application rate due primarily to the contribution of urea-C through hydrolysis to total CO2 emission. First-order kinetics parameters (C0 and k) became greater with increasing urea application rate; C0 increased from 665.1 to 780.3 mg C/kg and k from 0.024 to 0.069 day-1, determinately showing fertilizer-induced SOC mineralization. The relationship of C0 (non-linear) and k (linear) with urea-N application rate revealed different responses of C0 and k to increasing rate of fertilizer N.

CONCLUSION(s): The relationship of mineralizable SOC pool size and mineralization rate with urea-N application rate suggested that increasing N fertilization may accelerate decomposition of readily decomposable SOC; however, it may not always stimulate decomposition of non-readily decomposable SOC that is protected from microbial decomposition.

Key Words: First-order kinetics, CO2 emission, Carbon mineralization, Fertilizer application rate, Soil organic carbon

Introduction

The size of soil C pool, the largest C sink in the terrestrial ecosystem, is estimated to be 2500 Pg which is about 3.3 times greater than the atmospheric C pool (Lal, 2004). Therefore, any changes in soil C pool influence atmospheric CO2 concentration via a negative (CO2 sequestration) or positive (CO2 emission) feedback (Lal et al., 2007). In arable lands, many agricultural practices such as fertilization, tillage, cover crops, cropping system, and organic matter management have been proven to affect soil organic C (SOC) dynamics and thus C balance between soil and atmosphere (Lal, 2004; Sainju et al., 2008). Therefore, a better understanding
of the responses of SOC dynamics to different agricultural practices is necessary to enhance the role of SOC as a C sink under climate change (Lal, 2004).

As fertilization is one of the key agricultural activities that improve crop productivity, adequate fertilization may be helpful in increasing SOC pool size when plant residues are returned to the soil (Smith, 1999). Nitrogen is one of the macro-nutrients that are essential both to plants and soil microbes; however, as most of N is in the organic form that is not directly available (only 5% of N is available in most soils with moderate fertility), N is likely to be the element limiting plants growth and microbial activities (Jansson, 1996). Under such N deficient conditions as in most agricultural soils, N fertilization can not only enhance crop productivity but also stimulate soil heterotrophs that are responsible for decomposition of SOC. Therefore, if plant residues are not returned to the soils, SOC level is expected to decrease via C loss through fertilization-induced mineralization of SOC (Kuzyakov et al., 2000; Khalil et al., 2007).

Urea is one of the most widely used N fertilizers due to its high N content (ca. 46.7%), solubility, and nonpolarity, particularly in Asian countries (International Fertilizer Industry Association, http://www.fertilizer.org/ifa/homepage/statistics). Because elemental C content of urea ((NH₂)₂CO) is 20% that is converted to CO₂ during urea hydrolysis ((NH₂)₂CO + 3H₂O → 2NH₄⁺ + CO₂ + 2OH⁻), application of urea as a N fertilizer may further increase CO₂ emission from the soil (Choi et al., 2007; Jassal et al., 2010; Serrano-Silva et al., 2011). However, as far as our knowledge, no attempt has been made to investigate soil CO₂ emission responses to increasing rate of urea fertilization. In this context, CO₂ emission from soil in responding to different urea fertilization rate may be helpful in enlarging our understanding of SOC dynamics in urea-applied soils.

Materials and Methods

Soil
A sandy loam soil (around 10 kg) was collected from the surface layer (0-10 cm) of an experimental farm (126°36’08˝E, 35°10’21˝N) at Chonnam National University in Gwangju. The soil is classified as Fluventic Haplaquepts in the Soil Taxonomy. When the soil was collected, visible plant detritus and gravels were removed, and the soils were placed in a plastic box and homogenously mixed with a shovel. The soil was brought to the laboratory, and air-dried, passed through a 2-mm sieve, and used for the incubation experiment and analysis of some chemical properties; pH_water (1:5) of 5.7, total organic C of 14.0 g C/kg, total N of 1.4 g N/kg, NH₄⁺ of 3.2 mg N/kg, and NO₃⁻ of 5.3 mg N/kg.

Incubation experiment
Each 50 g of soil was placed into a 125-mL beaker and distilled water was added to bring the moisture content to 40% of the water holding capacity of the soil (0.36 kg/kg), and then pre-incubated for 5 days at 25±1°C in darkness to restore the microbial activity of the soils. A total of twelve bottles was prepared for four treatments with triplicates; the four treatments were control without fertilizer (code: N0), urea at 175 mg N/kg (N0.5), at 350 mg N/kg (N1), and at 700 mg N/kg (N2). Urea solutions were prepared by dissolving 0.1875, 0.375, and 0.75 g of urea in 100-mL distilled water for N0.5, N1, and N2, respectively, and 10 mL of the solution was added to the corresponding bottles at the initiation of the incubation. As C content of urea is 20%, the amounts of C added to the soil as urea were 75, 150, and 300 mg C/kg for N0.5, N1, and N2, respectively.

