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Carbon Dioxide Emission from Ferric Luvisols: The Role of Mineral Nitrogen Fertilizers and Soil Temperature in the Guinea Savanna Agro-ecological Zone of Ghana

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Authors' contributions

This work was carried out in collaboration between both authors. Author WKA wrote the protocol, designed the study, managed the analyses of the study and performed the statistical analysis and wrote the first draft of the manuscript. Author PKK reviewed the experimental design and all drafts of the manuscript and approved. Both authors read and approved the final manuscript.

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ABSTRACT

Soils in the Guinea Savanna Agro-ecological zone of Ghana are inherently low in fertility, especially nitrogen. Furthermore, organic matter is very low as a result of total removal of crop residue followed by animal grazing and annual phenomenal bush burning. This has led to a reduction in soil carbon content and poor soil C:N ratio. With increase crop production, soils are amended with mineral fertilizer in most cases. In order to improve the soil carbon stocks and determine its losses in the soil, many studies have been conducted on the use of both inorganic and organic fertilizers as soil amendments and their impact on soil carbon partitioning. However, in the Guinea Savanna Agro-ecological zone of Ghana, there is paucity of information on the effects of mineral fertilizers on soil carbon emissions. Also, there are few reports of $CO₂$ flux from soils in the Guinea Savanna

agro-ecological zone of Ghana. Furthermore, there is lack of research information on the influence of hydrothermal conditions on carbon stocks in the study area. This study, sought to investigate the influence of soil-water-temperature and application of mineral N fertilizers on $CO₂$ emissions in the Guinea Savanna agro-ecological zone of Ghana. It further determined soil CO₂ emissions released per maize grain produced. It was conducted on Ferric Luvisols in the Tolon District of the Northern region of Ghana to determine the influence of mineral nitrogen (N) fertilizers and soil-temperaturewater and chemical characteristics of the soil on $CO₂$ emissions. The treatments consisted of three sources of N fertilizers: urea(U), sulphate of ammonia (SA) at 60 and 120 kg ha⁻¹ yr⁻¹ each and 60 kg N ha⁻¹ yr⁻¹ and a control(N0) arranged in a randomized completely block design replicated thrice. Omankwa, a maize cultivar, was the test crop. A plot was left without mineral N application and was used as the control. The results of the study showed that, plots of NPK 60-40-40, U 120, SA 60 and U 60 kg N ha⁻¹ yr⁻¹ emitted 2 to 5 times less $CO₂$ flux compared to plots of SA 120. Additionally, application of NPK 60-40-40 kg ha⁻¹ yr⁻¹, SA 60 and U120 kg N ha⁻¹ yr⁻¹ resulted in the release of 0.9 kg $CO₂-C$ kg⁻¹ grain emitted which was significantly higher than plots that received no mineral fertilizer. This study, therefore, concludes that although N fertilizer type and quantities applied affected $CO₂$ emissions significantly, it was not enough to cause global warming.

Keywords: Carbon dioxide; emissions; fertilizers; soil.

1. INTRODUCTION

Sustainable increases in agricultural productivity and rural incomes are the basis for broad-based economic growth [1]. Africa's soils, Ghana not an exception, are much depleted and poor compared to other continents, and to produce on these soils, fertilizer is one of the major inputs needed to replenish the soil [2]. Replenishing soil fertility is important because soil nutrients are the number-one natural resource in Africa currently being depleted, and the nutrient capital of African soils is being mined just like mineral deposits of metals or fossil fuels [2]. [3] estimated the depletion rates of soil nutrients as 22 kg ha⁻¹ yr⁻¹ for nitrogen (N), 2.5 kg ha⁻¹ yr⁻¹ for phosphorus (P) and 15 kg ha⁻¹ yr⁻¹ for potassium. The challenges facing agriculture in Ghana are immense. With the uncontrolled increase in population over the past few decades, there has been increased pressure on arable land, and farmers can no longer fallow their fields to regain fertility like they used to, and therefore rely on inorganic fertilizers for increased crop productivity. From 1988 to 1990, fertilizer use in Ghana averaged about 11,000 metric tons. The implications for Ghana are clear: depletion of soil nutrients is becoming a serious constraint to soil fertility and crop productivity. Moreover, the level of depletion suggests that efficient and sustainable use of fertilizers was required to maintain soil fertility [4]. The Government of Ghana recognizes the critical role of effective application of fertilizers in increasing agricultural productivity and contributing to the achievement of national food security. Ghana imports all of its fertilizers

