

Research Article

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

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### Abstract

**BACKGROUND:** Application of urea may increase CO<sub>2</sub> emission from soils due both to CO<sub>2</sub> 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 CO<sub>2</sub> emission from soil and mineralization kinetics of indigenous SOC.

**METHODS AND RESULTS:** Emission of CO<sub>2</sub> 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 CO<sub>2</sub> emission (C<sub>cum</sub>) was linearly increased with urea application rate due primarily to the contribution of urea-C through hydrolysis to total CO<sub>2</sub> emission. First-order kinetics parameters (C<sub>0</sub>, mineralizable SOC pool size; k, mineralization rate) became greater with increasing urea application rate; C<sub>0</sub> increased from 665.1 to 780.3 mg C/kg and k from 0.024 to 0.069 day<sup>-1</sup>, determinately showing fertilizer-induced SOC mineralization. The relationship of C<sub>0</sub> (non-linear) and k (linear) with urea-N application rate revealed different

responses of C<sub>0</sub> 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, CO<sub>2</sub> 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 CO<sub>2</sub> concentration via a negative (CO<sub>2</sub> sequestration) or positive (CO<sub>2</sub> 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

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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 ((NH<sub>2</sub>)<sub>2</sub>CO) is 20% that is converted to CO<sub>2</sub> during urea hydrolysis ((NH<sub>2</sub>)<sub>2</sub>CO + 3H<sub>2</sub>O → 2NH<sub>4</sub><sup>+</sup> + CO<sub>2</sub> + 2OH<sup>-</sup>), application of urea as a N fertilizer may further increase CO<sub>2</sub> 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 CO<sub>2</sub> emission responses to increasing rate of urea fertilization. In this context, CO<sub>2</sub> emission from soil in responding to different urea fertilization rate may be helpful in enlarging our understanding of SOC dynamics in urea-applied soils. In this study, CO<sub>2</sub> emission was monitored over 110 days in an incubation experiment with an acidic loam-textured soil treated with urea at four different levels (0, 175, 350, and 700 mg N/kg soil) to investigate the effect of increasing urea application rate on CO<sub>2</sub> emission from soil and mineralization kinetics of indigenous SOC.

## 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 homogeneously 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<sub>water</sub> (1:5) of 5.7, total organic C of 14.0 g C/kg, total N of 1.4 g N/kg, NH<sub>4</sub><sup>+</sup> of 3.2 mg N/kg, and NO<sub>3</sub><sup>-</sup> 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 (CO<sub>2</sub> 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 O<sub>2</sub> 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 CO<sub>2</sub>, 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.

### CO<sub>2</sub> measurement and kinetic model fitting

The amount of CO<sub>2</sub>-C trapped within the NaOH

solution was determined via the titration of the solution with 1 N HCl solution after the addition of 20 mL of 1 N BaCl<sub>2</sub> (Choi *et al.*, 2005). Daily CO<sub>2</sub> emission rate was expressed as mg C/kg soil/day, and the cumulative CO<sub>2</sub>-C ( $C_{cum}$ ) evolved over the 110-day incubation was calculated. The amounts of CO<sub>2</sub> emitted during the aeration (for 10 minutes) were calculated from the daily mean CO<sub>2</sub> emission rate (see Fig. 1a) and the average values of CO<sub>2</sub> 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 CO<sub>2</sub> 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  $C_{cum}$ ; equivalent to 0.6, 0.62, 0.70, and 0.71% of  $C_{cum}$ , respectively.

To obtain kinetic parameters ( $C_0$ , mineralizable SOC pool size and  $k$ , rate constant) of SOC mineralization, the contribution of urea-derived CO<sub>2</sub> to the cumulative CO<sub>2</sub>-C evolution was eliminated by supposing that CO<sub>2</sub> originated from urea hydrolysis is emitted at a

uniform rate over the incubation period (Serrano-Silva *et al.*, 2011). The refined data on cumulative CO<sub>2</sub>-C evolution ( $C_{cum}$ ) was fitted to the single exponential first-order kinetic model,  $C_{cum} = C_0[1 - \exp(-kt)]$ , 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).

