Nitrogen fertilization and liming increased CO_2 and N_2O emissions from tropical ferralsols, but not from a vertisol

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Abstract

The application of nitrogen (N) fertilizers and liming ($CaCO_3$) to improve soil quality and crop productivity are regarded as effective and important agricultural practices. However, they may increase greenhouse gas (GHG) emissions. There is limited information on the GHG emissions of tropical soils, specifically when liming is combined with N fertilization. We therefore conducted a full factorial laboratory incubation experiment to investigate how N fertilizer (0 kg N ha $^{-1}$, 12.5 kg N ha $^{-1}$, and 50 kg N ha $^{-1}$) and liming (target pH=6.5) affect GHG emissions and soil N availability. We focused on three common acidic soils (two ferralsols and one vertisol) from the Lake Victoria (Kenya). After eight weeks, the most significant increase in cumulative carbon dioxide (CO_2) and nitrous oxide (N_2O) fluxes compared to the unfertilized control was found for the two ferralsols in the N+lime treatment, with five to six times higher CO_2 fluxes than the control. The $\delta^{13}C$ signature of soil-emitted CO_2 revealed that for the ferralsols, liming (i.e. the addition of $CaCO_3$) was the dominant source of CO_2, followed by urea (N fertilization), whereas no significant effect of liming or of N fertilization on CO_2 flux was found for the vertisol. In addition, the N_2O fluxes were most significantly increased by the high N+lime treatment in the two ferralsols, with four times and 13 times greater N_2O flux than that of the control. No treatment effects on N_2O fluxes were observed for the vertisol. Liming in combination with N fertilization significantly increased the final nitrate content by 14.5–39% compared to N fertilization alone in all treatment combinations and soils. We conclude that consideration should be given to the GHG budgets of agricultural ferralsols, since liming is associated with high liming-induced CO_2 and N_2O emissions. Therefore, nature-based and sustainable sources should be explored as an alternative to liming in order to manage the pH and the associated fertility of acidic tropical soils.

Keywords: Acidic soils; calcium carbonate; carbon dioxide; fossil CO_2 emissions; isotope signature; nitrous oxide.

1 Introduction

On a global level, increasing agricultural productivity without risking an increase in greenhouse gas (GHG) emissions or loss of soil quality remains a challenge (Ren et al., 2017). Agriculture contributes approximately 24% of the GHG fluxes worldwide. In developing countries, agriculture's GHG contribution is estimated to be up to 66% (Pelster et al., 2017). GHG emissions from agriculture and other land uses are estimated to account for 61% of Africa's total GHG emissions (Valentini et al., 2014). In addition, GHG emissions are predicted to further increase due to changing diets and a growing population, particularly in developing nations (Smith et al., 2007). The three major GHGs emitted as a result of agricultural practices are carbon dioxide (CO_2), nitrous oxide (N_2O), and methane (CH_4) (Nayak et al., 2015: Snyder et al., 2006). Carbon dioxide from soils is released primarily by the microbial decomposition of soil organic matter (SOM), which is caused by changes in soil structure during agricultural land preparation (Silva et al., 2022; Smith et al., 2008). Nitrous oxide is generated from the microbial transformation of soil N, which is stimulated by nitrogen (N) fertilization to improve crop performance. However, CH_4 is released through the decomposition of organic materials in oxygen-deprived environments (Smith et al., 2008). The global warming potential (GWP) of N_2O and CH_4 over a 100-year time horizon is estimated to be 265 times and 28 times higher than that of CO_2, respectively (IPCC, 2014). Although N_2O and CH_4 emissions on a mass and area basis are small compared to CO_2, the emissions have significant effects through their GWP on a global scale.

Nitrogen is an essential mineral nutrient for crop productivity, particularly in regions with nutrient-depleted soils or low nutrient status (Sun et al., 2020). The global N demand for crop production stood at 110 million tons in 2015, with an anticipated linear increase in the future (Lu & Tian, 2017). In Sub-Saharan Africa, farmers are highly encouraged to use N fertilizers to boost soil fertility and crop productivity (van Loon et al., 2019). The current average N fertilizer application rate is 12.5 kg N ha^{-1} in contrast to the recommended potential of 50 kg N ha^{-1} (Masso et al., 2017; Ntinyari et al., 2022). Low N input and continuous cropping without matching the crop N demand have led to widespread N mining and the depletion of soil N stocks in tropical soils (Leitner et al., 2020). The low N inputs and small crop production areas for most farmers in Sub-Saharan Africa contribute to significantly larger yield gaps compared to other regions of the world. Reducing the yield gaps in Sub-Saharan Africa by 50% will require nutrient deficiencies in the region to be addressed and remains a key challenge for smallholder farmers (Mueller et al., 2012). Solutions related to soil health, such as building up the soil organic carbon (SOC) stock, should be given priority in the region to reduce the existing yield gaps for major crops, such as maize and rice (Amelung et al., 2020). Closing the yield gaps would significantly reduce agricultural land expansion and the associated SOC loss. Conversely, with the recommendation to increase fertilizer use, particularly of N fertilizers, for higher yields and to alleviate the regional challenges of soil fertility, it is more likely that the GHG emissions will increase through increased rates of nitrification and denitrification, which are associated with increased N_2O emissions (Barton et al., 2013). As reported by Elrys et al. (2020), the projected amount of gaseous N emissions in Sub-Saharan Africa is predicted to increase from 8 kg N ha^{-1} yr^{-1} to 61 kg N ha^{-1} by 2050, if N input is increased to 181 kg N ha^{-1} yr^{-1} to achieve food self-sufficiency. In addition, nitrate (NO_3^-) is a highly mobile compound, and N is the macronutrient most susceptible to environmental loss. Unsustainable management practices, coupled with drought and flooding conditions, can trigger the loss of N through N_2O emissions, NO_3^- leaching, and ammonia (NH_3) volatilization, subsequently contributing to problems related to the environment, human health, and the economy (Zhao et al., 2017). Sub-Saharan Africa has experienced a continuous increase in GHG emissions from agriculture due to agricultural deforestation, as the population increases and there is growing pressure for food (van Loon et al., 2019). However, agriculture in Sub-Saharan Africa has so far depended mainly on the nutrient reserves stored in the soil after deforestation (Carter et al., 2017). To avoid future deforestation, fertilization and liming should be increasingly used to maintain and increase the fertility of the existing agricultural lands.

Aside from the low use of fertilizers in the region, soil acidity is another issue affecting soil quality and crop productivity. Approximately 40% of the world's soil is acidic – a severe threat affecting agricultural gross income, particularly in the tropics (Kunhikrishnan et al., 2016). In Africa, 22% of the land (659 million ha of land) out of 3.01 billion ha is acidic soil (Sumner & Noble, 2003). Soil acidification may also result from the nitrification of ammonium (NH_4^+)-based fertilizers to NO_3^--N through the release of protons and is common in soil with a low pH buffering capacity, particularly in the tropics and sub-tropical regions (Shi et al., 2019). Fageria & Nascente (2014) reported that soil acidity influences chemical and biological reactions that control plant nutrient availability and heavy metal toxicity. In strongly acidic soils, aluminium (Al) becomes mobile and leads to Al toxicity, thus limiting nutrient uptake by affecting crop root growth (Hijbeek et al., 2021, Leenaars et al., 2018). Liming is an agricultural practice for reducing soil acidification, improving soil structure and the uptake of the major plant nutrients N, phosphorus (P), and potassium (K) in acidic soils, and enhancing crop productivity and nutrient cycling (Senbayram et al., 2019). In addition, liming influences the soil microbial community and affects GHG balances (Abalos et al., 2020). In most agricultural systems, an optimal soil pH of about 6.5 is maintained by regular buffering with calcareous materials such as limestone and dolomite (Žurovec et al., 2021). In acidic soils, lime ($CaCO_3$) dissolves and increases the concentration of calcium (Ca^{2+}) and bicarbonate (HCO_3^-). The Ca^{2+} replaces the Al^{3+} ions present in the soil solution.

