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GREENHOUSE GAS EMISSIONS FROM *FERRIC LUVISOLS* UNDER NITROGEN FERTILIZATION IN NORTHERN GHANA

BY

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Thesis submitted to the Department of Soil Science of the School of Agriculture, College of Agriculture and Natural Sciences, University of Cape Coast in partial fulfilment of the requirements for the award of Doctor of Philosophy degree in Soil Science

MAY 2016

DECLARATION

Candidate Declaration

I hereby declare that this thesis is the result of my own original research and that

no part of it has been presented for another degree in this university or elsewhere.

Candidate signature ....   Date: 16/01/2017
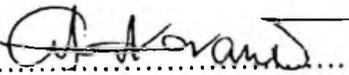
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Supervisors' Declaration

We hereby declare that the preparation and presentation of the thesis were

supervised in accordance with the guidelines on supervision of thesis laid down by

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ABSTRACT

Carbon dioxide and nitrous oxide are two important greenhouse gas that contribute to global warming. Farmers in Northern Ghana rely on mineral fertilizers mainly sulphate of ammonia, urea and NPK compound fertilizers to boost crop production due to low soil fertility. A study was conducted on *Ferric Luvisols* in Akukayilli in the Tolon District of the Northern Region of Ghana to assess the influence of physic-chemical properties and environmental factors (soil temperature and soil moisture characteristics) on CO_2, N_2O, NO NO_2 emissions. A randomized complete block design with three replications was used. Two nitrogenous fertilizer sources, sulphate of ammonia and urea at two rates of 60 and 120 kg N ha^{-1} y^{-1} and NPK (60-40-40) were used. Maize was the test crop, using the variety *omankwa*. The fate of excess N fertilizer in the soils were determined by ^{15}N procedures. Application of NPK 60-40-40, sulphate of ammonia 60 and urea 60 kg ha^{-1} y^{-1} produced substantial maize yield with minimum production of CO_2 and N_2O. A nitrous oxide emission factor (EF) of 0.15 % has been established for the Northern savanna zone of Ghana. A large substrate availability (120 kg N ha^{-1} y^{-1}) was found to contribute to the high emission of greenhouse gases, however, the levels of the greenhouse gases observed in this study are below the threshold that will lead to global warming. Observed $\delta^{15}N$ values of N_2O proved that the application of the compound fertilizer NPK fixed higher nitrogen in the soil than sulphate of ammonia and urea. Water filled pore spaces directly correlated with increase in emission of N gases. It is recommended that the emission factor be assessed for soils of other agro-climatic zone.

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KEY WORDS

Greenhouse gas

Emissions

Nitrous oxide

Emission factor

Yield scaled emissions

Carbon dioxide

Ferric Luvisols
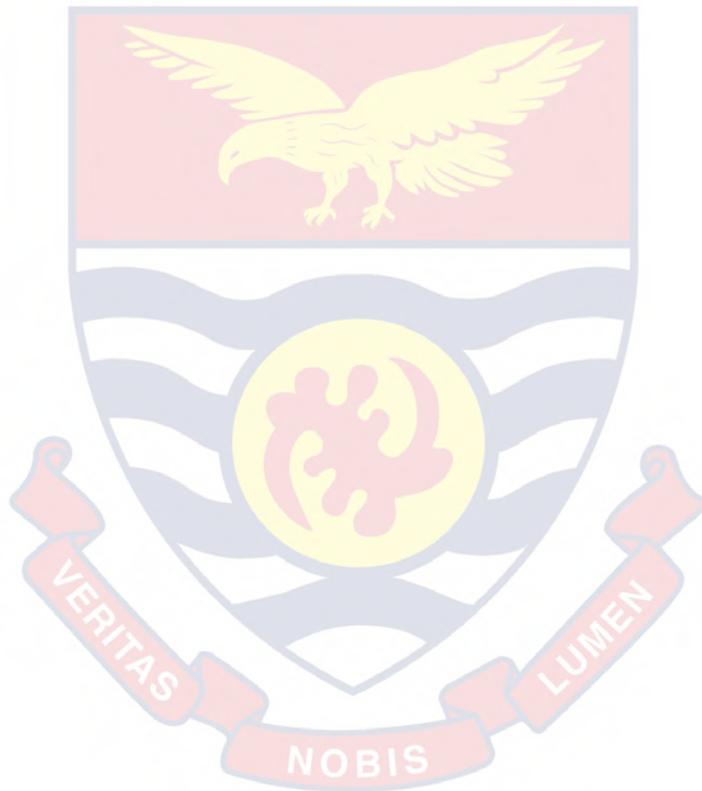
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DEDICATION

