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SOC Turnover and Lime-CO₂ Evolution during Liming of an Acid Andisol and Ultisol

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ABSTRACT

Agricultural liming contributes significantly to atmospheric CO_2 emission from soils but data on magnitude of lime-contributed CO_2 in a wide range of acid soils are still few. Data on lime-contributed CO_2 and SOC turnover for global acid soils are needed to estimate the potential contribution of agricultural liming to atmospheric CO_2. Using $Ca^{13}CO_3$ (^{13}C 99%) as lime and tracer, here we separated lime-contributed and SOC-originated CO_2 evolution in an acidic Kuroboku Andisol from Tanashi, Tokyo Prefecture (35°44′ N, 139°32′ E) and Kunigami Mahji Ultisol of Nakijin, Okinawa Prefecture, Japan (26°38′ N, 127°58′ E). On the average, lime-CO_2 was 76.84% (Kuroboku Andisol) and 66.36% (Kunigami Mahji Ultisol) of overall CO_2 emission after 36 days. There was increased SOC turnover in all limed soils, confirming priming effect (PE) of liming. The calculated PE of lime (Kuroboku Andisol, 51.97% - 114.95%; Kunigami Mahji Ultisol, 10.13% - 35.61%) was entirely ^{12}C turnover of stable soil organic carbon (SOC) since SMBC, a labile SOC pool, was suppressed by liming in our experiment. Our results confirmed that mineralization of lime-carbonates is the major source of CO_2 emission from acid soils during agricultural liming. Liming can influence the size of CO_2 evolution from agricultural ecosystems considering global extent of acid soils and current volume of lime utilization. We propose the inclusion of liming in simulating carbon dynamics in agricultural ecosystems.

Keywords: *Agricultural Liming, Soil Organic Carbon, SOC Turnover, Andisol, Ultisol*

1. Introduction

Agricultural liming has increased with agricultural intensification and periodic use has become necessary to counteract acidification of cultivated soils [1,2] brought by inorganic fertilization, cultivation of N-fixing crops, and crop removal. The chemical liberation of CO_2 from lime has been recognized to contribute significantly to the CO_2 emissions from agricultural soils [3,4]. However, the default methodology of the Intergovernmental Panel for Climate Change that assumes that all carbon in applied lime dissolve as CO_2 [5] tends to overestimate lime contribution to atmospheric CO_2. This is challenged by several authors [6,7]. Biological theory suggests that the dissolution of carbonate minerals can act as either a net source or sink for CO_2 [6], depending whether the reaction occurs with either strong acids or carbonic acid. The dissolved "soil CO_2", from root and microbial respiration exists in equilibrium with the weak acid H_2CO_3. Soil CO_2 reacts with the lime involving dolomite as an example:

$$CaMg(CO_3)_2 + 2H_2CO_3 \leftrightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^-.$$
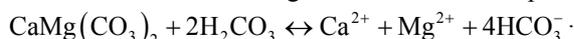
This case is a sink for soil CO_2 since the reaction produces two moles of CO_2-equivalent ($2HCO_2^-$) for every mole of gaseous CO_2 taken up. Most of the dissolution of carbonate minerals in moderately acid, neutral and alkaline soils can be pointed to carbonic acid weathering. This is the major natural process of limestone weathering and the primary source of alkalinity of most surface and groundwaters [8]. If, however, H^+ comes in contact with the HCO_3^-, it will be consumed and CO_2 will be produced [6]. During nitrification of NH_4^+ to NO_3^-, strong acids such as HNO_3 may be present, and the dissolution of carbonate minerals acts as a CO_2 source:

$$CaMg(CO_3)_2 + 4HNO_3 \leftrightarrow$$
$$Ca^{2+} + Mg^{2+} + 4NO_3^- + 2CO_2 + 2H_2O.$$
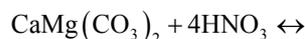
This reaction becomes important at pH < 5 and greatly enhances the dissolution rate of lime [9]. Experimental data is still insufficient to reliably estimate how much of the applied lime is released as CO_2 to the atmosphere [5], and its effect to the soil organic carbon (SOC) pools.