Consequently, the soil pH is reduced due to the acidic hydrolysis of the Al^{3+} (Kalkhoran et al., 2019).

Although the low input of the macronutrients N, P, and K by smallholder farmers in Kenya results in low CO_2 and N_2O emissions of the cropping systems, using N fertilizers and liming in Sub-Saharan Africa could help alleviate the challenge of low fertility and acidity. However, the combined effects of liming and N fertilizers are complex, as most studies conclude that liming and N fertilizers are complementary inputs (Kalkhoran et al., 2019; Holland et al*.,* 2018; Tumusiime et al., 2011). Moreover, there is limited information on the quantification of GHG fluxes as influenced by N fertilizer and liming practices from smallholder farms in Sub-Saharan Africa (Pelster et al., 2017). The current study aimed to evaluate the effect of increasing N fertilization and liming on the GHG emissions of three acidic soils from the Lake Victoria basin. This knowledge is required to inform policy on the best management practices for improving food security and environmental sustainability. We hypothesized that the potential for N loss and GHG emissions is increased by liming and further increases in combination with higher N inputs.

2 Materials and Methods

2.1 Soil sampling description

The three agricultural soil substrates used in this study were collected from the fields of smallholder farmers at the Lake Victoria basin in Kenya from three catchment areas: Yala (0.163675° N, 34.391973° E), Bukura (0.22324° N, 34.61912° E), and Nyando (0.172663° S, 34.807757° E; 0.171744° S, 34.914260° E). The soils were classified as ferralsol 1 (F1) (sample from Yala) with a sandy, loamy texture, a pH of 4.2 ($CaCl_2$), and a total organic carbon (TOC) content of 0.67%; ferralsol 2 (F2) (sample from Bukura) with a sandy clay loam texture, a pH of

4.6, and a TOC of 1.44%; and vertisol (sample from Nyando) with a silty clay texture, a pH of 5.9, and a TOC of 1.61%. The Lake Victoria basin receives a bimodal rainfall in a year, with long rains from March to June and short rains from September to December. The average annual precipitation is 1750 mm. Approximately 70% of the population at the Lake Victoria basin engages in small-scale mixed farming with a wide range of commodities including maize, rice, and livestock.

The soil samples were collected according to standard soil sampling procedures. At each location within the field, a spade was used to collect soil samples from depths of 0–20 cm. The soil samples were sorted manually to remove any stones and clods bigger than 2 mm before homogenizing them by hand in a bucket. The collected samples were air-dried, crushed, sieved at 2 mm, and stored at room temperature until the start of the experiment. Before the incubation experiment was set up, selected initial physical and chemical characteristics of the soils were analyzed, as shown in Table 1.

2.2 Experimental design

A 57-day incubation experiment was carried out at the Institute of Bio- and Geosciences, Forschungszentrum Jülich, Germany. The measurements of GHG fluxes were performed on incubation days 1, 2, 3, 5, 8, 15, 22, 29, 36, 43, 50, and 57. Five different treatments (n=4) were applied to three soil substrates, namely ferralsol 1 (F1), ferralsol 2 (F2), and vertisol. The treatments included: (i) a low nitrogen (N) level with an equivalent of 12.5 kg N ha^{-1} (SL), (ii) a high N level with an equivalent of 50 kg N ha^{-1} (SH), (iii) a low N level with an equivalent of 12.5 kg N ha^{-1} and calcium carbonate ($CaCO_3$) (SLC), (iv) a high N level with an equivalent of 50 kg N ha^{-1} and $CaCO_3$ (SHC), and (v) control without N fertilizer and liming. The $CaCO_3$ used was in the form of marble granular (A233866, Merck KGaA, Darmstadt, Germany), while N was in the form of urea sourced from Merck KGaA. The N fertilizer rate of 12.5 kg N ha^{-1} represents the current rate used by smallholder farmers in Sub-Saharan Africa, while 50 kg N ha^{-1} is a recommendation for improved soil fertility (African Union, 2006).

Soil substrates (with and without N and $CaCO_3$) were thoroughly mixed, filled in incubation PVC tubes (150 mm height, 50 mm diameter) as described in Cao et al. (2021), and recompacted to the original bulk density, as reported in Table 1. The soil moisture was adjusted to 50% of the water holding capacity, and the water content was adjusted by weekly weighing and replacing the evaporative water loss by using distilled water. Urea, a commonly used form of N fertilizers by farmers in the Lake Victoria basin in Kenya, was used as the source for mineral N, and its equivalence per ha was calculated for the area of the incubation tubes. Throughout the incubation period, the temperature was set at 23°C, the average soil temperature in the Lake Victoria basin.

2.3 Soil analyses

The soil pH and electrical conductivity (EC) were determined with a pH and EC meter (multi 340i, WTW GmbH, Weilheim, Germany) in soil suspensions with 0.01 M $CaCl_2$ (1:2.5 w/v, VDLUFA 1991), respectively. Soil mineral N (NH_4^+ and NO_3^-) was extracted with 0.01 M $CaCl_2$ (1:4 w/v) by shaking at 200 rpm for one hour (VDLUFA 1991) and centrifuged at a relative centrifugal force (RCF) of 690 for 15 min. The supernatant was decanted into a filtration unit and filtered through a membrane filter with a pore size of 0.45 µm (47 mm diameter, Macherey-Nagel, Germany) and stored at -20 °C until analysis. The concentrations of NH_4^+ and NO_3^- in soil extracts were measured by ion chromatography (Dionex DX-500, ThermoScientific, Massachusetts, USA). To extract plant-accessible P and K, 2 g of air-dried soil was weighed in 50 ml tubes, and 40 ml of an acidic (pH 4.5) Calcium acetate lactate solution (CAL: 0.05 mol/L Ca-lactate and Ca-acetate) was added, shaken for 1.5 h, and centrifuged at 690 x *g* for 15 min (VDLUFA 1991). The supernatant was decanted into a filtration unit and filtered through a membrane filter with a pore size of 0.45 µm (47 mm diameter, Macherey-Nagel, German). P and K were determined by inductively coupled plasma optical emission spectrometry (iCAP™ 7600 ICP-OES Analyzer, ThermoScientific, Massachusetts, USA).

The maximum water holding capacity (% WHC) of the soil samples was determined using the procedure described by Schinner et al. (1996). The lime demand of each soil was determined as described in the LUFA methods handbook (VDLUFA, 1991). In brief, 10 g of air-dried soil was mixed with 25 ml of a 0.5 M calcium acetate lactate solution (1:2.5, w/v) and incubated overnight at room temperature. The pH of soil in both 0.5 M Calcium-acetate soil extract and in 0.01 M $CaCl_2$ soil extract (Table 1) were used to estimate the lime demand for a target soil pH of 6.5. Based on this, the amounts of $CaCO_3$ for the lime treatments were 5.5 t ha^{-1}, 8.5 t ha^{-1}, and 3 t ha^{-1} for treatments with lime for F1, F2, and vertisol, respectively

Microbial biomass C (C_{mic}) was determined at the end of the incubation using the slightly modified chloroform fumigation–extraction method as described by Joergensen (1996). Ten grams of unfumigated and fumigated soil were extracted with 40 ml 0.01 M $CaCl_2$ (shaking for 30 min at 200 rpm), centrifuged at 690 x *g* for 10 min, and filtered through a 0.45 µm polypropylene membrane filter (47 mm diameter, Macherey-Nagel, Germany). Soil samples for fumigation were incubated in a vacuum desiccator for 24 h at room temperature. Dissolved organic carbon (DOC) was analyzed with a TOC-VcPH + TNM-1 + ASI-V analyzer (Shimadzu, Japan). Microbial biomass C (C_{mic}) was determined based on the difference in DOC concentration between fumigated and non-fumigated samples. Results were corrected with a factor of 0.45.