and in 2003, imported about 150,000 metric tons of fertilizer [5]. The northern region of Ghana uses 27% of the total fertilizer import [6]. The use of nitrogenous mineral N fertilizers is a significant source of $N₂O$ gas emissions and contributes greatly to climate change through the destruction of stratospheric ozone [7,8]. Gaseous N losses can also represent a significant loss of fertility from nutrient-poor soils that in many cases are have a severe negative nutrient balance [9]. Energy and chemical-intensive farming has led to increased levels of greenhouse gas emissions, primarily as a result of the overuse of fertilizers (not in Africa), land clearance, soil degradation, and intensive animal farming. Excessive use of fertilizer is responsible for the highest single share of agriculture in direct greenhouse gas emissions, currently equal to some 2.1 billion tons of $CO₂$ annually [10]. The study therefore, sought to quantify carbon dioxide emissions from rain fed maize fields in the Guinea Savannah agro-ecological zone in relation to type of fertilizer and rate applied and also determined the influence of soil moisture and soil temperature on $CO₂$ and $N₂O$ emissions.

Carbon dioxide $(CO₂)$ emissions contribute to a lesser extent agricultural emissions and are mainly attributed to soil and crop management practices that reduce soil organic carbon stocks. Forest activities impact on $CO₂$ emissions and deforestation mainly for cultivation negatively affects C storage, uptake and loss from woody biomass and soils. $CO₂$ is produced in agricultural and forest ecosystems through autotrophic or heterotrophic oxidation of carbon in organic compounds and chemical weathering

of inorganic carbonate containing minerals in soils. As a result of uptake of $CO₂$ through photosynthesis, organic carbon is present in plants as well as soil organic matter through root turn over, litter decomposition and organic amendment. However, in arable soils, the largest carbon stock is predominantly found in the soil [11]. Soil inorganic carbon (SIC) is comprised of primary carbonate minerals, such as calcite $(CaCO₃)$ or dolomite $(CaMg$ $(CO₃)₂)$, or secondary minerals formed when carbonate (CO_3^2) , derived from soil CO_2 , combines with base cations (e.g., Ca^{2+} , Mg²⁺) and precipitates within the soil profile in arid and semi‐arid ecosystems. The balance between soil organic carbon (SOC) losses induced by microbial decomposition of soil organic matter (SOM) and organic C inputs to soils as crop residues and manures [12] are identified as the major regulator of the SOC stock in the soil. Furthermore, SOM decomposition is affected by physical, chemical and biological factors that affect the activity of soil microorganisms and soil fauna which include temperature, moisture, soil properties including soil pH, nutrients, aeration, soil texture and clay mineralogy, and soil physical disturbance), substrate quality and quantity, and microbial community composition and enzymatic capacity [13]. Also, land use and management of agricultural systems have considerably changed SOC stocks in agricultural land through disparities in land use, tillage, cropping practices (intensity and types of crops), irrigation, fertilization, and other activities affecting the balance between C inputs and SOM decomposition. Additionally, long term cultivation reduces SOC stocks in most agricultural lands. This happens as a result of stimulation of SOM decomposition through tillage which releases organic matter protected in aggregates and redistributes it in the soil profile where environmental conditions are more favorable for decomposition [13,14]. Soil organic C has been shown to decline significantly following even one tillage event (1–11% of soil C lost) [11].

Soil C losses are typically lower under less frequent and less intensive tillage management whereas no tillage has been found to increase soil C stocks in surface layers relative to plough tillage systems [15,10,16,17] and as a consequence, is being promoted as an alternative management practice in mitigating GHG emissions from agricultural systems (CAST, 2004; T‐AGG, 2010). Management of C stock and $CO₂$ emissions can therefore be targeted on cropping system and crop management practices that influence $CO₂$ emissions by affecting the quantity of C inputs to the soil and the quality of crop residue returned to the soil. Management practices such as irrigation and fertilization are normally applied with the purpose of increasing crop productivity, which directly controls the amount of C input to the soil. Other management practices of increasing C inputs to the soil include green manuring and organic manure application. Furthermore, changes in agricultural practices for the purpose of sequestering C must either increase organic matter inputs to the soil, stabilize a larger proportion of C in longer-term C pools in the soil, slow down decomposition of SOM, or a combination thereof. Soil C sequestration will therefore be favored under crop and soil management systems that maximize amounts of crop residue return to the soil and minimize soil disturbance and erosion (CAST, 2004). For cropland, these practices include reducing tillage intensity, crop rotation, including perennial crops in rotations or altering soil inputs to increase primary production (fertilizers, pesticides and irrigation) and restoring highly degraded soils, e.g., by setting aside in the Conservation Reserve Program (CRP) [12,18]. This study sought to determine the impact of different source, rate of application and soil characteristics on $CO₂$ emissions from soils.