To my daughters and spouse, Harriet Hatty Williams, Maya Afia Maanu Atakora

and Comfort Yeboah Boafo Williams.

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LIST OF ACRONYMS

Abbreviations	Meaning
μg	Microgram
DEA	Denitrification Enzyme Activity
C	Carbon
CEC	Cation Exchange Capacity
cm	Centimeter
CO_2	Carbon Dioxide
h^{-1}	Per hour
h	Hour
IPCC	Intergovernmental Panel on Climate Change
kg	Kilogram
m^2	Square Meter
mg	Milligram
N	Nitrogen
N_2O	Nitrous Oxide
NH_4^+	Ammonium
NO	Nitric Oxide
NO_2	Nitrogen Dioxide
NO_3^-	Nitrate
NO_X	NO and NO_2
O_3	Ozone
P	Phosphorus

s^{-1}	Per Second
WFPS	Water Filled Pore Space
TCD	Thermal Conductivity Detector
DNDC	Denitrification Decomposition Model
TEB	Total Exchangeable Bases
EEC	Equilibrium Equivalent Concentration
EMB	Electro Mechanical Brake
NASA	National Aeronautics and Space Administration
GISS	Goddard Institute for Space Studies
IFPRI	International Food Policy Research Institute
y^{-1}	Per Year
VSMOW	Vienna Standard Mean Ocean Water

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CHAPTER ONE

INTRODUCTION

Climate change affects agriculture through changes in average temperatures, rainfall, and climate extremes, changes in atmospheric nitrous oxide, carbon dioxide and ground-level ozone concentrations. Higher CO_2 levels can affect crop yields. However, research findings suggest that elevated CO_2 levels can increase plant growth but other features, such as temperature variability, water and nutrient constraints, may thwart these potential increases in yield (United States Global Change Research Program (USGCRP), 2014).

More so there is little information on the amount of N_2O derived from nitrogen applied to agricultural soils from atmospheric deposition, mineral N fertilizer, organic source or biologically fixed N as this amounts to 20–30% of the total N_2O emitted annually from the earth's surface. Although unknown, but probably significant, amount of N_2O is generated indirectly in on and off farm activities associated with food production and consumption (Mosier, 1994). Management options to limit direct N_2O emissions from N-fertilized soils should emphasize improving N-use efficiency. These management options include but not limited to timing and quantity of N application only to meet crop demand through multiple applications during the growing season. The extent at which the emission of these greenhouse gases occur have not been thoroughly researched into in the Guinea Savanna agro-ecological zone of Ghana. This study evaluates the influence

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of N fertilizer type and rate of application on soil CO_2, N_2O and NOx emissions from fertilized and unfertilized maize fields.

Background to the Study

More than 70 % of Africans live in rural areas and agriculture is their most important economic activity (Camara & Heinemann, 2006). It is, therefore, clear that sustainable increase in agricultural productivity and rural incomes are the basis for broad-based economic growth (Zhang & Zhang, 2007). The challenge, however, remains how best to create conditions under which farmers can intensify their production and link them to markets. Achieving this will help reduce food insecurity on the   continent (Ackah, Agyemang & Anim, 2011) and (Tiwari, 2011). However, history shows that no region in the world achieved food security and substantial productivity increases without significantly expanding fertilizer use (Food and Agricultural Organization (FAO), 2006; Zhang and Zhang).