2.4 Greenhouse gas measurements

Gas (N_2O, CO_2, and CH_4) concentrations were measured using an infrared laser absorption gas analyzer (G2508, Picarro, Inc., Santa Clara, USA) in closed-loop mode. A gas-tight headspace chamber with a vent tube was placed on top of the PVC column containing the soil sample. The headspace was connected to the gas analyzer (G2508, Picarro, Inc., Santa Clara, USA) in closed-loop mode. This allowed the change in CO_2, CH_4, and N_2O concentration to be quantified over a 10-minute period, as described by Cao et al. (2021). The measurements of GHG fluxes were performed on incubation days 1, 2, 3, 5, 8, 15, 22, 29, 36, 43, 50, and 57.

Gas fluxes were determined as shown by equation (Eq) 1.

$$F = \frac{\frac{\Delta C}{\Delta t} x V \, x T_o \, x M}{\mathrm{A}_{\mathrm{ch}}(K + T) x V_m} \qquad Eq\,1$$

where F represents the gas emission flux, $\frac{\Delta C}{\Delta t}$ the change in gas concentration over time in ppmv for CO_2 and ppbv for N_2O and CH_4, *V* the headspace volume, *M* the molar mass of N in N_2O or C in CO_2 and CH_4, respectively, and V_m is the molar volume of the gases corrected for the gas sample temperature using *K* (273.15 K) and *T* (air temperature in °C).

The global warming potential among the treatments was determined as a sum of the CO_2-C and CO_2-C equivalent of N_2O. To convert N_2O-N to CO_2-C equivalent, the cumulative emissions were multiplied by 265, divided by 28 (representing the atomic mass of two N atoms of N_2O) and multiplied by 12 (representing the atomic mass of one atom of carbon) according to Reichel et al. (2018) and the IPCC (2014) (Eq. 2):

$$GWP = CO_2 - C + (N_2O - N * \frac{265*12}{28}) \qquad \mathrm{Eq}\,2$$

The emission factor (EF) for N_2O was determined by the difference between the treatments with and without N fertilizers and divided by the N fertilizer application rate (kg N ha $^{-1}$) in the respective treatments (Eq. 3).

$$EF\% = \frac{(N_2O\,fertilized - N_2O\,control)}{Rate\ N\,applied(kgNha^{-1})}\ x100 \qquad Eq\ 3$$

where *EF (%)* represents the N_2O emission factor, *N_2O fertilized* the N_2O flux from treatments with N fertilizers, and *N_2O control* the N_2O flux from treatments without N fertilizers.

2.5 $\delta^{13}C$-CO_2 analysis

For the three soil substrates, 1 g of air-dried soil was incubated in 12 ml glass vials with soil moisture retained at 50% WHC. All five treatments for each soil substrate described in incubation above were considered for $\delta^{13}C_{VPDB}$ analysis. Marble granular was used as the source of $CaCO_3$, while urea (Merck KGaA) was used as the source of N. The $\delta^{13}C$ of CO_2 evolving from all the treatments was determined for an incubation time of 0 h and 48 h by measuring gas samples on an isotope ratio mass spectrometer, as described in Zhao et al. (2022). CO_2 evolving from each source was calculated using a 2-end-member mixing model. In the 2-end-member mixing model, the ratio of CO_2 was calculated from each of the sources and that of the combined sample containing urea, $CaCO_3$, and soil.

2.6 Statistical analyses

All statistical analyses were performed with the R software (R Core Team, 2021). Data on cumulative gas fluxes and mineral N dynamics were analyzed using a one-way analysis of variance (ANOVA), while Tukey's post hoc test at $P < 0.05$ was used to analyze the significance of the difference between treatments. The computation of least squares means was performed using the lsmeans package, followed by mean separation using the adjusted Tukey's method implemented using the cld of the Multicomp View package.

3 Results

3.1 CO_2 and CH_4 fluxes and cumulative emissions

The highest CO_2 fluxes occurred during day 1 of the incubation in all soil substrates. Mean CO_2-C values on the first day of measurements for F1 and F2 with SHC treatments were 3271 mg m^{-2} h^{-1} and 2672 mg m^{-2} h^{-1}, while the mean values of the control were 98 m^{-2} h^{-1} and 75 mg m^{-2} h^{-1} for F1 and F2, respectively (Fig. 1A, 1B). The initial CO_2 fluxes of the treatments SH-F1 (225 mg m^{-2} h^{-1}) and SH-F2 (202 mg m^{-2} h^{-1}) were 14 or 13 times less than for SHC for F1 and F2, respectively. The CO_2 fluxes of the vertisol were lower than those of F1 and F2 on the first day of the experiment, with mean values of 434 mg m^{-2} h^{-1} and 311 mg m^{-2} h^{-1} for SHC and SLC, respectively (Fig. 1C). On day 2, CO_2 fluxes increased further in all treatments except for SHC. However, from day 3 onwards, CO_2 fluxes declined gradually until the end of the incubation period on day 57. Overall, CO_2 fluxes decreased gradually over the incubation period for all soils and treatments.

[Insert fig. 1 approximately here}

In general, cumulative CO_2 emissions varied significantly between the soils and treatments (Fig. 1D). In F1, SHC had significantly higher CO_2 emissions, with a mean value of 217 g m^{-2} and was 30.2% higher than the CO_2 emissions of the SLC treatment, whereas SH did not show any significant differences in CO_2 emissions compared to SL and the control. Compared to the control, the high and low N applications increased cumulative CO_2 emissions by 26.4% and 17.5%, respectively.

In F2, the application of lime with both high N (SHC) and low N (SLC) increased CO_2 emissions by threefold compared to SH, SL, and the control (Fig. 1D). Although not significantly different from each other, the cumulative CO_2 emissions of SH and SL were 15.8% and 6.8% higher than in the control, respectively. In the vertisol, both SHC and SLC exhibited significant differences in cumulative CO_2 emissions compared to SH and SL, equivalent to an increase of 46.1% and 75.2%, respectively (Fig. 1D). Daily CH_4 fluxes and cumulative CH_4 emissions were negligible for all soils and treatments (Fig.S1).

3.2 Isotopic signatures ($\delta^{13}C$) of CO_2

The soils used for incubation had $\delta^{13}C_{VPDB}$ values of -19.2‰ (F1), -18.9‰ (F2), and -20.4‰ for the vertisol. Due to the low inorganic C content of the soils, CO_2 emissions originating from inorganic sources were assumed to be negligible in all soils. The primary sources of CO_2 were soil organic carbon (SOC) in all soils, and additionally $CaCO_3$ with a $\delta^{13}C_{VPDB}$ of +2.2‰ and N fertilizer (urea) with a $\delta^{13}C_{VPDB}$ of -46.3‰ in the treatments with lime and N fertilizer addition (Fig. 2). The variations in $\delta^{13}C$ values for SL and SH are likely due to additional CO_2 emanating from urea applied at a low or higher N level, reducing the emissions. In both F1 and F2, the dominant source of CO_2 was a combination of urea and $CaCO_3$, which exhibited higher $\delta^{13}C$ values (Figs. 2A, 2B). However, in the vertisol, the $\delta^{13}C$ values of the emitted CO_2 did not show any significant difference between the treatments (Fig. 2C).

[Insert fig. 2 approximately here]

3.3 N_2O fluxes and cumulative emissions

During the first week of incubation, N_2O-N fluxes were not detected in any of the F1 treatments. However, F1 showed a peak of N_2O-N fluxes on days 15 and 22 in the SHC treatment, with mean values of 274 µg N_2O-N m^{-2} h^{-1} and 173 µg N_2O-N m^{-2} h^{-1}, respectively (Fig. 3A). A similar trend was observed for the SLC and SH treatments. In F2, the SHC treatment showed an initial flush of N_2O during the first day of measurement, followed by a decline, and another peak on days 8 and 15, with mean values of 84 N_2O-N m^{-2} h^{-1} and 119 µg N_2O-N m^{-2} h^{-1}, respectively. In the vertisol, the SHC treatment had an initial peak of N_2O fluxes during days 1, 2, and 3 of the experiment, with mean values of 68 µg N_2O-N m^{-2} h^{-1}, 104 µg N_2O-N m^{-2} h^{-1}, and 49 µg N_2O-N m^{-2} h^{-1}, respectively. However, after the 3rd day of the experiment, N_2O fluxes were no longer detectable throughout the remainder of the incubation period. For the treatments SH and SL, N_2O peaks occurred on days 2, 3, and 8 of the experiment, but no more N_2O-N fluxes were subsequently detected until the end of the experiment. In the SHC treatment, the highest mean value was 129 µg N_2O-N m^{-2} h^{-1} on day 8, while for SLC the highest N_2O flux was observed on day 2 with a mean value of 101µg N_2O-N m^{-2} h^{-1}.