2. METHODOLOGY

The study was carried out at Akukayilli, N 09° 23 ′ 38.2″ and W 001 00′ 18.4″ located in the Tolon district of the Northern region of Ghana. The climate of the region is relatively dry, with a single rainy season that begins in May and ends in October sometimes with few scattered rains in November [19]. The amount of rainfall recorded annually varies between 750 mm and 1100 mm. The dry season starts in November and ends in March or April with maximum temperatures occurring towards the end of the dry season (March-April) and minimum night temperatures in December and January. The harmattan winds, which occur during the months of December to early February, have a considerable effect on the temperatures in the region, which may vary between 14°C at night and 40°C during the day [19]. Humidity, however, which is very low at this time, mitigates the effect of the daytime heat.

Vegetation cover is mainly Guinea savannah. Farming forms the main occupation of about 70% of the people in the region. Among the crops

grown are maize, rice sorghum, yams, tomatoes and tree crops such as shea-nut, cotton and kapok. The soil at the experimental site was profiled and classified as ferric Luvisols/ Kumayilli series. The parent material is Voltaian clay; well to moderately drained. The top soil is strong brown with occasional iron and manganese concretions. It has an average depth of 0-90 cm.

2.1 Experimental Design and Approach

Two types/sources of N fertilizer; ammonium sulphate (SA) and urea (U) each at two levels of 60 and 120 kg N ha⁻¹ yr^{-1 '}plus NPK 15-15-15 at 60-40-40 kg N ha $^{-1}$ yr $^{-1}$ and a control were laid in a randomized complete block design with three replications. Triple superphosphate and muriate of potash each at the rate of 40 kg ha $^{-1}$ yr $^{-1}$ of P_2O_5 and K_2O , respectively were applied together with the N fertilizer by dibbling. The NPK 60-40-40 is the current fertilizer recommendation fertilizer for maize in Ghana [20]. Plot size was 5 $m \times 5$ m. Each plot was separated by a buffer zone of 1 m which was left bare throughout the experimental period. A maize cultivar, Omankwa was sown on 28 and 30 of July for years 2013 and 2014, respectively. Seven days after planting, plant numbers around the chamber base areas were adjusted, by either thinning or filling in, to reflect the average plant density in the field (6.25 plants $m²$), where plant germination was found to be uneven. Fifty percent of mineral N fertilizer and 100 % of P and K fertilizers were incorporated into the soil by dibbling two weeks after planting on August 12 and 14, for years 2013 and 2014 respectively as basal, the remaining 50% of mineral N fertilizer was applied on August 28 and 30, for years 2013 and 2014: Respectively (six weeks after planting, which is the recommended practice in Ghana). Weeding was done manually after crop establishment and whenever needed throughout the season.

An area of 16 m^2 within each plot was designated for measuring $CO₂$ fluxes, while the remaining plot was used for plant sampling. Weeding was done manually.

2.2 Data Collection

2.2.1 Chamber measurements of CO2 fluxes

An improvised static chamber technique [21] was used to sample gas from each plot. The chamber measured 0.50 m in length, 0.25 m width and a height of 0.17 m. It was fitted on to collars of 0.50 m long, 0.25 m wide and 0.06 m high covering an area of 0.1256 m^2 , and used for CO_2 and N_2 O flux. Collars were inserted into the soil permanently at a depth of 0.003 m, a week after planting in each experimental year. Chambers were fitted to the collars at the time of gas sampling each day and were removed after flux measurements. Four gas samples were taken during each measurement day at times 0, 20, 40 and 60 minutes. Volume of 20 ml was collected with a syringe through a three-way stop cock which was fitted gas-tight to the chamber and transferred to a vial with septum. The syringe was flushed three times before sampling in order to mix the chamber air. Samples were transferred into vials with septum, which had been pre-evacuated of air using a vacuum pump of 0.3 mbar and a capacity of 3.5 m^3 h⁻¹ and transported to the laboratory for analysis. Samples were analyzed for $CO₂$ using a Clarus 580, PerkinElmer, Rodgau, Germany, fitted with an electron capture detector. Chamber closure and gas sampling were conducted between 09:00 and 16:00 h each gas sampling.