Soils of Africa, Ghana not an exception, are much depleted and inherently poor compared to other continents, and to produce on these soils, fertilizer is one of the major inputs that is needed to replenish the soil (FAO, 2006). 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 (FAO). Smaling (1993), estimated the depletion rates of soil nutrients as 22 kg ha^{-1} y^{-1} for nitrogen (N), 2.5 kg ha^{-1} y^{-1} for phosphorus (P) and 15 kg ha^{-1} y^{-1} for potassium (K) in Africa.

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Challenges facing agriculture in Ghana are immense. With the increasing population over the past several few decades, there has been increased pressure on arable land, and farmers can no longer fallow their fields long enough 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 per annum. However, the nutrient requirements for the various crops for the same period was estimated to be 90,000 metric tons (Mwangi, 1995).

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 (Mwangi, 1996). The Government of Ghana recognizes the critical role that application of fertilizers increases agricultural productivity and contribute to the achievement of national food security. Farmers throughout the country must, therefore, have access to good quality fertilizers at reasonable costs. The fertilizers should be appropriate for the local conditions, effective in use according to the quality standards as per the product recommendation. Ghana imports all of its fertilizers with about 150,000 metric tons of fertilizer being imported in 2003 (Enti-Brown et al., 2012). These are mostly mineral or inorganic fertilizers that contain the macro nutrients required by plants. The Northern Region of Ghana use 27 % of the total fertilizer import into the country (Bonsu, Fosu & Kwakye, 1996.).

The use of inorganic Nitrogen fertilizers is a significant source of N_2O gas emissions that contribute greatly to climate change through the destruction of

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stratospheric ozone (Mosier *et al.*, 1998); (Intergovernmental Panel on Climate Change (IPCC), 2001) and (IPCC, 2014). Gaseous N losses can also represent a significant loss of fertility from nutrient-poor soils that in many cases have a severe negative nutrient balance (Smaling & Braun, 1996). Tropical savannas are thought to contribute around 16 % of the global production of N_2O from terrestrial systems (IPCC, 2014). However, these estimates are based upon relatively few observations, and processes contributing to N_2O-N loss in the tropics are known to be substantially different from those in temperate regions where much of the research on greenhouse gas emissions from soils have been based.

Statement of Problem

Energy and chemical-intensive farming has led to increased levels of greenhouse gas emissions, primarily as a result of the overuse of N fertilizers, land clearing, soil degradation, and intensive animal farming. The total global contribution of agriculture to climate change, including deforestation for farmland and other land use changes, is estimated to be equivalent to between 8.5-16.5 billion tons of carbon dioxide or between 17- 32 % of all human-induced greenhouse gas emissions (Skinner et al., 20014). Overuse 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 CO_2 annually (Smith et al., 2006). Excess N fertilizer results in the emission of greenhouse, nitrous oxide (N_2O), which is 298 times more potent than carbon dioxide in a 100-year time frame (Smith, et al.).

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Nitrous oxide has important effects both on the climate system and on stratospheric ozone (Wuebbles, 2009). It is produced in the soil predominantly by the microbial processes of nitrification (ammonia oxidation) and denitrification (nitrate reduction); (Robertson and Groffman, 2007). Processes that control N_2O production in soil include those that regulate denitrification and nitrification, available carbon, inorganic N, and oxygen as affected by soil moisture, porosity, and aggregate structure (Robertson & Groffman, 2007). Management practices that can influence emissions of N_2O from agricultural soils include fertilizer N (rate, type, timing and application method), crop, tillage, residue management, and irrigation (Parkin & Kaspar, 2006). Given that N_2O in agricultural soil is emitted predominantly through the microbial transformations of inorganic N, the potential to produce and emit N_2O increases with the increasing availability of N (Bouwman, Fung, Matthews & John, 1993). Man's need for more food, as a result of an expanding global population, has inevitably led to an increase in the use of both synthetic fertilizer and the wider application of animal waste on agricultural lands. However, the application of such N based fertilizers in many areas has been excessive, with large proportions of the added fertilizer providing no benefit to crop yield, but inducing elevated nitrous oxide emissions.