Overall, irrespective of the N level, treatments with N and $CaCO_3$ addition (SHC and SLC) exhibited the highest cumulative N_2O emissions over the 8-week incubation period. For F1, the highest mean value was recorded for SHC at 81 mg N_2O-N m^{-2}, which was four times higher than for SH. N_2O emissions from SLC were 25 mg N_2O-N m^{-2}, with no significant differences between SH and SL. The control had the lowest cumulative N_2O emissions, with a mean value of 6 mg N_2O-N m^{-2} (Fig. 3B). A similar trend was evident for F2, with significant differences between the treatments. The SHC treatment had a significantly higher mean cumulative N_2O flux (39 mg m^{-2}) than the control (9 mg N_2O-N m^{-2}).

[Insert fig. 3 approximately here]

In the vertisol, there were no significant differences in cumulative N_2O emissions between the treatments, with mean values ranging between 16 mg N_2O-N m^{-2} and 31 mg N_2O-N m^{-2} **(**Fig. 3F). The N_2O emission factors (EF) observed in our study varied significantly across the different soils and treatments. In F1, SLC had the highest EF of 1.8%, while the lowest was found for SH with 0.4 %. In F2, SLC had the highest EF of 1.8%, while in the vertisol, the same treatment had an EF of 1.3% (Table 2).

[Insert Table 2 approximately here}

3.4 Total greenhouse gas balance

The total greenhouse gas balance, determined as the sum of CO_2-C plus the CO_2-C equivalents (CO_2-C-eq) of the cumulative CH_4 and N_2O emissions, calculated on the basis of their respective global warming potential, showed a significant response to the treatment factors (i.e, liming and N fertilization) in the three soils (Fig.4). In F1, SHC had a significantly higher total greenhouse gas balance compared to the other treatments, with a mean value of 228 g CO_2-C-eq m^{-2}, while the lowest total greenhouse gas balance was found for the control, with a mean value of 33 g CO_2-C-eq m^{-2} (Fig. 4A).

[Insert Fig. 4 approximately here]

In F2, the total greenhouse gas balance was not significantly different between SHC and SLC, but both were significantly higher than in the other treatments (SH, SL, and control), with mean values of 220 mg CO_2-C-eq m^{-2} and 201 mg CO_2-C-eq m^{-2}, respectively (Fig. 4B). In the vertisol, the total greenhouse gas balance was relatively lower than in the two ferralsols, with mean values of 92 mg m^{-2} and 101 mg m^{-2} for the SHC and SLC treatments, respectively (Fig. 4C). Despite its lower values, the SHC and SLC treatments of the vertisol showed a similar pattern to the ferrasols and were significantly higher than the other three treatments.

3.5 Mineral N and microbial biomass C after incubation

In all three soils, the SHC treatment had a significantly higher NO_3^- content than all other treatments, with mean values of 127 mg N kg^{-1}, 152 mg N kg^{-1}, and 168 mg N kg^{-1} for F1, F2, and vertisol, respectively (Table 3). In contrast, the lowest NO_3^- content was found in the control of all experimental soils. Despite the same amount of N being added, the SHC treatment exhibited a higher final NO_3^- content than the corresponding SH treatment without the addition of lime in all three soils. The same pattern was found for the SLC–SC pairs in all soils.

[Insert Table 3 approximately here]

In F1, the SH treatment had the highest final NH_4^+ concentration (3 mg N kg ^{1}), while all other treatments had much lower final NH_4^+ contents and did not show any significant differences compared to the control. In F2 and the vertisol, NH_4^+ concentrations exhibited no significant differences at the end of the incubation period. Microbial biomass C did not show significant differences between fertilized, limed + fertilized, and control soils. However, individual soils had significant differences, with the vertisol having a higher MBC than F1 and F2 (Table S1).

4 Discussion

The neutralization of soil acidity through the dissolution of the added $CaCO_3$ led to an increase in CO_2 efflux in our study, which was significant for the two acidic ferralsols, reflecting their lower pH compared to the vertisol (Fig. 1D). Fuentes et al. (2006) and Dumale et al. (2011) reported similar results on CO_2 emission rates to our study, with high CO_2 emissions during the first few days after the liming of acidic soil, and with a subsequent decrease in the remainder of the incubation period. The IPCC (2006) recognized liming as one of the sources of CO_2 in calculating the GHG emissions in the global budget. From this study, it can be confirmed that the liming of acidic soils increases CO_2 emissions in cropping systems, thereby contributing to global warming due to $CaCO_3$ containing fossil CO_2, which is released into the atmosphere following the application of lime.

The amendment of agricultural soils with urea is known to stimulate microbial activity and thus to enhance the emission of CO_2, primarily due to urea hydrolysis to NH_4^+ and carbonic acid with the subsequent release of CO_2 (Serrano-Silva et al., 2011), resulting in adverse effects on the global atmospheric CO_2 budget and global warming (Zamanian et al*.,* 2018; Raza et al., 2020). The application of urea to soils is one of the major sources of GHG emissions in the agricultural sector, for which a CO_2 emission factor of 0.2 Mg per Mg of urea was proposed (IPCC, 2006). However, in our study, N fertilization with urea alone (i.e., without additional liming) did not contribute to the increase in CO_2 efflux to the atmosphere compared to the control. This might have been due to a low urease activity, i.e., the enzyme that catalyzes the hydrolysis of urea to NH_4^+ and carbonic acid due to low pH levels and the low N status of tropical soils (Rana et al., 2021; Chatterjee et al., 2018). In contrast, in the treatments with combined N fertilization and liming we found a further increase in CO_2 emissions at a higher N level. This suggests that N fertilization with ammonium-based fertilizers produces more acidity in the soil due to nitrification, during which nitric acid is formed, thus increasing the dissolution of the added $CaCO_3$ and leading to even higher CO_2 efflux (Kunhikrishnan et al., 2016). However, this additional increase in CO_2 emissions due to combined N fertilization and liming was found only in the two ferralsols (Fig. 1D), but not in the vertisol, which was very likely due to the differences in pH between the ferralsols and the vertisol. Finally, the increase in CO_2 fluxes by liming might also have been due to the optimized soil pH, which stimulates microbial activity along with increases in the availability of labile C and the decomposition of SOC in soils that may have been limited by a low pH (Wu et al., 2020). However, we did not observe a significant increase in microbial biomass, which would have been indicative of such a pH-related stimulation of microbial growth and activity. Our results agree with Adnan et al. (2018) and Shaaban et al. (2017) on increasing CO_2 emissions after liming due to induced soil respiration. Enhanced mineralization of organic matter by the application of calcium carbonate ($CaCO_3$) may have contributed to the increase in CO_2 observed in our study. Previous research has demonstrated that $CaCO_3$ can stimulate microbial activity and enhance the breakdown of organic matter (Chen et al., 2022). However, the effect of $CaCO_3$ on soil organic matter mineralization and CO_2 emissions may be influenced by various other factors, including the type and quality of organic matter present in the soil and the intensity of liming (Ramesh et al., 2019). These findings highlight the importance of considering the role of $CaCO_3$ in the carbon cycle when developing strategies to predict and mitigate CO_2 emissions.