Carbon dioxide concentration was calculated and corrected for the chamber temperature at the time of sampling. This was done by multiplying the change in gas concentration by the ratio $(275.15/(275.15+T))$; where T is the temperature in \mathfrak{C} . The rate of $CO₂$ increase at the deployment time was calculated using a linear model. Rate of $CO₂$ increase was calculated by the difference in concentration between 60 and zero minutes of sampling divided by the sampling time and the rate of $CO₂$ increase was divided by 22.4 and multiplied by 44 to transform ppm to micrograms of $CO₂$. The value obtained was finally multiplied with the internal chamber height in m to obtain the $CO₂$ flux in mg $CO₂$ m⁻² h⁻¹. The chamber height was measured from the soil surface to the top of the chamber. Annual cumulative $CO₂-C$ fluxes were calculated by interpolating the $CO₂$ fluxes measured between sampling periods [22].

2.2.2 Soil sampling and analysis

Soils were sampled from plots after field layout and before planting and were analyzed for pH, organic carbon, total nitrogen, exchangeable
cations and particle size distribution. cations and particle size distribution. Approximately, a composite sample of 200 g soil was taken from each plot and air dried. It was sieved through 0.2 mm sieve and used for the analysis. A separate soil sampling was done for

soil moisture determination. Soil sampling for ammonium, nitrate, moisture content and soil temperature measurement was conducted on each day of gas sampling until the end of the season in both years. Soil surface temperature was determined using an infrared thermometer (voltcraft IR 1000-30D, K-Type -50 to 1370°C, Germany) while soil temperature at 10 cm depth was measured with a temperature probe inserted 10 cm below the soil surface.

Particle size analysis was done by the hydrometer method as outlined by [23]. Soil moisture was determined gravimetrically. Moisture content in field soil sample was determined by oven-drying a previously weighed sample at 105°C till it attained a constant weight usually after 24 hours. In this method, the loss in weight after oven-drying at 105°C for 24 hours expressed as a fraction of the oven-dried soil represented the moisture content. Based on the gravimetric moisture content, volumetric water content was also estimated. Organic carbon was determined by the modified [24]. Total N was determined by the Kjeldahl procedure modified to include the mineral nitrates in the soil by the use of salicylic acid to convert all the nitrates into ammonium salts [25,26]. The exchangeable base cations Ca^{2+} , Mg²⁺, K⁺ and Na⁺ were extracted with 1.0 M neutral NH₄OAc solution [24]. The Bray 1 extraction solution procedure [27] was used for available phosphorus. Furthermore, Berthelot procedure as outlined by [28] was used to measure soil ammonium content whereas the colorimetric method of [29] was used for soil nitrate concentration.

3. RESULTS AND DISCUSSION

The initial soil physical and chemical properties of the experimental are shown in Table 1a and 1b, respectively. The soil is characterized by sandy loam texture, moderately drained with a bulk density of 1.3 g $cm⁻³$ (Table 1a). These physical attributes would allow good air-moisture relationship that is conducive to easy root penetration, crop establishment and growth. The soil water properties were determined to assess drainage and moisture conditions before imposing fertilizer treatments. These results suggest that the soil water properties were homogeneous across the experimental plots and would not likely affect the emission of gases. However, the research of [30] saturated water content and drained upper limit of available water have been found to influence N_2O and CO_2 fluxes.

Mean stones determined from a composite sample was $3.42\% \pm 0.02$, respectively (Table 1a). Again mean lower limit of available soil water, drained upper limit and saturation were 0.05, 0.16 and 0.45 mm³/mm³ respectively (Table 1a).

The results of chemical analysis (Table 1b) revealed that the soil was slightly acidic with a mean pH of 5.18±0.46 and 5.28±0.009 for 2013 and 2014, respectively (Table 1b). The results in Table 1b indicate that the soil at the experimental site is characterized by low inherent fertility typical of the West African Savannas. The results also show low levels of organic carbon in the soil. Mean values were 0.57±0.04 and 0.59±0.02% for 2013 and 2014, respectively. The average organic carbon and water content showed no significant differences among plots ($P > 0.05$) in 2013 and 2014. Similarly, mean effective cation exchange capacity was also low with mean values of 3.87±0.10 and 3.59±0.12 cmol/kg soil in 2013 and 2014, respectively. This is consistent with characteristics of soils in northern Ghana as described by [31]. The low organic carbon content suggests low $CO₂$ emissions. Furthermore, the low organic carbon and cation exchange capacity coupled with the low clay point to the poor buffering capacity of the soil.

Finally, the total N, available P, except exchangeable K are all below the critical levels 0.15% N, 8.5 mg kg⁻¹ P and 0.16 cmol kg⁻¹ K [32,33]. Maximizing crop production on these soils will require integrated nutrient management comprising application of inorganic and organic fertilizers.