Although the emission of CO_2, NO and N_2O is expected to be high from soils under wetting conditions, the quantification of CO_2, NO_x and N_2O emissions from soil previously cropped with maize under mineral fertilizer application has not been attempted or quantified in the Guinea Savanna agro-ecological zone of Ghana. Additionally, there is inadequate knowledge on other soil chemical factors

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that influence greenhouse effect such as nitrate accumulation in the dry season fallow following early rains. Although under normal agricultural practices on slightly acidic soils, the instability of nitrite usually does not lead to significant N losses from soils, the compounds formed through its degradation or interaction with other soil components are linked to environmental problems such as tropospheric ozone formation, acid rain, the greenhouse effect and the destruction of the stratospheric ozone.

Research Objectives, Hypothesis and Questions

Objective of the study

The main objective of this study is to determine the contribution of N fertilizer type and rate of application to nitrous oxide and carbon dioxide emissions in the Guinea savanna agro-ecological zone of northern Ghana.

Specific objectives of the study

The specific objectives of the study were to:

- Quantify nitrous oxide and carbon dioxide emissions from rain fed maize fields in the Guinea Savannah agro-ecological zone and estimate the proportion of applied N fertilizer lost through N_2O emissions in relation to source and amount of fertilizer applied

- Determine the influence of soil moisture and soil temperature on CO_2 and N_2O emissions

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- To determine the relationship between ammonium (NH_4^+) fertilizers and N_2O emissions

- Determine N_2O emission in relationship to grain yield under fertilized and unfertilized maize plots

- Measure NO_x and N_2O emissions following drying and rewetting of previously fertilized soil.

- Determine the fate of excess N fertilizer in soils employing ^{15}N approach

Research hypothesis

The main hypotheses of the study are:

Ho_1: Different types of N fertilizer increase N_2O, NO and NO_2 emissions from soils;

Ho_2: Application of N fertilizer at higher levels increase N_2O, NO and NO_2 emissions from soils; and

Ho_3: Increases soil moisture increase N_2O, NO and NO_2 emissions in soils.

Research questions

To be able to test these hypothesis, the following research questions were addressed.

a) What are the different N fertilizer types commonly used in the Guinea Savanna agro-ecological zone of Ghana?

b) What are the levels of the N fertilizer used by smallholder and commercial maize farmers?

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c) Which soil characteristics affect soil N_2O and CO_2 emissions?

Significance of Study

Due to the strong influence of available soil N on N_2O emissions, some emissions of N_2O is an unavoidable consequence of maintaining highly productive cropland (Mosier, 2002). Consequently, anthropogenic activities that lower the input of N into cropland agriculture or reduce N availability can reduce emissions of N_2O. Nitrogen is generally the most limiting nutrient in intensive crop production systems (Robertson & Vitousek, 2009), and N fertilizer is commonly applied to maize, rice, wheat and other non-leguminous crops. Knowledge of the trade-offs between N_2O emissions, N fertilizer management practice, and crop yield is, therefore, an essential requirement for informing management strategies that aim to reduce the agricultural N_2O burden without compromising productivity and economic returns.

The improved targeting of fertilizer applications, both in rate and type, can significantly reduce nitrous oxide emissions from agricultural lands. Land-management strategies which accurately take account of the optimum amounts of fertilizer addition necessary for maximum crop yield are crucial both environmentally and economically. It is estimated that only a percentage of mineral N fertilizer applied are used by plants. It is, therefore, worth knowing the radiative forcing and mitigation potential in relation to N_2O emitted by mineral N fertilizers from agricultural production systems undertaken in Ghana especially the Guinea savanna agro-ecological zone. Furthermore, there are less relative measurements of

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N_2O emission from developing countries of which Ghana is not an exception and even in less diversified and complex landscapes. This is, a useful indicator of environmental and long term sustainability in improving soil fertility for increased yields and will also help in developing sustainable food production.