Increasing N fertilization in agricultural systems affects global warming due to increased emissions of N_2O, a very potent GHG (Hergoualc'h et al., 2021). The findings of this study (Fig. 4) agree with Pittelkow et al. (2014), who found the contribution of N_2O to GWP to be very little (10-18%). However, despite the low values reported here, they should not be underestimated since the cumulative effect of N_2O on the atmosphere will increase as farmers increase their farm inputs. Mitigation potentials should therefore be explored.

The analysis of the $\delta^{13}C$ of CO_2 from the different soils and treatments in our experiment helped to distinguish between the fraction of CO_2 originating from SOM, urea (N fertilizer), and $CaCO_3$ (liming material). The dominant sources of $\delta^{13}C$ variation in our experiment were liming ($CaCO_3$) and N fertilization applied at different levels, specifically for the two ferralsols (Fig. 2A, B) with CO_2 evolving from SOM, urea (N fertilizers), and $CaCO_3$. The results emphasize the relevance of liming ($CaCO_3$) for the total CO_2 efflux of limed acidic soils and their potential contribution to the global GHG budget (Bertrand et al., 2007). This therefore poses an important dilemma, as both liming and N fertilization are crucial for improving the productivity of acidic tropical soils. Similar findings were reported by Tamir et al. (2011) on the production of CO_2 through carbonate dissolution in soils and due to the hydrolysis of N fertilizers. In addition, Perrin et al. (2008) reported about the potential impact of N fertilizers on increasing CO_2 emissions through the dissolution of $CaCO_3$. Our study found evidence of an additional contribution of CO_2 from urea fertilizers through the analysis of $\delta^{13}C$-CO_2. This suggests that ureolysis, the conversion of urea into ammonium ions (NH_4^+) and CO_2, may be a significant source of CO_2 emissions.

Our results also revealed higher N_2O emissions due to liming and N fertilizer application (Fig. 3). Soil pH was a critical factor influencing emissions of N_2O from the soil, with the highest stimulation of N_2O emissions caused by liming of the most acidic ferralsol (F1, Fig. 3A, 3B). The use of nitrogen fertilizer enhances soil N_2O emissions through increased nitrification and denitrification rates (Li et al., 2020). When fertilizer is applied as urea to soil, it is hydrolyzed to NH_4^+, which is then oxidized by ammonia-oxidizing bacteria and archaea to nitrate, thus leading to the formation of N_2O during nitrification (Yin et al., 2022).

Without N fertilization and liming, the tropical soils of our experiment had minimal N_2O fluxes, possibly due to the depletion of N stocks in the untreated soil (Fig. 3). The N_2O peaks were different for the different soil types, with F1 having the highest daily fluxes for the SHC treatment (274 µg N_2O-N m^{-2} h^{-1} and 173 µg N_2O-N m^{-2} h^{-1}) on days 15 and 22, respectively (Fig. 3A). Since F1 was the most acidic soil used in the study, raising its pH had a significant influence on microbial activity, leading to the highest observed fluxes in the treatment with high N application rates.

The differences in N_2O peaks are influenced by the level of N concentrations in the soils, which were very low in our untreated soils, leaving no potential for significant N_2O production during the experimental period. This corresponds to the situation in the Lake Victoria basin, but also in other Sub-Saharan African countries, where the amount of N fertilizer used by the farmers in the fields is very low, resulting in very low N_2O emissions. Table 4 summarizes some of the empirical studies conducted in Kenya and other Sub-Saharan African countries on GHG fluxes for comparison.

[Insert Table 4 approximately here here]

The increase in N_2O emissions upon the application of lime could be due to favoring ammonia-oxidizing bacteria that have a higher potential for N_2O production compared to ammonia-oxidizing archaea (Abalos et al., 2020). Similar results were reported by Brümmer et al. (2008), who found low emissions of N_2O in natural savannas and cropland with very low N levels.

The effect of N fertilizers on N_2O emissions is due to higher mineral N availability in the soil, providing a substrate for the bacterial or archaeal production of N_2O (Ullah et al., 2016). In contrast to what has been recommended for smallholder farmers in sub-Saharan Africa to mitigate soil N depletion and to enhance soil fertility for food security, an increase in the use of N fertilizer will increase N_2O emissions. As revealed by our study, raising the soil pH of acidic soils to an optimal value of 6.5 will significantly increase N_2O emissions due to higher coupled nitrification and denitrification rates, leading to the rapid depletion of available soil NO_3^- at neighboring nitrifying–denitrifying microsites (Senbayram et al., 2019).

The findings of this study agree with Galbally et al. (2010) that N_2O emissions in soil could increase by 10 % when soil pH is increased from <5.5 to 7.3. Liming creates a favorable environment for both denitrification and nitrification, and therefore significantly increases the fluxes of N_2O. As observed in our study, elevated pH led to higher N_2O production – especially in the acidic ferralsols. According to Wang et al. (2021), the liming of acidic soils at a high N level stimulates N_2O emissions due to increased nitrification leading to the increased production of N_2O and increased NO_3^- availability, which in turn is a substrate for N_2O production through the process of denitrification. Due to the high buffer capacity of the soil and the large CEC, the addition of N to vertisol would not result in a significant change in soil acidity and would not affect the N_2O emissions. The availability of N would be retained for a longer time, thus reducing the rate of denitrification – which is the main process that produces N_2O.

The N_2O EFs obtained in our study were partly lower and partly higher than the IPCC tier 1 EF (1 % default value) for the developing countries (Table 2). There was a tendency to higher EFs with liming, but only significantly higher for the SL–SLC pair in F2 (Table 2). Interestingly, in two cases, a higher N level led to lower EFs, i.e. for the SL–SH pairs in F1 and for SLC–SHC in F2. Such an increase in EF might potentially have policy implications for the management of soil pH and fertility towards minimizing N_2O emission rates. However, for a more robust statement, the data basis would have to be enhanced in order to obtain a clearer picture.

There was higher residual NO_3^- in the limed treatment compared to non-limed treatments at the end of the experiment (Table 3). The higher residual N benefits the soil and offers a viable management strategy for the acidic soils in the Lake Victoria basin, since more N is available for plant uptake for growth and development – with the caveat that nitrate can also become easily lost during/after heavy rains. Raising the soil pH enhances the nitrification process, resulting in more NO_3^- in the soils, as this study shows. The higher concentration of NO_3^- was due to an improved environment for the growth and development of nitrifiers at a higher pH, leading to the enhanced nitrification of applied urea-N. Consistent with our study, Sahrawat (2008) reported that the application of $CaCO_3$ promotes the formation of NO_3^- when the pH is raised. According to Senbayram et al. (2019), liming acidic soils stimulates nitrification, resulting in higher NO^-_3 in the soil. Liming has been reported to increase fertilizer efficiency and microbial activity, enhancing the release of organic N and other crop N nutrients (Kreišmane et al., 2016). With more N retained in the soil, liming can have the beneficial effect of minimizing N input to cropping systems due to improved N mineralization and nitrification (Holland et al., 2018).

5 Conclusions

Soil management practices were evaluated in our study to better inform policy making and help prioritize low fertility and acidity management in Sub-Saharan Africa. According to our results, there is a potential risk of increased GHG emissions with increasing N fertilization and liming in Sub-Saharan Africa. The combination of liming and N fertilization can increase CO_2 emissions, and the effect is more pronounced in highly acidic soils, such as ferralsols. This highlights the need for alternative approaches to improve soil fertility in the region that minimize negative environmental impacts. The results of our study suggest that the individual and combined effects of N fertilization and liming on GHG emissions may vary depending on the soil type. This is an important consideration because Sub-Saharan Africa has many soil types, which also have different characteristics that affect their susceptibility to GHG emissions.