3.1 General Environmental Conditions at the Experimental Site

Weather data for 2013 and 2014 were obtained from CSIR-Savanna Agricultural Research Institute's weather station located 2.5 km away from the experimental site. Average air temperature, relative humidity and total rainfall recorded in 2013 and 2014 are presented in Figs. 1a and 1b, respectively. Daily weather conditions during the growing seasons are also presented in Figs. 2a and 2b, respectively. An annual average minimum and maximum air temperature of 24 and 38° C was recorded in both 2013 and 2014, respectively. Temperatures were, however, low in January and December in each year. High temperatures were recorded between February and late April prior to the beginning of the growing season in each year.

Relative humidity followed a similar pattern. Relative humidity was initially low at the beginning and end of the years. However, it increased at the onset of the rains, from June and reached maximum in September in both years where rainfall was at its peak.

The rainfall pattern observed in year 2013 was not different from year 2014, although higher rainfall was recorded in 2014 compared with 2013. However, there was an early start of rains in 2014 (Fig. 1b). Rainfall values recorded were 964 and 1168 mm for 2013 and 2014, respectively. As a result of the higher rainfall in 2014 in August and October, relative humidity was also comparatively higher within the same period compared to year 2013. Similar to total annual rainfall for the years, rainfall values recorded during the 2013 and 2014 growing seasons were 601 and 862 mm, respectively (Figs. 2a and 2b). This indicates that 62 and 73%

of the total annual rainfall occurred during the growing season between June and November in 2013 and 2014, respectively.

Average maximum and minimum temperatures recorded during the 2013 growing seasons were 22 and 33° C, respectively (Fig. 2a). Temperatures increased from November to December. Similar data were also recorded during the 2014 growing season. Average minimum and maximum temperatures were 21 and 32°C, respectively (Fig. 2b).

Similarly, highest relative humidity of 80 and 90% was recorded during the 2013 and 2014 growing seasons, respectively. This occurred between September and end of October of both years. However, relative humidity decreased from the first week of November with an expectant increase in daytime temperatures and reduced rainfall.

Table 1b. Mean chemical properties of a ferric luvisol at the experimental site

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Fig. 1a. Daily maximum and minimum air temperature, daily relative humidity and daily rainfall recorded in year 2013

Fig. 1b. Daily maximum and minimum air temperature, daily relative humidity and daily rainfall recorded in year 2014

Fig. 2a. Daily maximum and minimum air temperature, daily relative humidity and daily rainfall recorded during the growing season in year 2013

Fig. 2b. Daily maximum and minimum air temperature, daily relative humidity and daily rainfall recorded during the growing season in year 2014

3.2 Soil Temperature Measurement

Soil temperature data taken each day of gas sampling both at the surface and also at 10 cm depth, are presented in Figs. 3a – 4b for both years. Minimum soil surface temperature observed during 2013 was 24 \mathbb{C} , with 33 \mathbb{C} as the maximum temperature. This occurred in late August and early September (Fig. 3a). Soil temperatures in both years were similar. The differences in the mean values among the treatment groups were not statistically significant (P > 0.05) between 2013 and 2014.

Soil surface temperature stabilized at an average of 32°C from the end of October in year 2013. Plots that received 120 kg N ha⁻¹ yr⁻¹ exhibited a reduced soil surface temperature from October in 2013. However, it was not significantly different $(P > 0.05)$ from the other plots including the control plots. Similar to 2013, minimum soil surface temperature of 25°C was observed between mid-August and mid-September of 2014 (Fig. 3b). Unlike year 2013, plots that were treated with 60 kg N ha $^{-1}$ yr $^{-1}$ showed a decline in soil surface temperature from September onwards (Fig. 3b). However, as in 2013, the trend was not from the other treatments. Soil surface temperatures recorded after heavy rains were, however, affected by fertilization.

Soil temperature measured at 10 cm depth showed similar trends as surface temperature. Plots that received 120 kg N ha⁻¹yr⁻¹ had the lowest temperature from September to December in 2013 (Fig. 4a), although it was not statistically different (\overline{P} > 0.05) from the other plots. Similar to soil surface temperature measured in 2014, plots that received 60 N kg ha^{-1} yr⁻¹ urea showed the lowest soil temperature measured at 10 cm depth. This decline in soil temperature at 10 cm depth by plots of the SA 120 and U 60 in 2013 and 2014, respectively, could be attributed to higher biomass establishment that provided lush canopy protecting the soil surface from direct heating.