Selection of soil type, amount of mineral N applied and used by the crop will not only reduce input cost per unit of product harvested but would also increase crop yields. Similarly, the exact form of N based fertilizer and rate of application are a key information on which to base fertilization campaigns.

Delimitations

The study was conducted at Akukayilli, in the Tolon District of Northern Region of Ghana. The experimental site is located between N 09^0 23′ 38.2″ and W 001 00′ 18.4″ and belongs to the Guinea Savannah agro-ecological zone of West Africa.

The study was conducted on upland *Ferric Luvisols* where maize is mostly cultivated to determine the influence different types and rate of nitrogen fertilizer application on N_2O and CO_2 emissions; NOx emissions from previously fertilized maize fields following subsequent drying and rewetting. Also, the fate of excess N fertilizer was determined using ^{15}N technique. The study was not conducted in lowlands. Other greenhouse gas such as methane was not quantified in the study.

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Limitations

Nitrous oxide and CO_2 measurements were conducted by placing the air-tight improvised chambers fixed on collars intra-rows. Measurements of soil N_2O and CO_2 with improved chambers placed intra and inter-rows in each experimental plot instead of only intra-rows may capture more accurately the spatial variability of N_2O and CO_2 fluxes in each experimental plot.

Definition of Terms

Greenhouse gas

A greenhouse gas (GHG) is a gas in an atmosphere that absorbs and emits radiation within the thermal infrared range. This process is the fundamental cause of the greenhouse effect. The primary greenhouse gases in Earth's atmosphere are water vapor, carbon dioxide, methane, nitrous oxide, and ozone. Without greenhouse gases, the average temperature of Earth's surface would be about -18 °C (Berbert et al., 1977).

Nitrous oxide emission

Nitrous oxide emission in this study refers to the discharge of an oxide of nitrogen into the atmosphere. At room temperature, it is a colorless, odorless non-flammable gas, with a slightly sweet taste. At elevated temperatures, nitrous oxide is a powerful oxidizer similar to molecular oxygen. It is also a major greenhouse gas and air pollutant. Considered over a 100-year period, it is calculated to have

between 265 and 310 times more impact per unit mass global-warming potential than carbon dioxide (Overview of Greenhouse Gases – Nitrous Oxide, 2014).

Carbon dioxide emission

Carbon dioxide emission in this study refers to the discharge of an oxide of carbon into the atmosphere. There are both natural and human sources of carbon dioxide emissions. In this study emphasis on the source of CO_2 emission is on organic matter decomposition and soil respiration. Carbon dioxide makes up the largest share of "greenhouse gases". Elevated levels in the atmosphere disturbs the earth's radiative balance. This is leading to an increase in the earth's surface temperature and to related effects on climate, sea level rise and world agriculture.

Fertilizers

A fertilizer is any material of natural or synthetic origin (other than liming materials) that is applied to soils or to plant tissues (usually leaves) to supply one or more plant nutrients essential to the growth of plants. Fertilizers are classified in several ways. They are classified according to whether they provide "straight fertilizers "or "Multi-nutrient fertilizers".

In this study fertilizers used were nitrogen fertilizers made from ammonia and NPK fertilizers (i.e. NPK 15-15-15) which is a three-component fertilizer providing nitrogen, phosphorus, and potassium. The first number represents the percentage of nitrogen in the product; the second number, P_2O_5; the third, K_2O. This fertilizer does not actually contain P_2O_5 or K_2O, but the system is a

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conventional shorthand for the amount of the phosphorus (P) or potassium (K) in a fertilizer. A 50-kg bag of the fertilizer labeled 15-15-15 contains 7.5 kg each of nitrogen, phosphorus and potassium (15% of the 50-kg bag), an amount of phosphorus equivalent to 17.21 kg of P_2O_5 (15% of 50-kg), and 9.04 kg of K_2O (15% of 50-kg bag).