The increased use of synthetic fertilizers is a key management tool to improve nutrient-poor soils in Sub-Saharan Africa, as this leads to increased yields and a reduction in regional food insecurity. However, this must be done in a way that avoids negative environmental impacts, such as increased GHG emissions. This therefore highlights the need to implement sustainable soil pH management strategies that have less of an impact on increasing GHG emissions. Further studies are needed to understand the combined mechanisms by which N fertilization and liming affect the emission of GHGs in order to develop more environmentally friendly farming practices in different soil types. Future studies should also investigate how climate change, such as temperature variation in tropical soils and the presence of crops, affects the emission of GHGs and the availability of nutrients in limed and N-fertilized soils. Understanding these complex interactions can facilitate the development of sustainable farming practices for different soil types.

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Declarations

Conflicts of interest: The authors declare no competing interest.

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Tables

Table 1. Soil physical and chemical characteristics of the three soils used in the experiment.

Mean values (unit)	Ferralsol 1	Ferralsol 2	Vertisol
pH (0.01 M $CaCl_2$)	4.25	4.63	5.9
EC (mS cm^{-1})	2.27	2.24	2.20
pH (calcium acetate)	6.27	6.09	6.43
Bulk density (g cm^{-3})	1.28	1.29	1.01
Texture	Sandy loam	Sandy clay loam	Silty clay
WHC (% w/w)	36.4	46.3	67.2
P (CAL) (mg kg^{-1})	18 (A-low)	24 (B-low)	42 (B-low)
Mg (mg kg^{-1})	33.50	90.11	180.49
K (mg kg^{-1})	94.9	89.9	614.1
NO_3^- (mg kg^{-1})	2.76	4.86	6.29
NH_4^+ (mg kg^{-1})	2.33	2.11	1.51
TOC (% w/w)	0.67	1.49	1.75
TN (% w/w)	0.06	0.13	0.13
C:N ratio	11.0	11.6	13.8

Table 2. Mean N_2O emission factors (EF = fraction of N_2O-N of fertilizer N added in % ± 1 standard error of the mean) for the different treatments and experimental soils.

Treatments	Ferralsol 1	Ferralsol 2	Vertisol
SHC	1.6±0.5 [ab]	0.7±0.1 [b]	0.5±0.7 [a]
SLC	1.8±0.7 [a]	1.8±0.4 [a]	1.3±0.4 [a]
SH	0.4±0.2 [b]	0.2±0.2 [b]	0.2±0.1 [a]
SL	1.6±0.7 [a]	0.7±0.7 [b]	1.3±1.2 [a]
Control	-	-	-

Letters indicate significant differences at the $p < 0.05$ level between treatments. SHC = high N + $CaCO_3$, SLC = low N+ $CaCO_3$, SH = high N, and SL = low N. The IPCC default EF value is (1 % default values) according to tier 1 methodology.

Table 3: NH_4^+ and NO_3^- concentrations in different soil samples at the end of the incubation period.

Ferralsol 1	Treatments	NH_4^+ (mg N kg^{-1})	NO_3^- (mg N kg^{-1})
	SHC	0.18^b	127.4^a
	SLC	0.11^b	93.8^b
	SH	3.24^a	98.4^b
	SL	0.11^b	67.5^c
	Control	0.11^b	42.8^d
Ferralsol 2			
	SHC	0.12^a	152.3^a
	SLC	0.12^a	107.0^{bc}
	SH	0.12^a	120.3^b
	SL	0.11^a	88.1^c
	Control	0.11^a	62.5^d
Vertisol			
	SHC	0.13^a	168.0^a
	SLC	0.12^a	97.8^b
	SH	0.12^a	127.2^b
	SL	0.12^a	85.4^c
	Control	0.12^a	63.2^d

Letters indicate significant differences at the $p < 0.05$ level between treatments. SHC = high N + $CaCO_3$, SLC = low N+ $CaCO_3$, SH = high N, and SL = low N.

Table 4: Summary of empirical studies in Kenya and selected Sub-Saharan African countries on GHG emissions.

Location	CO_2 fluxes (kg ha^{-1} yr^{-1})	N_2O fluxes (g ha^{-1} yr^{-1})	CH_4 fluxes (g ha^{-1} yr^{-1})	Soil pH	Crops grown	Reference
Kenya	1800-2300	200-600	100-300	5.9	Intercrop maize agro-forestry	Baggs et al. (2006)
Burkina Faso	-	190-670	-	4.9-5.9	Sorghum, cotton, peanuts	Brummer et al. (2008)
Kenya	-	100-300	-	4.6	maize	Hickman et al. (2014)
Tanzania	900-4000	-	-	5.5-6.3	maize	Sugihara et al. (2012)
Zimbabwe	700-1600	100-500	-2,600-5800	5.4-6.4	maize	Mapanda et al. (2011)
Kenya	-	3-29	-	5.4	maize	Kimetu et al. (2007)
Kenya	194-766	5.2-50	-70- +40	5.4-6.6	maize, sorghum, greengrams	Pelster et al. (2015)
Kenya	-	0.16-316	0.024-240	4.8-5.1	maize	Musafiri et al. (2020)
Kenya	-	180-270	-	5.21	Coffee-dairy system	Ortiz-Gonzalo et al. (2018)
Mali	-	900-1500	-	-	Pearl millet, legume beans	Dick et al., (2008)

A dash (-) indicates that measurements were not available for the respective studies.

Figures

Fig. 1. Mean values of daily CO_2-C emission trends during the 8-week incubation experiment with A – ferralsol 1, B – ferralsol 2, and C – vertisol with different treatments: SHC = high N + $CaCO_3$, SLC = low N + $CaCO_3$, SH = high N, SL = low N, and control. D represents mean values and the standard deviation of cumulative CO_2-C emissions; different lowercase letters denote significant differences between the different treatments at $p < 0.05$.

Fig. 2. The ^{13}C signatures ($\delta^{13}C_{VPDB}$) of the CO_2 evolved from the experimental treatments in the three soils: A – ferralsol 1, B – ferralsol 2, and C – vertisol for the different treatments: SHC = high N + $CaCO_3$, SLC = low N + $CaCO_3$, SH = high N, and SL = low N. Different lowercase letters denote significant differences between the different treatments at $p < 0.05$. The black arrows show the ($\delta^{13}C_{VPDB}$) of $CaCO_3$ and the grey arrow indicates the ($\delta^{13}C_{VPDB}$) of urea used as a source of N fertilization for the three soil types.

Fig. 3. Mean N_2O emissions of A – ferralsol 1, C – ferrasol 2, and E – vertisol, and cumulative N_2O emissions of B – ferralsol 1, D – ferralsol 2, and F – vertisol during the 8-week incubation experiment for the different treatments: SHC = high N + $CaCO_3$, SLC = low N + $CaCO_3$, SH = high N, and SL = low N. Different lowercase letters denote significant differences between the different treatments at $p < 0.05$

Fig. 4. Mean cumulative total greenhouse gas emissions in CO_2-C-eq: A – ferralsol 1, B – ferralsol 2, and C – vertisol; treatments: SHC = high N + $CaCO_3$, SLC = low (N + $CaCO_3$), SH = high N, and SL = low N. Different uppercase letters denote significant differences between the contributions of CO_2 from different treatments. Different lowercase letters denote significant differences between the contributions of N_2O from different treatments $p < 0.05$.