Results on effects of lime on CO$_2$ emissions are highly diverse [10]; hence, a refinement of the CO$_2$ emissions as a consequence of liming in acid soils is needed. The use of tracers allows the separation of lime and SOC-CO$_2$, which is impossible using conventional methods. In the present study, we separated lime- and SOC-CO$_2$ using Ca^{13}CO$_3$ (^{13}C 99%) as lime and tracer. Specifically, the study aimed to determine (1) the relative contribution of applied lime and SOC to CO$_2$ evolution; and (2) measure the priming effect (PE) of lime to SOC.

2. Materials and Methods

2.1. Soil Sampling and Incubation Experiment

Two acid soils high and low in carbon content (**Table 1**): a Kuroboku Andisol from Tanashi, Tokyo Prefecture (35°44′ N 139°32′ E) and Kunigami Mahji Ultisol of Nakijin, Okinawa Prefecture, Japan (26°38′ N 127°58′ E) were used. The soil samples were sieved in 2-mm copper sieve after air drying for two to three days. Visible roots and other organic debris were handpicked during sieving. In a separate experiment, the field capacity (FC) of the samples was measured for moisture adjustments in the experimental treatments. To determine the amount of lime (Ca^{13}CO$_3$; ^{13}C 99 %) needed to raise the soil pH to 6.5 (results in **Table 1**), a separate liming experiment using the calcium carbonate and aeration method [11] was done. Laboratory incubation was conducted at 20°C constant temperature for 36 days in transparent 500-ml glass bottles [12]. Experimental units consisted of 10 g soil adjusted to 70 (FC70) and 30% (FC30) of the soils' field capacity. The lime was incorporated to the soil before sealing the bottles. Air and moisture were replenished inside the bottles every six days. This was done by passing the air in a canister of de-ionized water. The inlet and outlet valves of the experimental bottles were allowed open for two minutes for this purpose. Sufficient number of experimental units was prepared to allow for three replicates per treatment.

2.2. Gas Chromatography-Mass Spectrometry

CO$_2$ evolution was measured once every 24 hours during the first 12 days and thereafter at three days interval. Gas samples (3 ml) were obtained using a 5-ml plastic syringe (Nipro, Japan) fitted with 0.70 × 38.00 mm needle (Nipro, Japan). These were injected in transparent 3-ml capacity pre-evacuated glass vials fitted with a rubber septum. From there, 0.3 milliliter gas sample was in-

jected into a GCMS2010 chromatograph (Shimadzu Corporation, Japan) coupled to a GCMS 2010Plus gas chromatograph mass spectrometer (Shimadzu Corporation, Japan) to distinguish ^{12}CO$_2$ and ^{13}CO$_2$ evolution. Priming effect (PE, %) was calculated as:

$$PE = 100[(^{12}CO_2 - C_{limed} - {}^{12}CO_2 - C_{non\text{-}limed})/{}^{12}CO_2 - C_{non\text{-}limed}].$$

2.3. Soil Microbial Biomass Carbon

Before and after incubation, soil microbial biomass carbon (SMBC) was measured using the chloroform-fumigation method [13] to determine the effect of lime to microbial growth. The organic carbon in the extracts was measured using a TOC-VCSN organic carbon analyzer (Shimadzu Corporation, Japan). SMBC was calculated using the formula [14]:

$$SMBC(mg \cdot kg^{-1}) = 0.45[TOC_{fumigated} - TOC_{non\text{-}fumigated}].$$

3. Results and Discussion

3.1. Lime-C (^{13}CO$_2$-C) in Evolved CO$_2$

Lime solubilization was highly dependent on the availability of sufficient soil moisture which influenced lime-CO$_2$ evolution (**Figure 1**). In Kuroboku Andisol at FC70, ^{13}CO$_2$-C evolution was dramatic in the first 24 hours after lime application, where 83. 93 mg·kg^{-1} has evolved. Cumulative ^{13}CO$_2$-C evolution after 36 days was 292.87 mg·kg^{-1}, which was 22.8% of applied Ca^{13}CO$_3$-C. At FC30, the slope of increase of cumulative ^{13}CO$_2$-C was almost uniform during the first 12 days after lime application. Cumulative ^{13}CO$_2$-C was 297.28 mg·kg^{-1}, which corresponded to 23.1% of the Ca^{13}CO$_3$-C. The wide difference in ^{13}CO$_2$-C evolution between FC70 and FC30 was only highly evident during the early stage of incubation. At latter stage (starting at 12 days), the difference in ^{13}CO$_2$-C between FC70 and FC30 was small. At this stage, soil moisture would have been similar, explaining the nearly equivalent amounts of solubilized Ca^{13}CO$_3$ and evolved ^{13}CO$_2$-C. This trend was also observed in Kunigami Mahji Ultisol, where abrupt lime solubilization also occurred within 24 hours. Cumulative ^{13}CO$_2$-C evolution was 79.44 mg·kg^{-1}, which was 14.1% of applied Ca^{13}CO$_3$-C at FC70. At FC30, the slope was almost uniform starting from 48 hours (2 days) after liming. Cumulative ^{13}CO$_2$-C evolution was 29.93 mg·kg^{-1}, which corresponded to 5.3% of applied Ca^{13}CO$_3$-C. Our data showed that when the soil tends to be dry, the applied

