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Evaluation of carbon dioxide emission factor from urea during rice cropping season: A case study in Korean paddy soil

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HIGHLIGHTS

- IPCC proposed 0.2 Mg CO_2–C per Mg urea as the CO_2 emission factor from urea in soil.
- 0.0143–0.0156 Mg CO_2–C per Mg urea was emitted from urea during rice cultivation.
- CO_2 emission factor of urea should be revised with 0.0143–0.0156 Mg CO_2–C per Mg urea in Korean rice paddy.

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ABSTRACT

Fertilization with urea can lead to a loss of carbon dioxide (CO_2) that was fixed during the industrial production process. The extent of atmospheric CO_2 removal from urea manufacturing was estimated by the Industrial Processes and Product Use sector (IPPU sector). On its basis, the Intergovernmental Panel on Climate Change (IPCC) has proposed a value of 0.2 Mg C per Mg urea (available in 2006 revised IPCC guidelines for greenhouse gas inventories), which is the mass fractions of C in urea, as the CO_2 emission coefficient from urea for the agricultural sector. Notably, due to the possibility of bicarbonate leaching to waters, all C in urea might not get released as CO_2 to the atmosphere. Hence, in order to provide an accurate value of the CO_2 emission coefficient from applied urea in the rice ecosystem, the CO_2 emission factors were characterized under different levels of ^{13}C-urea applied paddy field in the current study. The total CO_2 fluxes and rice grain yields increased significantly with increasing urea application (110–130 kg N ha^{-1}) and thereafter, decreased. However, with increasing ^{13}C-urea application, a significant and proportional increase of the $^{13}CO_2$–C emissions from ^{13}C-urea was also observed. From the relationships between urea application levels and $^{13}CO_2$–C fluxes from ^{13}C-urea, the CO_2–C emission factor from urea was estimated to range between 0.0143 and 0.0156 Mg C per Mg urea. Thus, the CO_2–C emission factor of this study is less than that of the value proposed by IPCC. Therefore, for the first time, we propose to revise the current IPCC guideline value of CO_2–C emission factor from urea as 0.0143–0.0156 Mg C per Mg urea for Korean paddy soils.

1. Introduction

Urea [$CO(NH_2)_2$] is the most widely used source of nitrogen (N) fertilizer in the world. However, adding urea to soils during fertilization can lead to a loss of carbon dioxide (CO_2) that was fixed during the industrial production process. Generally, in the presence of water and urease enzymes, urea gets converted to ammonium (NH_4^+), hydroxyl ion (OH^-) and bicarbonates (HCO_3^-), as can be seen below (Eq. (1)) (Mizutani et al., 2001).

$$(NH_2)_2CO + 3H_2O \rightarrow 2NH_4^+ + HCO_3^- + OH^- \quad (1)$$

The above reaction resulting in the formation of bicarbonates in the solution phase produces one mole of CO_2-equivalent (HCO_3^-) for every mole of gaseous CO_2 consumed. Bicarbonates formed may either remain in the soil or get flushed through the soil profile.

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Bicarbonates remaining in the soil are expected to react with the available hydrogen (H^+) ions and forms carbonic acid (H_2CO_3), which subsequently result in the acidification of the soil. Since carbonic acid in soil water is in equilibrium with soil CO_2, the overall reaction yields CO_2 that gets released to the atmosphere (Eq. (2)) (West and McBride, 2005).

$$H_2CO_3 \leftrightarrow CO_2 + H_2O \quad (2)$$

To derive a comparable per-hectare figure for the dissolution of urea, we used the emission coefficients developed by the Intergovernmental Panel on Climate Change (IPCC) (IPCC, 2006b). The IPCC emission coefficient of 0.2 Mg C per Mg urea is the mass fractions of C in urea. This source category was included because CO_2 removal from the atmosphere during urea manufacturing is estimated by the Industrial Processes and Product Use Sector (IPPU Sector) (IPCC, 2006a). However, the assumption that all C in urea is released to the atmosphere as CO_2 seems unlikely based on current knowledge of carbonate dissolution and transport through soil. Carbon dioxide emissions from urea applications could be estimated with more detailed measurements that incorporate the possibility of bicarbonate leaching into waters, thereby not contributing to CO_2 emissions, at least not immediately. Also, the specific CO_2 emission factor from urea application is so far not developed for arable soils.

The current field study was hence undertaken to provide the first approximation of the ultimate fate of the C contained in urea applied soil. Urea was applied in a typical temperate paddy soil at different levels, and CO_2 emissions were recorded during rice cropping. Finally, CO_2–C emission factor from urea was estimated from the relationships between urea application levels and $^{13}CO_2$–C fluxes from ^{13}C-urea.