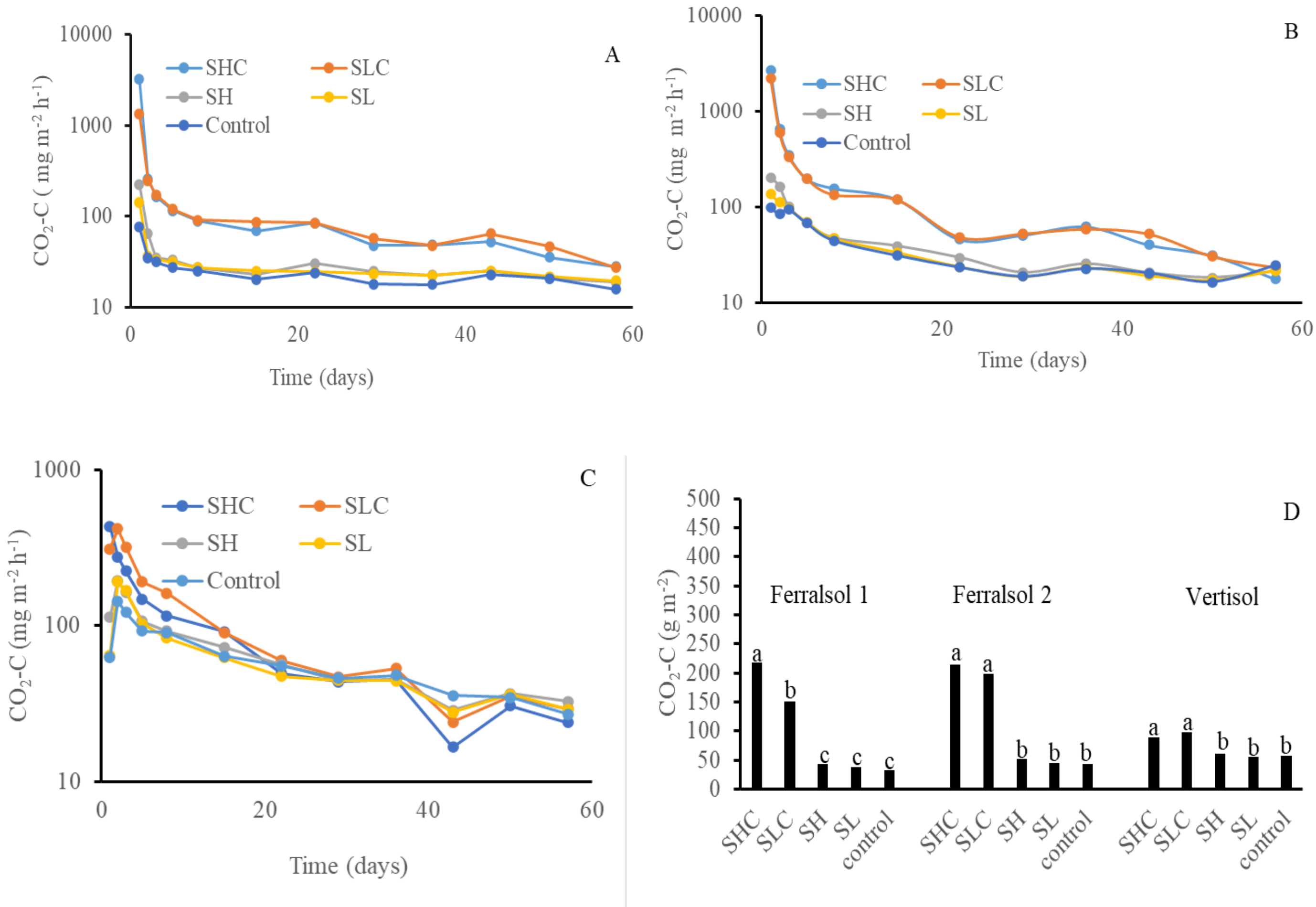
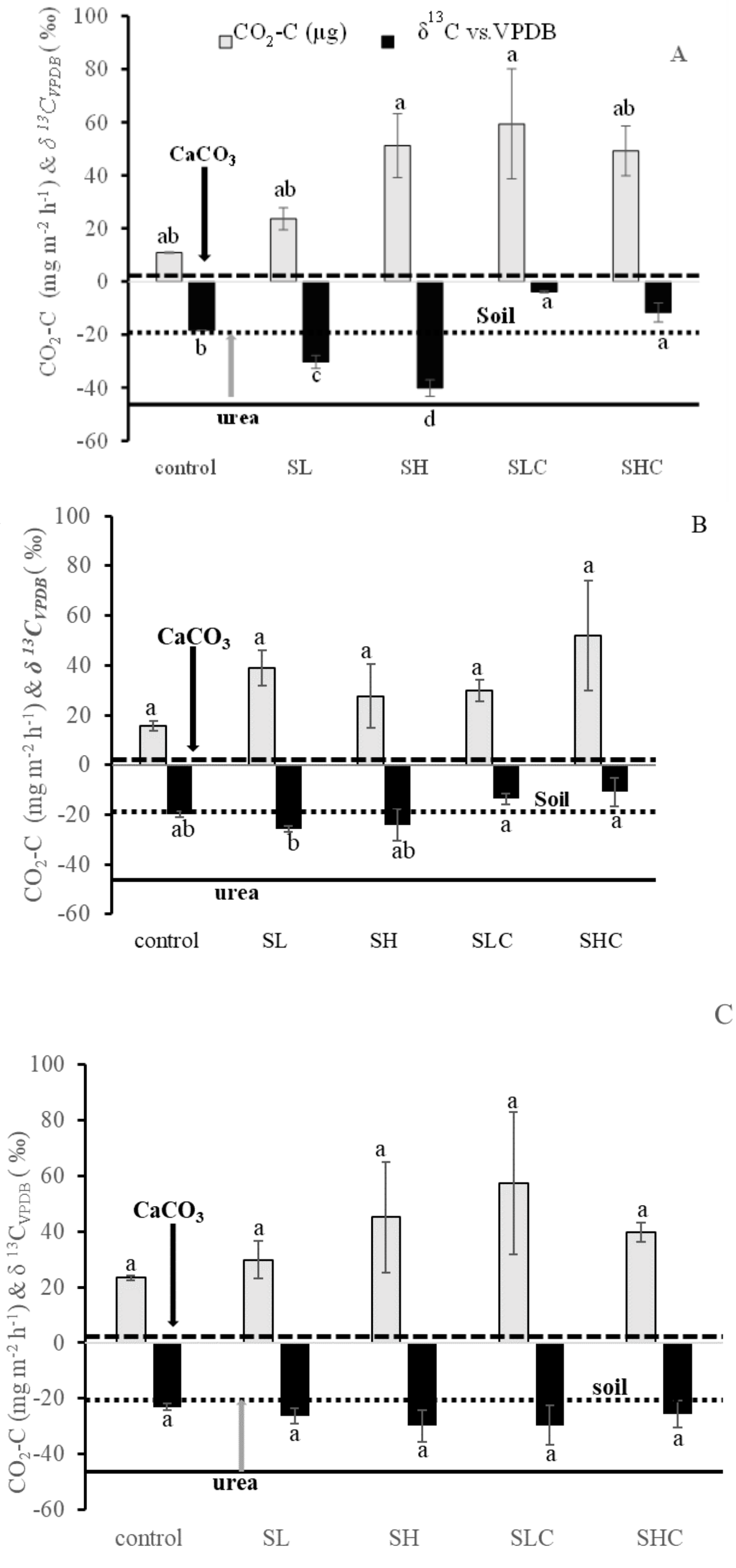

A
B
C
D
SHC
SLC
SH
SL
Control
CO2-C (mg m-2 h-1)
Time (days)
CO2-C (g m-2)
Ferralsol 1
Ferralsol 2
Vertisol
control

Fig. 1



CO_2-C (μg)
δ[13]C vs.VPDB
A
B
C
CO_2-C (mg m^{-2} h^{-1}) & δ $^{13}C_{VPDB}$ (‰)
$CaCO_3$
Soil
soil
urea
100
80
60
40
20
0
-20
-40
-60
control
SL
SH
SLC
SHC