Both the beaker containing the soils and a 25-mL vial containing 20 mL of 1 N NaOH (CO₂ trap) were placed into a 1-L Mason jar with air-tight screw-top lids. The jars were incubated for 110 days in darkness at 25±1°C. During incubation, the jars were opened for 10 minutes every other day to maintain an adequate O₂ level. At 3, 10, 17, 24, 31, 38, 45, 60, 80, and 110 days of incubation, the vial containing the NaOH solution was removed from the jar and utilized for acid-base titration to determine entrapped CO₂, and a new vial with fresh NaOH solution was placed back into the jar at each sampling except at 110 days. Soil water content was adjusted via addition of distilled water to the initial weight of the beaker at each sampling.

CO₂ measurement and kinetic model fitting
The amount of CO₂-C trapped within the NaOH
solution was determined via the titration of the solution with 1 M HCl solution after the addition of 20 mL of 1 M BaCl₂ (Choi et al., 2005). Daily CO₂ emission rate was expressed as mg C/kg soil/day, and the cumulative CO₂-C (Ccum) evolved over the 110-day incubation was calculated. The amounts of CO₂ emitted during the aeration (for 10 minutes) were calculated from the daily mean CO₂ emission rate (see Fig. 1a) and the average values of CO₂ loss at each aeration event over the entire incubation period were between 0.06 and 0.13 mg C/kg. Therefore, the total amounts of CO₂ lost (i.e. not entrapped) during the aeration over 110-day estimated to be 3.4, 4.9, 6.1, and 7.3 mg C/kg for N0, N0.5, N1, and N2, respectively, and these are negligible compared to the Ccum, equivalent to 0.6, 0.62, 0.70, and 0.71% of Ccum respectively.

To obtain kinetic parameters (C₀, mineralizable SOC pool size and k, rate constant) of SOC mineralization, the contribution of urea-derived CO₂ to the cumulative CO₂-C evolution was eliminated by supposing that CO₂ originated from urea hydrolysis is emitted at a uniform rate over the incubation period (Serrano-Silva et al., 2011). The refined data on cumulative CO₂-C evolution (Ccum) was fitted to the single exponential first-order kinetic model, \( C_{\text{cum}} = C_0 [1 - \exp(-kt)] \), with the Fit Curve procedures of SigmaPlot 10.0 (Systat Software Inc., IL), which uses the Marquardt-Levenberg algorithm and an iterative process to determine the parameter values that minimize the residual sum of squares (Boyle and Paul, 1989; Ajwa and Tabatabai, 1994).

**Statistical analysis**

Analysis of variance (ANOVA) on cumulative CO₂ emission (Cm) and kinetics parameters (C₀ and k₀) using the GLM procedure in the SPSS 17.0 package (SPSS Inc., Chicago, IL, USA) was conducted in order to evaluate the effects of urea application rate. When the treatment effect was significant, the means were separated via Duncan's multiple range tests. The significance of the first-order kinetic model was analyzed via an F-test. The level of significance established for all statistical tests was \( \alpha = 0.05 \).

**Results and Discussion**

During the first 3 days of incubation, CO₂ emission rates were as high as 26.8, 44.5, 68.8, and 89.1 mg C/kg/day for N0, N0.5, N1, and N2, respectively (Fig. 1a). Thereafter, it decreased gradually over the remaining incubation period. An initial flush of CO₂ emission in the early incubation period followed by a gradual decrease is widely reported by others (Ajwa and Tabatabai, 1994; Bernal et al., 1998; Aslam et al., 2008). This was attributable to rapid mineralization of readily decomposable SOC immediately after the initiation of incubation (Bernal and Kirchmann, 1992; Bernal et al., 1998; Rochette et al., 2006).

The Ccum over the whole incubation period were 618.8, 827.3, 933.0, and 1091.5 mg C/kg for N0, N0.5, N1, and N2, respectively when urea-derived CO₂ was included (Table 1). Although added N might activate heterotrophs that decompose SOC, the increasing pattern of Ccum with increasing urea application should be ascribed primarily to CO₂ produced from urea hydrolysis (Khalil et al., 2007). Hydrolysis of urea is known to be very rapid; e.g. Choi et al. (2007) reported that urea was hydrolyzed completely within 3 days of application into the same soil used in the present study. Therefore, these results suggest that application of urea may result in a higher CO₂ emission from soils compared
Table 1. Treatment description and cumulative CO₂ emission from the soils over the 110-days incubation

<table>
<thead>
<tr>
<th>Treatment code</th>
<th>Urea application (mg urea/kg soil)a</th>
<th>Cumulative CO₂ emission (mg C/kg)b Including CO₂ from urea hydrolysis</th>
<th>Excluding CO₂ from urea hydrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>N0</td>
<td>0</td>
<td>618.8a</td>
<td>618.8a</td>
</tr>
<tr>
<td>N0.5</td>
<td>375</td>
<td>827.3b</td>
<td>752.3b</td>
</tr>
<tr>
<td>N1</td>
<td>750</td>
<td>933.0c</td>
<td>783.0c</td>
</tr>
<tr>
<td>N2</td>
<td>1500</td>
<td>1091.5d</td>
<td>791.5c</td>
</tr>
</tbody>
</table>