2. Materials and methods

2.1. Experimental plot preparation and rice cultivation

The experiment was conducted at the agronomy field of *Gyeongsang National University* (35° 06′ N and 128° 07′ E), Jinju, South Korea for 2 years (2014 and 2015). Soil in this experimental site belongs to the *Pyeongtaeg* series (fine-silty, mixed, nonacid, mesic Typic haplaquent with somewhat impeded drainage). The soil pH was 5.6 ± 0.2 (1:5 with H_2O). Organic C content of the soil was 8.9 ± 0.6 g kg^{-1} and the total N content was 0.65 ± 0.08 g kg^{-1}.

Based on the recommendation level of N fertilizer for rice in Korea (90 kg N ha^{-1}), four different levels (0, 45, 90 and 180 kg N ha^{-1}) of urea treatments were arranged in the experimental plots (10 m × 10 m) following randomized block design with three replications. The concrete barrier was laid down between each treatment as buffer zones (0.6 m) to avoid the mixing effect. However, the same levels of P_2O_5 (45 kg ha^{-1}) and K_2O (58 kg ha^{-1}) were applied in all treatments following the recommended doses for Korean rice cultivation (RDA, 1999). The sources of P_2O_5 and K_2O were superphosphate and potassium chloride, respectively. We applied 50% of N, 100% of P_2O_5 and 70% of K_2O as the basal fertilizers, one day before transplanting. Split doses of fertilizers were applied on the 15th (20% of N) and the 42nd day (30% of N and K_2O) after transplanting.

Thirty days old seedlings (3 plants per hill) of rice (*Dongjinbyeo* cultivar, Japonica) were transplanted by hand with a spacing of 30 cm × 15 cm in the late May 2014 and 2015. Irrigation water was controlled at 5–7 cm depth during the cropping season and drained 3 weeks before rice harvesting. Rice was harvested by early October, and its productivity was recorded following the RDA methods (RDA, 1995).

2.2. Investigation of carbon dioxide emission characteristics

A closed-chamber method (Xiao et al., 2005; Iqbal et al., 2008; Haque et al., 2015) was used to investigate the CO_2 flux from the soil during rice cultivation. Opaque acryl chambers of 24 cm in diameter and 25 cm in height were placed in each plot between rice hills without rice plant (Supplementary material-1). The rice root intrusion was prohibited and aquatic weeds inside the chamber were properly removed at every gas sampling. The chamber remained open in the field during rice cultivation, except for the gas sampling time. Same level of ^{13}C labelled urea [$(NH_2)_2^{13}CO$] (Sigma Aldrich, 99.99%) with that of each treatment was applied inside the closed chamber to characterize the emission rates of CO_2 induced from urea. Gas was sampled three times a day (08:00, 12:00 and 16:00 h) during the rice cropping season. Gas samples in triplicates were collected once a week using 50-ml air-tight plastic syringes at 0, 15 and 30 min intervals after closing the chamber manually (Haque et al., 2015). The collected gas samples were transferred into 30 ml air-evacuated glass vials sealed with a butyl rubber septum.

A Shimadzu QP 2010 Plus GC/MS system equipped with a silica capillary column (SH-Rt-Q-BOND, 30 m × 0.32 mm x 10 μm film thickness) in the splitless mode was used to separate the gaseous components. The detector operated at 1.10^{-5} torr and 70 eV. The GC oven program was isothermal at 120 °C. Using the single ion monitoring mode, the detector was able to simultaneously quantify $^{12}CO_2$ (m/z = 44) from $^{13}CO_2$ (m/z = 45). CO_2 quantification was based on standards (Supelco Inc., Bellefonte, Pa.) and serial dilutions prepared therefrom.

The carbon dioxide emission rate was calculated from the increase in each gas concentration per unit surface area of the chamber for a specific time interval (Eq. (3)) (Rolston, 1986; Lou et al., 2004).

$$F = \rho \times (V/A) \times (\Delta c/\Delta t) \times (273/T) \quad (3)$$

where, F is the CO_2 (g m^{-2} d^{-1}), ρ is the gas density of CO_2 under a standardized state (1.977 mg cm^{-3}), V is the volume of the chamber (m^3), A is the surface area of chamber (m^2), Δc/Δt is the rate of CO_2 increase in the chamber (g m^{-3} d^{-1}) and T (absolute temperature) is the 273 + mean temperature in °C of the chamber.

The seasonal CO_2 flux for the entire cropping period was computed as reported by Singh et al. (1999) (Eq. (4)).

$$\text{Seasonal } CO_2 \text{ flux} = \sum_i^n (F_i \times D_i) \quad (4)$$

where F_i is the rate of CO_2 emission (g m^{-2} d^{-1}) in the ith sampling interval, D_i is the number of days in the ith sampling interval and n is the number of sampling.

2.3. Investigation of meteorological and rice yield properties, and statistical analysis

Weather data were corrected from the automatic weather station (AWS) at the field. Soil temperature was constantly recorded using a thermometer placed at a 3–5 cm depth in the soil during rice cultivation. Rice growth and yield characteristics were investigated at maturing stage. Yield components were determined following Korean standard methods (RDA, 1995). Statistical analyses were performed using SAS package, version 9.1 (SAS Institute, 2003). A two-way ANOVA was carried out to compare the means of different treatments.