3.3 Soil CO2 Flux from Fertilized and Unfertilized Plots

The time course of $CO₂-C$ fluxes measured in years 2013 and 2014 are presented in Figs. 5a and 5b, respectively. In 2013, plots of NPK 60- 40-40, SA 120 and U 60 had a higher $CO₂$ flux than the plots that received no N fertilizer until the mid of October (Fig. 5a). Thereafter, $CO₂$ fluxes from N fertilized plots were lower than from the control plots, except, plots that received SA 120 and U 60. Mean $CO₂$ fluxes recorded ranged between 1 and 140 mg m^2 h⁻¹.

Maximum $CO₂$ (140 mg m⁻² h⁻¹) flux emitted was observed between August and September on plots where SA 120 and NPK 60-40-40 were applied. Carbon dioxide emissions were significantly higher $(P = 0.002;$ LSD = 18.730) than emissions from SA 60 and NPK 60-40-40 as well as the control plots throughout 2013. In 2014, $CO₂$ emissions followed similar trend as 2013. However, in 2014, higher $CO₂$ fluxes occurred later between September and October, compared to year 2013 (Fig. 5b). Furthermore, the peaks of $CO₂$ fluxes occurred in September on the control plots. These results are in agreement with findings of [34], who reported $CO₂$ fluxes without mineral N fertilizer under tropical conditions.

Fig. 3a. Soil surface temperature measured in 2013 growing season

Fig. 3b. Soil temperature at 10 cm depth measured in 2013 growing season

Fig. 4a. Soil surface temperature measured in 2014 growing season

Fig. 4b. Soil temperature at 10 cm depth measured in 2014 growing season

Fig. 5a. Time course of CO2 flux (mg m-2 h-1) in the 2013 growing season (error bars represent standard deviation)

Fig. 5b. Time course of CO2 flux (mg m-2 h-1) in the 2014 growing season (error bars represent standard deviation)

Carbon dioxide emission at the beginning of the growing season was low but increased albeit not significantly, when the crops had been established and growth had been boosted by the application of N fertilizer. This increase in $CO₂$ flux after N fertilization could be attributed to higher $CO₂$ sequestration from the atmosphere by the plants to meet their photosynthetic needs. This indicates that $CO₂$ could be greatly reduced from the atmosphere through carbon sequestration. It can therefore be suggested from this study that, carbon dioxide uptake probably occurred on application of N fertilizer resulting in an increase in plant biomass; and, thus, did not result in higher $CO₂$ release because it was later consumed in the process of photosynthesis by the plants. This shows that $CO₂$ uptake could potentially provide a strong negative feedback on changing $CO₂$ concentrations in the atmosphere by adopting agronomic practices that enhance higher biomass production.

Also, the marginal increase in $CO₂$ emission could be attributed to increased heterotrophic and autotrophic (root) respiration, as plant growth is stimulated by the N fertilization as well as increase in soil moisture content. The results imply that microbial respiration might have been increased with the application of N at a rate of 60 and 120 kg ha⁻¹, irrespective of the N source, leading to increased $CO₂$ flux. However, other factors such as pH of the soil might have influenced the decline of $CO₂$ with increased application of N fertilizer to a certain thresh hold. The results also indicate that microbial respiration, although not studied under this experiment was significantly enhanced when 120 sulphate of ammonia was applied, giving rise to an increase in the soil $CO₂$ flux. On the contrary, application of 120 kg ha⁻¹yr⁻¹ as urea resulted in $CO₂$ fluxes that were not significantly different from applying the lower rate of the N fertilizer and control. This observation might be attributed to high N volatilization from urea compared with sulphate of ammonia.

The cumulative $CO₂$ fluxes for the growing seasons of 2013 and 2014 are presented in Figs. 5a and 5b, respectively. The cumulative flux illustrates total $CO₂$ flux cumulatively emitted since the beginning of the growing season taking into account the time interval between measurements. Cumulative $CO₂$ fluxes for year 2013 ranged between 200000 and 400000 mg C $m²$ (Fig. 6a). Cumulative CO₂ fluxes of SA 120 and U 60 treatments were higher than from the control plots, NPK 60-40-40 and SA 60 plots. In

2013, plots of SA 120 had cumulative $CO₂$ fluxes that were higher than SA 60, NPK 60-40-40 as well as the control plots. However, the latter was not significantly different from the application of 60 kg ha $^{-1}$ yr $^{-1}$ as urea.

Cumulative $CO₂$ flux in 2014 followed a similar pattern as 2013. However, in 2014, fluxes in the latter year were measured only until October and may not be very well comparable with 2013. Cumulative $CO₂$ flux ranged between 150000 and 250000 mg C m² (Fig. 6b). Similar to 2013, the cumulative $CO₂$ flux computed from SA 120 was higher than from SA 60, U 120 and NPK 60- 40-40 as well as from U 60 and the control plots.