Table 1. Some physico-chemical properties of Kuroboku Andisol and Kunigami Mahji Ultisol.

Soil	Texture	Field capacity (%)	Total C (%)	Total N (%)	pH	Lime requirement (tons·ha^{-1})
Kuroboku Andisol	light clay	52.00	11.1	0.75	5.2	6.0
Kunigami Mahji Ultisol	light clay	28.13	0.25	-	4.2	4.8
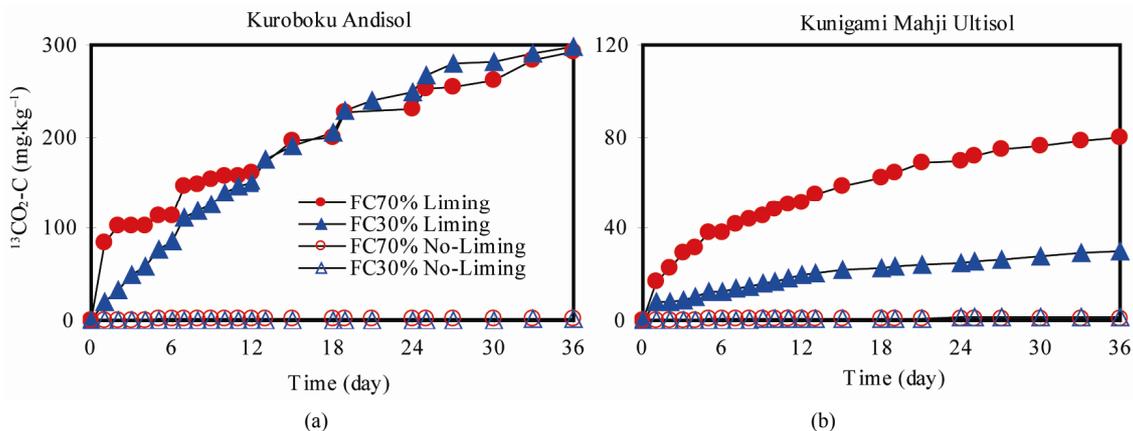
**Figure 1. $^{13}CO_2$-C evolution in (a) Kuroboku Andisol and (b) Kunigami Mahji Ultisol after lime (Ca$^{13}CO_3$; 99% ^{13}C) application.**

lime may not be solubilized at once. After 36 days, less than 25% of applied Ca$^{13}CO_3$-C evolved as CO$_2$ in all limed soils, indicating that most of the lime was retained in soil. However, lime-CO$_2$ was 74.37% - 79.32%, and 62.32% - 70.4% of CO$_2$-C evolutions from Kuroboku Andisol, and Kunigami Mahji Ultisol, respectively. This showed that most of the CO$_2$ evolution in limed soils originated from lime. Biasi *et al*. [15], found that "more than 50%" of CO$_2$ release was attributable to lime-carbonates in a similar short-term incubation study.

3.2. ^{12}C Turnover and Soil Microbial Biomass Carbon

In our experiment, evolved $^{12}CO_2$-C entirely originated from SOC turnover, since there was no source of ^{12}C other than the SOC. Cumulative $^{12}CO_2$-C was consistently higher in limed treatments of both soils (**Figure 2**). In Kuroboku Andisol, cumulative $^{12}CO_2$-C at FC70, 36 days after liming was 100.91, compared to 66.4 mg·kg^{-1}