Oxides of nitrogen (NOx)

NOx is a generic term for the mono-nitrogen oxides NO and NO_2 (nitric oxide and nitrogen dioxide) (Mollenhauer, Klaus; Tschöke & Helmut, 2010). They are produced from the reaction among nitrogen, oxygen and even hydrocarbons (during combustion), especially at high temperatures (Mollenhauer *et al*. 2010); (Annamalai, Kalyan, Puri, & Ishwar, 2006). In this context, NOx refers to the total concentration of NO and NO_2. Oxides of nitrogen gases react to form smog and acid rain as well as being central to the formation of tropospheric ozone.
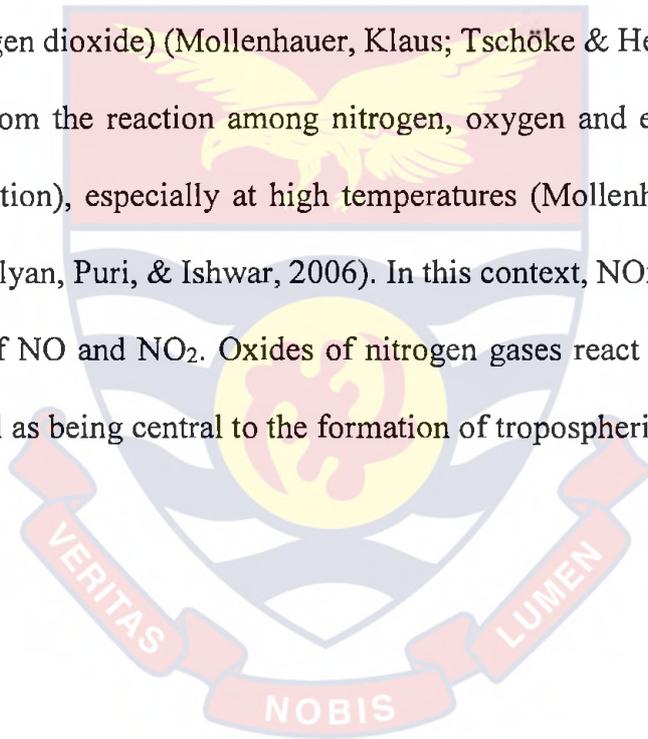
Yield Scaled emission

Yield scaled emission in this study refers to the amount of greenhouse gas produced per kilogram grain from N fertilized and unfertilized fields

Emission factor

In this study, emission factor refers to the average amount of N_2O-N discharged into the atmosphere by application of nitrogen fertilizers. It is expressed as number of microgram of N_2O-N unit amount of N fertilizer applied.

Organization of the Study

This thesis is organized into five chapters. The first chapter presents the background to the study, the statement of the problem, objectives and research questions, significance of the study, the delimitations, the limitations and the definition of terms. The second chapter presents the literature review focusing on impact of agriculture on climate change, fertilizer use in Sub-Saharan Africa, greenhouse gases (CO_2, N_2O, NO and NO_2) emission and processes of N_2O losses.

The third chapter details the climatic conditions, vegetation cover and soil properties of the study area. This chapter also presents in details the methodologies used in this study, data collection techniques and analytical procedures.

The fourth chapter presents the results and discussion of each specific objective whereas the fifth chapter presents the summary of the research findings, conclusions as well as recommendations as a result of finding from this study.

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Summary of Chapter One

Chapter one details the inter relationship between climate change and agriculture and how the latter is affected. It describes the potential effect of rising atmospheric nitrous oxide and carbon dioxide on crop yields and the environment. Furthermore, this chapter discusses the scantiness of information regarding greenhouse gas emission measurement in the tropics and efforts by other researches to mitigate the effect of climate change on agriculture and its associated knowledge gabs. Finally, the chapter also presents the main objective of the study as well as specific objectives, research questions and the significance of the study. Delimitations, limitations, definitions of terms as used within the context of this study and the organization of the entire thesis are also presented in chapter one.