The results further showed that cumulative $CO₂$ flux from plots of NPK 60-40-40 and U 120 were lower compared with the control. This suggests that application of NPK, U 120 either grossly reduced microbial activities in the soil or enhanced $CO₂$ uptake that resulted in the decline in $CO₂$ -C emission. Furthermore, the differences that existed between treatments and the time of measurements showed that a significant amount of $CO₂$ flux was lost when fluxes were taken in 0, 20, 40 and 60 minutes.

3.4 Relationship between Soil Temperature and CO2 Fluxes from Fertilized and Unfertilized Fields

Linear correlation between soil temperature and $CO₂$ was computed using a linear model. The results are presented in Figs. 7-10. Results from the two year study indicated that fluxes from all plots showed no correlation (P = 0.6915) and r^2 = 0.051) between $CO₂$ flux and soil surface temperature (Fig. 7). A similar result was also found for $CO₂$ flux and soil temperature measured at 10 cm depth which even showed a weaker correlation (P = 0.8372 and r^2 of 0.003) (Fig. 8). Field measurements of soil temperature both at the surface and at 10 cm depth did not show any significant differences among treatments as well as days of measurement. Therefore, this was not expected to influence $CO₂$ fluxes. This result suggests a water limited
microbial activity throughout the flux activity throughout the flux measurement period hence the lack correlation. Microbial activities are expected to be elevated with increased soil temperature thereby increasing $CO₂$ emitted by soil respiration and producing a positive feedback to global warming as reported by [35], but in this study, soil temperatures measured within sampling period were not significantly different among different

times of the day. For instance, soil surface temperature measured in the first 14 days when maximum $CO₂$ flux was observed ranged between 24 and 26°C (Figs. 3a, 3b, 4a and 4b). Also, soil temperature measured between September and October remained constant between 30 and 32°C.

The rise in temperature from an average of 24°C in the first 14 days of flux measurement to an average maximum of 32°C from September to November in both years should have been associated with an increase in $CO₂$ emissions but was found otherwise in this study. This inadequate response of $CO₂$ emission to temperature change could be attributed to reduced soil microbial respiration due to high temperatures. This is consistent with reports that suggest that increase in respiration may not persist as temperatures continue to rise.

3.5 Response of Grain and Stover Yields to Mineral N Fertilizer Application

Results of mean grain and stover yields obtained from this study are presented in Table 2. Grain yields from plots that received mineral N fertilizer were significantly superior ($P = < 0.001$ for both years). Those from plots that received no mineral N fertilizer. In both years maximum grain yield of 2246 and 2446 $kg.ha^{-1}$ was obtained from plots of U 120. In most instances, maize grain yields N fertilized plots were not significantly different (LSD = 748.7 and 648.7 for 2013 and 2014, respectively) from each other in both years except plots that received NPK 60-40-40 and SA

120 in 2013. Mean stover biomass obtained were 4542 and 5142 kg ha $^{-1}$ respectively.

Also, plots that received mineral N fertilizer produced stover biomass that were significantly higher ($P = 0.02$) than from plots that received no mineral N fertilizer in both years. Although statistical analysis showed no significant difference $(P = 0.394)$ between grain yields produced in both years among treatments, grain yields in year 2014 was found to be higher than the previous year. Lower rainfall and uneven distribution in 2013 might have accounted for the differences in yields in that year. Again, the relatively short drought that occurred following fertilizer application possibly affected mineral N fertilizer dissolution and transport to the plant roots making it unavailable for plant use, resulting in a delayed crop physiological activity at silking and/ or tasseling that resulted in reduced grain yield. Total rainfall recorded in the 2013 growing season was 513 mm (June-November) and most of it occurred between late August and September with scattered rainfall occurring in October (Fig. 2a) when crops were tasselling whereas 690mm of rainfall was recorded in 2014 (Fig. 2b) at the same period.