in the non-limed treatment. At FC30, cumulative $^{12}CO_2$-C was 77.51 and 36.06 mg·kg^{-1} in the limed and non-limed treatments, respectively. In Kunigami Mahji Ultisol, cumulative $^{12}CO_2$-C was 33.4 in the limed treatment and 24.63 mg·kg^{-1} in the non-limed at FC70. At FC30, limed and non-limed soils had cumulative $^{12}CO_2$-C of 18.1 and 16.43 mg·kg^{-1}, respectively. The higher emission in Kuroboku Andisol than in Kunigami Mahji Ultisol can be explained by the difference in their carbon contents (**Table 1**). The rate of SOC loss is higher in soils with high initial SOC levels than those with low initial levels [16]. Our data confirmed that there was increase in SOC turnover when lime is added to acid soils. This is priming effect of lime application. *Priming effects* are strong short-term changes in the turnover of soil organic matter caused by comparatively moderate treatments of the soil [17].

To determine whether the increases in $^{12}CO_2$-C evolution in the limed soils were a result of the flush in micro-
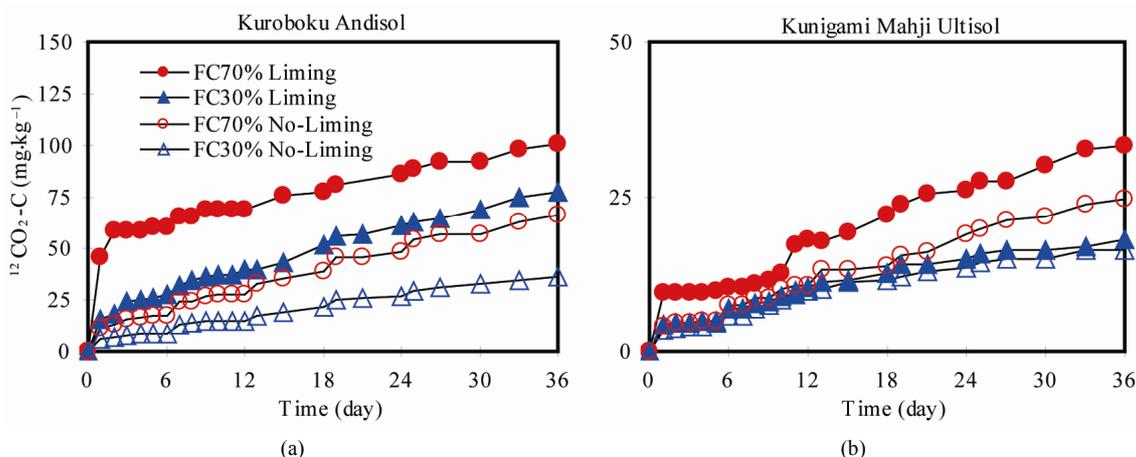

Figure 2. $^{12}CO_2$-C evolution in (a) Kuroboku Andisol and (b) Kunigami Mahji Ultisol after lime (Ca$^{13}CO_3$; 99% ^{13}C) application.

bial population, we compared SMBC in limed and non-limed soils at the end of incubation. SMBC is a measurable fraction of labile SOC, having turnover times of days to months [18]. It is generally accepted that lime application to soil causes a change in microbial biomass, and microbial dynamics and diversity [19,20]. Some workers reported 20-fold increase in bacterial population in 32 days [21] and by about 12% increase in SMBC [22].

SMBC was suppressed in all limed treatments (**Figure 3**), contrary to previous findings [e.g. 23]. This confirmed the suppressive effect of liming on microbial growth. Bååth *et al*. [24] also found a strong decrease in the number of fungi and bacteria after the use of lime in a spruce forest, despite an increase in pH. At higher soil pH, fungi cannot function optimally and as the acidic habitat changes, their role is taken over by different microorganisms, possibly prokaryotes [20]. New populations could have been activated with the rise in pH. After liming, the increase in pH allowed a wide range of prokaryotes to develop. This consequently limited thespectrum of fungal species and resulted to the decrease in SMBC in our experiment. The rise in soil pH may have allowed microbial communities able to use SOC. Fontaine *et al*. [25] proposed a similar mechanism involving organic matter. Therefore, the extra $^{12}CO_2$-C in limed treatments cannot be explained by increase in SMBC, since liming significantly suppressed the microbial population in our experiment. According to the theory of stressed ecosystems [26], the rise in CO$_2$ was a result of increased respiration of the stressed microbial community due to liming.