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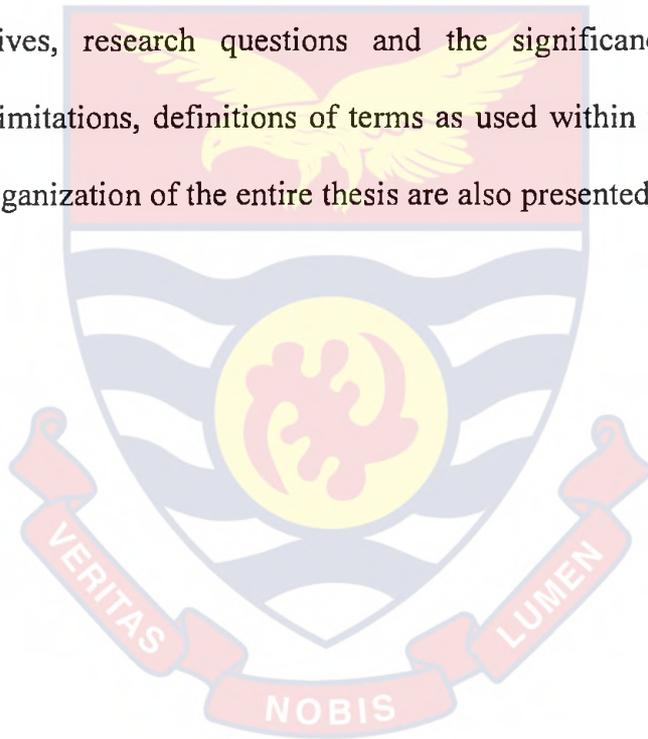
CHAPTER TWO

LITERATURE REVIEW

The susceptibility of the agricultural sector to both climate change and variability is well established in the literature. The general consent is that changes in temperature and precipitation will result in changes in land and water regimes that will subsequently affect agricultural productivity. Research has also shown that specifically in tropical regions, with many of the poorest countries, impacts on agricultural productivity are expected to be particularly harmful. The vulnerability of these countries is also especially likely to be acute in light of technological, resource, and institutional constraints.

Even though estimates points to the fact that global food production is likely to be increased, experts predict tropical regions will see both a reduction in agricultural yields and a rise in poverty levels as livelihood opportunities for many engaged in the agricultural sector become increasingly susceptible to expected climate pressures. This chapter presents a review of climate change and its inter-relationship with agriculture, factors emulating from agricultural activities that affects climate change and potential mitigation measures.

Climate Change and Agriculture

Climate change and agriculture are interrelated processes, both of which take place on a global scale (Bernstein et al., 2007). Global warming is projected to have significant impacts on conditions affecting agriculture, including temperature, carbon dioxide, glacial run-off, precipitation and the interaction of these elements

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(Bradford & Fraser, 2008). These conditions determine the carrying capacity of the biosphere to produce enough food for the human population and domesticated animals. The overall effect of climate change on agriculture will depend on the balance of these effects. Assessment of the effects of global climate changes on agriculture might help to properly anticipate and adapt farming to maximize agricultural production (Fraser).

At the same time, agriculture has been shown to exert significant effects on climate change, primarily through the production and release of greenhouse gases such as carbon dioxide, methane, and nitrous oxide, but also by altering the earth's land cover, which can change its ability to absorb or reflect heat and light, to assimilate carbon dioxide and to release water vapour, thus contributing to a change in radiative forcing. Land use change such as deforestation and desertification, together with use of fossil fuels, are the major anthropogenic sources of carbon dioxide; agriculture itself is the major contributor to increasing methane and nitrous oxide concentrations in earth's atmosphere (United Nations (UN), 2007).