Fig. 2

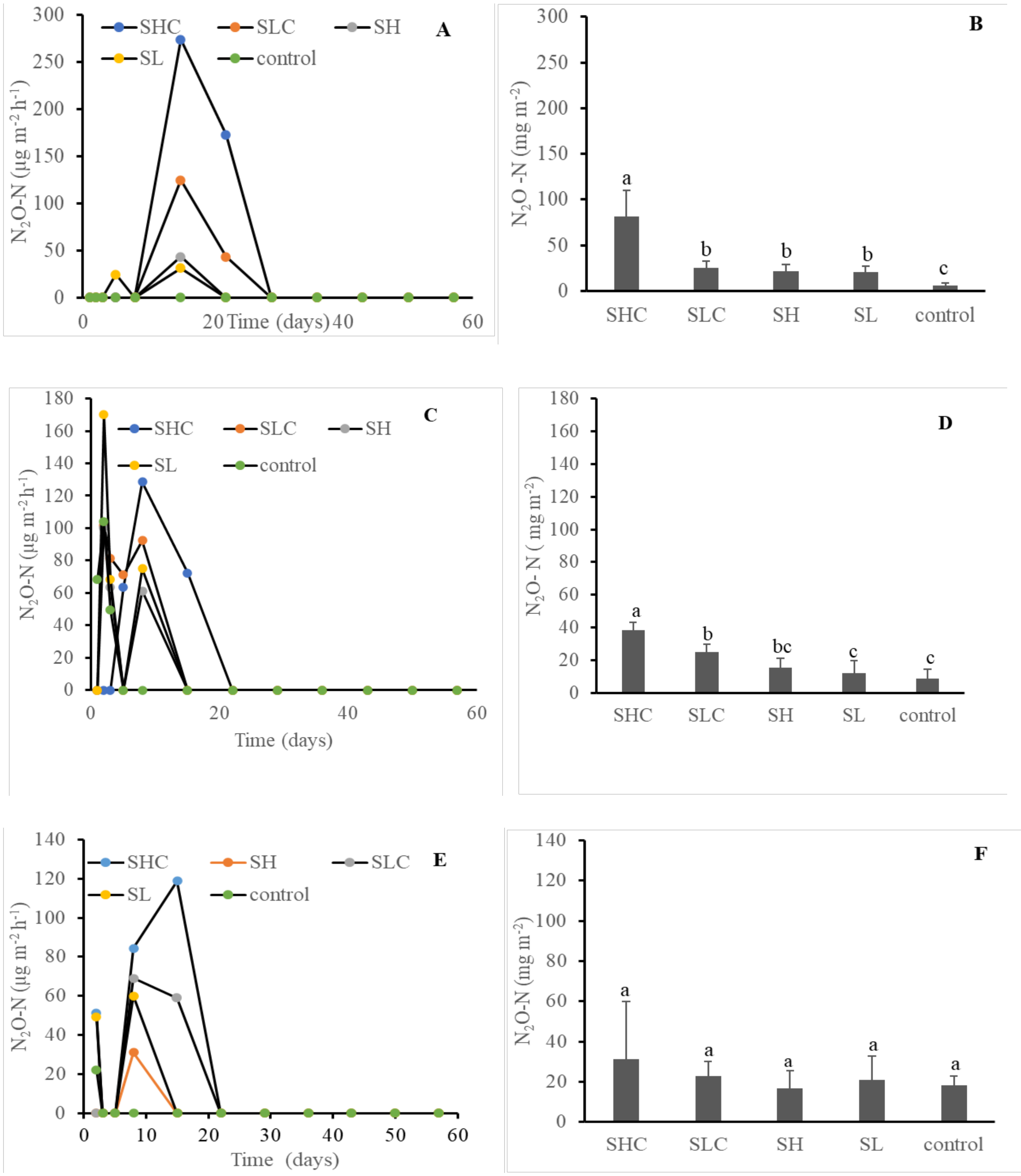

A
SHC
SLC
SH
SL
control
N2O-N (μg m-2 h-1)
Time (days)
B
N2O -N (mg m-2)
SHC
SLC
SH
SL
control
a
b
b
b
c
C
SHC
SLC
SH
SL
control
N2O-N (μg m-2h-1)
Time (days)
D
N2O- N (mg m-2)
SHC
SLC
SH
SL
control
a
b
bc
c
c
E
SHC
SH
SLC
SL
control
N2O-N (μg m-2 h-1)
Time (days)
F
N2O-N (mg m-2)
SHC
SLC
SH
SL
control
a
a
a
a
a

Fig 3

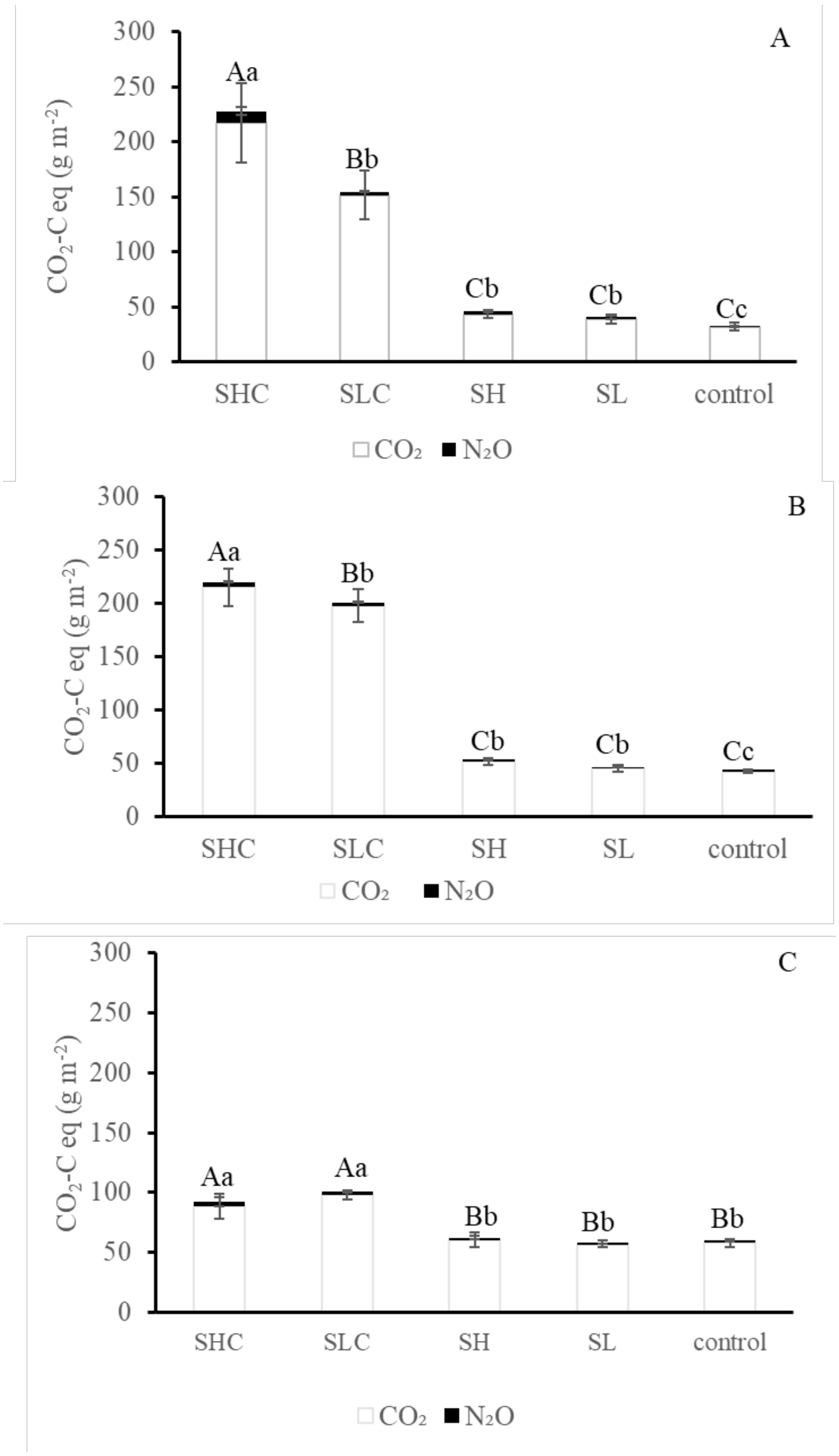

A
B
C
300
250
200
150
100
50
0
CO_2-C eq (g m^{-2})
Aa
Bb
Cb
Cb
Cc
Aa
Bb
Cb
Cb
Cc
Aa
Aa
Bb
Bb
Bb
SHC
SLC
SH
SL
control
CO_2
N_2O

Fig. 4