3.3. Priming Effect of Lime Application

Extra $^{12}CO_2$-C evolution from Kuroboku Andisol was 34.51 and 41.45 mg·kg^{-1} in the FC70 and F30 treatments,
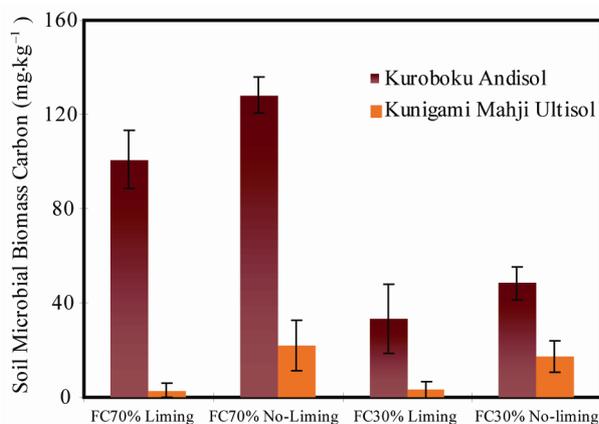
respectively (**Figure 4**). In Kunigami Mahji Ultisol, lime-induced extra $^{12}CO_2$-C evolution was 8.77 (FC70) and 1.66 (FC30) mg·kg^{-1}. Calculated PE for Kuroboku Andisol was 51.97% - 114.95%, while 10.13% - 35.61% for Kunigami Mahji Ultisol. These corresponded to 0.03% - 0.04% and 0.07% - 0.35% of SOC, respectively. Priming effect of this magnitude can significantly contribute to atmospheric CO$_2$ concentrations considering present global area of acid soils that periodically receive lime. Small SOC turnover could significantly alter CO$_2$ concentration in the atmosphere [27].

For example, in the US in 2001, an estimated 4.4 - 6.6 million tons CO$_2$ was produced from the total lime applications, equivalent to 22% of applied lime [7]. In Brazil, average lime-derived CO$_2$ emission during 1990-2000 was 7.2 million tons·y^{-1} [28] which was almost 1% of the total greenhouse gas emissions of Brazil in 1994 [29]. Reports of agronomically significant increases in mineralization after liming [4,23] did not identify which specific SOC pool was the source of extra CO$_2$ evolution. Here we have confirmed that the extra $^{12}CO_2$-C evolution in our limed treatments is real priming effect [17]. This originated from a stable SOC pool, and not from the labile SOC, as evidenced by the decrease in SMBC (**Figure 3**). Dumale *et al*. [12] put forward earlier observations after finding significant decline in mineral-associated organic carbon, a stable SOC fraction, after fresh organic matter is added to the soil.

4. Conclusions

The magnitude of lime-CO$_2$ during liming of acid soils could significantly impact global CO$_2$ emissions from agricultural ecosystems considering present global volume of lime utilization and continued increase in area of

Figure 3. Change in soil microbial biomass carbon (SMBC) after 36 days.
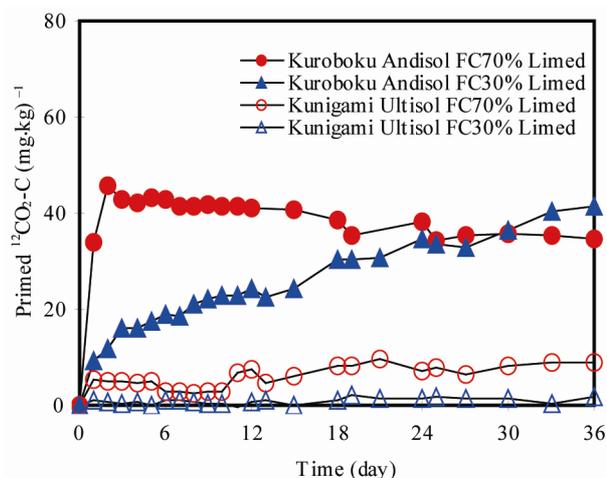
Figure 4. Primed $^{12}CO_2$-C in limed Kuroboku Andisol and Kunigami Mahji Ultisol.

world's acid soils. Further, brief and small SOC turnover (priming effect) from limed acid soils can also influence global atmospheric CO_2 and could alter carbon storage capacities of these soils. To this end, data on SOC turnover and the extent of lime-contributed CO_2 emission in the world's major acid soils are needed. More research must be done in this area. We need to incorporate the effect of lime utilization in our present soil organic matter models and CO_2 cycling simulation studies in agricultural ecosystems.

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