Values in the same column followed by a different letter are significantly different at α = 0.05.
a The amounts of N and C incorporated to soil as urea were equivalent to 0, 175, 350, and 700 mg N/kg, and 0, 75, 150, and 300 mg C/kg for N0, N0.5, N1, and N2, respectively.
b Cumulative CO₂ emission was calculated for both cases when CO₂ produced from urea hydrolysis was included and excluded. For the latter, C contained in the applied urea (75, 150, 300 mg C/kg for N0.5, N1, and N2, respectively) was subtracted from the first.

with other fertilizer N species such as (NH₄)₂SO₄ and KNO₃ due to its C content. Meanwhile, assuming that urea-C (20% w/w) incorporated additionally to the urea-treated soils was completely emitted from the soils via urea hydrolysis during the incubation period, the Ccum evolved from the indigenous SOC that calculated by excluding urea-derived C (75, 150, and 300 mg C/kg for N0.5, N1, and N2, respectively) from the whole Ccum was estimated to be 752.3, 783.0, and 791.5 mg C/kg, respectively (Table 1). Such an increasing pattern of Ccum after removing urea-C contribution supports increased soil respiration by fertilizer N-induced stimulation of heterotrophs (Kuzyakov et al., 2000; Khalil et al., 2007).

To evaluate the effect of increasing rate of fertilizer N on kinetic parameters of indigenous SOC mineralization, the measured Ccum was refined by subtracting urea-derived CO₂ from the Ccum as described earlier. The refined cumulative CO₂ emission increased gradually during the incubation period (Fig. 1b). Such CO₂ emission from decomposition of SOC can be described with the double exponential kinetic model that separates SOC pool into rapidly and slowly mineralizable pools particularly when exogenous organics such as composts and plant residues are amended (Boyle and Paul, 1989; Ajwa and Tabatabai, 1994). As exogenous organic C was not added into soils in our study, however, double exponential model resulted in k greater than a few orders of magnitude (data not shown). Meanwhile, the Ccum was better fit with the single exponential model that does not discriminate SOC pool in terms of decomposability (Table 2) and this is often the case for the soil into which a fresh organic matter is not incorporated (Lim, 2009). Kinetic parameters (C₀ and k) of SOC mineralization explored by the single exponential model became greater with increasing rate of urea-N application, indicating that urea application increased both mineralizable SOC pool and its mineralization rate.

The relationship of kinetic parameters (C₀ and k) with urea-N application rate, however, revealed different responses of C₀ and k to increasing rate of fertilizer N; k was linearly correlated with urea-N rate, but C₀ was not (Fig. 2). The pattern of k in responding to increasing urea-N suggests that application of fertilizer N tends to accelerate SOC decomposition rate in a linear fashion. Meanwhile, the non-linear relationship between C₀ and urea-N rate indicates that fertilizer-induced stimulation of SOC mineralization (i.e. increase of mineralizable SOC pool size) is not proportional to fertilization rate. In a similar fashion, Han et al. (2004) and Choi et al. (2005) reported that co-application of fertilizer increased microbial mineralization of compost applied in soils with relatively low mineral N availability;

Table 2. Kinetic parameter values (C₀, mineralizable soil organic C pool size; k, mineralization rate constant) of the single exponential first-order equation model and F-values for soil organic C mineralization in the soils

<table>
<thead>
<tr>
<th>Treatmenta</th>
<th>C₀ (mg C/kg)</th>
<th>k (day⁻¹)</th>
<th>RMS</th>
<th>Fb</th>
</tr>
</thead>
<tbody>
<tr>
<td>N0</td>
<td>665.1a</td>
<td>0.024a</td>
<td>186</td>
<td>2160**</td>
</tr>
<tr>
<td>N0.5</td>
<td>750.7b</td>
<td>0.036b</td>
<td>536</td>
<td>1159**</td>
</tr>
<tr>
<td>N1</td>
<td>767.1bc</td>
<td>0.048c</td>
<td>1308</td>
<td>475**</td>
</tr>
<tr>
<td>N2</td>
<td>780.3c</td>
<td>0.069d</td>
<td>1879</td>
<td>340**</td>
</tr>
</tbody>
</table>

Values in the same column followed by a different letter are significantly different at α = 0.05.
a See Table 1 for the details of the treatments.
b ***, P < 0.001
Fig. 2. Relationship between urea-N application rate and kinetic parameters (C_0, mineralizable soil organic C pool size; k, mineralization rate constant) of soil organic C mineralization.

however, such effect was negligible when mineral N concentration of indigenous soil was high. Therefore, our results in combination with the previous studies suggest that SOC mineralization rate is more sensitive than mineralizable SOC pool size to N fertilization.

**Conclusion**

Our study shows that application of urea may substantially increases CO_2 emission from soil due both to CO_2 generation from urea hydrolysis and fertilizer N-induced mineralization of SOC. The relationship of mineralizable SOC pool size and mineralization rate with urea-N application rate suggested that increased N fertilization may accelerate soil CO_2 emission rate in a linear fashion; however mineralizable SOC pool size may not be enlarged in corresponding to increasing N fertilization rate.

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**References**