The non-linear increase in grain yield with increasing mineral N application from 60 to 120 kg N ha $^{-1}$ yr $^{-1}$ could be explained by higher N loss from plots that received 120 kg ha $^{-1}$ yr $^{-1}$ N irrespective of the N form. Analysis of agronomic N use efficiency indicated higher N use efficiencies when 60 kg $^{-1}$ ha $^{-1}$ N was applied irrespective of the N form. Average agronomic N use efficiencies of 29.63, 27.66, 27.50, 16.19 and

Fig. 6a. Time course of cumulative CO2 flux (mg C m-2) in the 2013 growing season

Fig. 6b. Time course of cumulative CO2 flux (mg C m-2) in the 2014 growing season

15.60 kg kg $^{-1}$ was found from plots in the order U 60 > NPK 60-40-40 > SA 60 > U 120 > SA 12060, respectively. This means that beyond 60 kg N ha⁻¹, grain yield increase produced by N fertilization was not economic. Agronomic N use efficiency was calculated using a modified

procedure of [36]. This result showed that increased use of mineral N fertilizer reduces N use efficiency. This result supports the findings of [37], who also reported decline in agronomic N use efficiency with increasing N application from $60 - 180$ kg.ha⁻¹.

Fig. 7. CO₂ flux (mg m⁻² h⁻¹) as a function of soil surface temperature (°C) (f = y0+a*x)

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Fig. 8. CO₂ flux (mg m⁻² h⁻¹) as a function of soil temperature ($^{\circ}$ C) at 10 cm depth (f = y0+a*x)

Fig. 9. Cumulative CO2 flux (kg ha-1) of fertilized and unfertilized maize field (Bars with the same letters are not significantly different (P > 0.05) from each other)

Fig. 10. Yield-scaled cumulative CO2 emissions (kg CO2-C.kg-1 grain) yield-scaled ratio as kg per kg of grain emitted (Bars with the same letters are not significantly different (P >0.05) from each other)

3.6 Growing Season CO2 Cumulative Gas Fluxes from Experimental Fields

Total cumulative $CO₂$ fluxes from this two-year study were averaged and are presented in Figs. 9 and 10, respectively. Plots of SA 120 had a total of 400 $kg.ha^{-1}CO_2-C$ at the end of the growing season. This was followed by U 120 with 300 kg.ha⁻¹ CO₂-C. Total cumulative CO₂-C from the different treatments is in the order SA 120 > U 120 > Control > U 60 > NPK 60-40-40 > SA 60, (Fig. 9). Application of SA 120 significantly (P $<$ 0.05) emitted higher cumulative CO₂-C than the other plots except plots that were treated with U 120.

However, considering the demand for food to feed Ghana´s increasing population coupled with poor soil fertility in the Guinea Savanna agroecological zone, production of crops, especially maize, without mineral N fertilization should be discouraged. Therefore, the use of optimum N fertilizer rates that increased crop productivity with minimum $CO₂$ emissions should be considered. Furthermore, when cumulative $CO₂$ fluxes emitted were related to grain yields produced, the unfertilized fields emitted the highest $CO₂$ per grain yield (4.0 mg g⁻¹) (Fig. 10). Although application of SA 120 and U 120 resulted in the highest amount of $CO₂$ emitted per hectare of cropped field, which was comparatively higher than plots that received no mineral N fertilizer, $CO₂$ emitted per kg grain produced was lower. Contrary to the cumulative $CO₂$ fluxes on an area basis, which were not significantly different between the treatments (Fig. 9), grain-yield-related cumulative $CO₂$ fluxes were significantly lower in NPK, U60 and U120 as compared to the non-fertilized plots. These results are therefore in agreement with studies by [38] who reported that crop production caused GHG emissions, but at the same time the crops fixed about 1.6 t of $CO₂$ per t of biomass produced.

Good agronomic practices that improve crop productivity could improve soil carbon sequestration even though practices such as higher fertilizer application could increase GHG emissions per area, but may also prevent other lands such as forest reserves from being converted into agricultural land because intensive crop production allows for high yields per hectare and also increased $CO₂$ sequestration.

4. CONCLUSION

Considering additional future growth in global population accompanied by increasing demand for food, it will almost certainly be necessary to use more mineral N fertilizers in the future to boost crop production. Limited land resources further confirm the need for intensive crop production with optimal input of plant nutrients. The results of this study conducted in a Guinea Savanna agro-ecological environment of Ghana dominated by Ferric Luvisols support some conclusions that will have agronomic and environmental significance. It has been established in this study that comparable amounts of $CO₂$ were emitted with or without mineral N fertilization suggesting that the use of urea, ammonium sulphate or mixed NPK at the rate of 60 kg ha $^{-1}$ is an environmentally friendly practice that would not likely to significantly change $CO₂$ release into the atmosphere to cause global warming. Increased $CO₂$ flux observed following N fertilization is indicative of high $CO₂$ sequestration by the maize plant during photosynthesis. It is concluded that management of mineral N fertilizer must consider the source and optimum rate that will likely result in increased crop productivity and $CO₂$ sequestration.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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