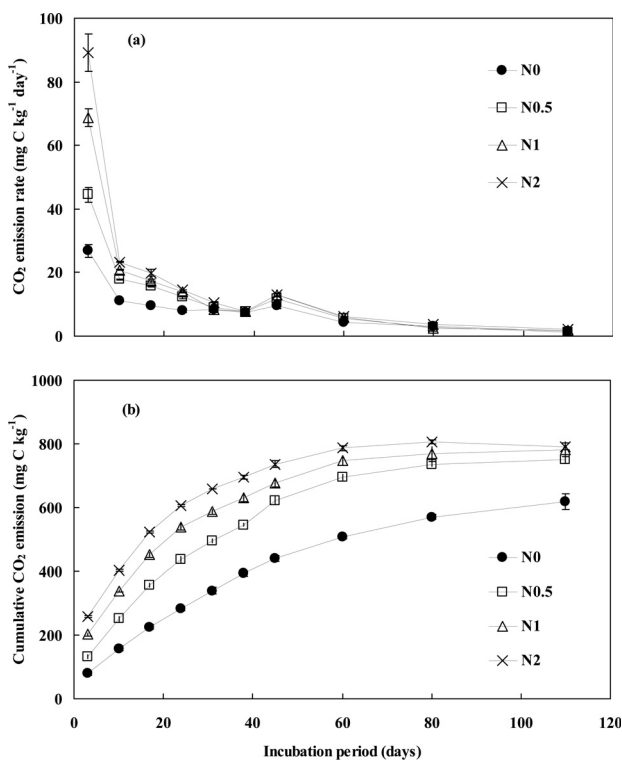
### Statistical analysis

Analysis of variance (ANOVA) on cumulative CO<sub>2</sub> emission ( $C_m$ ) and kinetics parameters ( $C_0$  and  $k_0$ ) 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, CO<sub>2</sub> 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 CO<sub>2</sub> 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  $C_{cum}$  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 CO<sub>2</sub> was included (Table 1). Although added N might activate heterotrophs that decompose SOC, the increasing pattern of  $C_{cum}$  with increasing urea application should be ascribed primarily to CO<sub>2</sub> 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 CO<sub>2</sub> emission from soils compared



**Fig. 1.** (a) CO<sub>2</sub> emission rate from soils with or without urea application and (b) cumulative amount of CO<sub>2</sub> emission through decomposition of indigenous SOC during the 110-day incubation (see Table 1 for details of treatment codes). For the cumulative CO<sub>2</sub> emission, contribution of CO<sub>2</sub> derived from urea hydrolysis was eliminated (details are provided in the text). The values are the means of triplicates and the vertical bars are standard deviations of the means.

**Table 1. Treatment description and cumulative CO<sub>2</sub> emission from the soils over the 110-days incubation**

Treatment code	Urea application (mg urea/kg soil) <sup>a</sup>	Cumulative CO <sub>2</sub> emission (mg C/kg) <sup>b</sup>	
		Including CO <sub>2</sub> from urea hydrolysis	Excluding CO <sub>2</sub> from urea hydrolysis
N0	0	618.8a	618.8a
N0.5	375	827.3b	752.3b
N1	750	933.0c	783.0c
N2	1500	1091.5d	791.5c

Values in the same column followed by a different letter are significantly different at  $\alpha=0.05$ .

<sup>a</sup> 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.

<sup>b</sup> Cumulative CO<sub>2</sub> emission was calculated for both cases when CO<sub>2</sub> 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 (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and KNO<sub>3</sub> 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 C<sub>cum</sub> 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 C<sub>cum</sub> was estimated to be 752.3, 783.0, and 791.5 mg C/kg, respectively (Table 1). Such an increasing pattern of C<sub>cum</sub> 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 C<sub>cum</sub> was refined by subtracting urea-derived CO<sub>2</sub> from the C<sub>cum</sub> as described earlier. The refined cumulative CO<sub>2</sub> emission increased gradually during the incubation period (Fig. 1b). Such CO<sub>2</sub> 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 C<sub>cum</sub> 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 (C<sub>0</sub> and

**Table 2. Kinetic parameter values (C<sub>0</sub>, 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**

Treatment <sup>a</sup>	Kinetics parameters			
	C <sub>0</sub> (mg C/kg)	k (day <sup>-1</sup> )	RMS	F <sup>b</sup>
N0	665.1a	0.024a	186	2160***
N0.5	750.7b	0.036b	536	1159***
N1	767.1bc	0.048c	1308	475***
N2	780.3c	0.069d	1879	340***

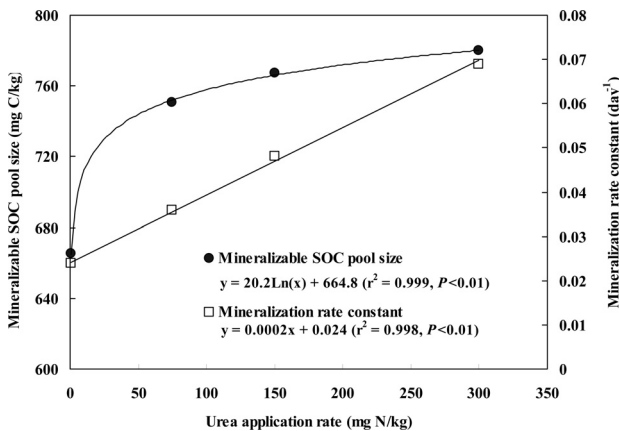
Values in the same column followed by a different letter are significantly different at  $\alpha=0.05$ .

<sup>a</sup> See Table 1 for the details of the treatments.

<sup>b</sup> \*\*\*,  $P<0.001$

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 (C<sub>0</sub> and k) with urea-N application rate, however, revealed different responses of C<sub>0</sub> and k to increasing rate of fertilizer N; k was linearly correlated with urea-N rate, but C<sub>0</sub> 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 C<sub>0</sub> 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;



**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 increase  $CO_2$  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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