Impact of Agriculture on Climate Change

The agricultural sector is a driving force of increase in the CO_2 and N_2O emissions and land use effects thought to cause climate change. In addition to being a significant user of land and consumer of fossil fuel, agriculture contributes directly to greenhouse gas emissions through practices such as rice production and the raising of livestock (Howden et al., 2007), according to the Intergovernmental Panel on Climate Change (IPCC), the three main causes of the increase in

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greenhouse gases observed over the past 250 years have been fossil fuels, land use change, and agriculture (Bernstein et al., 2007).

Agriculture contributes to the increase in greenhouse gas emissions through land use and land use change in four main ways: CO_2 releases linked to deforestation, methane releases from rice cultivation, methane releases from enteric fermentation in cattle and nitrous oxide releases from fertilizer application. Together, these agricultural processes comprise 54 % of methane emissions, roughly 80 % of nitrous oxide emissions, and virtually all carbon dioxide emissions tied to land use (Bernstein et al., 2007).

The planet's major changes to land cover since the year 1750 have resulted from deforestation in temperate regions: when forests and woodlands are cleared to make room for fields and pastures, the albedo of the affected area increases, which can result in either warming or cooling effects, depending on local conditions (Bernstein et al., 2007). Deforestation also affects regional carbon reuptake, which can result in increased concentrations of CO_2, the dominant greenhouse gas (Bernstein et al., 2007). Land-clearing methods such as slash and burn aggravate these effects by burning biomass, which directly releases greenhouse gases and particulate matter such as soot into the air. Factors contributing to CO_2 and N_2O emissions are reviewed extensively in this chapter.

Fertilizer Use in Sub-Saharan Africa

As is well known, food production in sub-Saharan Africa continues to lag behind population growth. Soil fertility must be managed more efficiently if Africa

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is to overcome its food-production problems. Mineral fertilizers and improved nutrient management strategies are crucial to such efficiency. New nutrient sources and more responsive crop varieties are also important. Maize combines widespread importance as a food staple with relatively high fertilizer responsiveness. As a result, maize production and fertilizer use are likely to become even more closely linked than they have been in the immediate past.

Though the appropriateness of seed-fertilizer technology for sub-Saharan Africa will continue to be debated, the continent can no longer be regarded as land-abundant. That characterization has been one of the major arguments against relying on a seed-fertilizer strategy for agricultural development. Though conditions vary widely, many African countries can now be classified as land-scarce (Binswanger & Pingali, 1988). Yield increases, rather than area expansion, will thus become progressively more important as a means of increasing crop production.

Mineral fertilizers must be included in any agricultural development strategy with a hope of reversing Africa's unfavorable food-production trends. Fertilizers also complement other major inputs and practices (e.g., improved seeds, better water control) that have had the greatest impact on yield. Soil nutrient depletion is a common consequence of most African agriculture (Smaling, 1993); (Stoorvogel, Smaling, & Janssen, 1993). For the foreseeable future, "the environmental consequences of continued low use of fertilizers" through nutrient mining and increased use of marginal lands "are more inevitable and devastating than those anticipated from increased fertilizer use" (Dudal & Byrnes 1993);

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(Matlon & Spencer, 1984). In the light of these considerations, many observers have called for increases in sub-Saharan fertilizer consumption of 15 % or more per annum (Mellor, Delgado, & Blackie, 1987); Vlek, (1990); (Desai & Gandhi, 1990); (Larson, 1993).

Fertilizer Use in Ghana

Over the last 30 years, fertilizer consumption in sub-Saharan Africa has increased. In recent years, growth in fertilizer on cereals, particularly maize has contributed substantially to this increase. Nonetheless, current application rates remain low. Fertilization in tropical agriculture has the potential to dramatically increase production due to the highly weathered soils and the limited reserves of nutrients (Stewart, Dibb, Johnston & Smyth, 2005), yet increased nutrient application is rarely managed by recommendations derived from soil testing and consequently this leads to misuse and associated economic (Chase, Duffy, Webb & Voss 1991) and environmental risks (Bundy, Andraski &Powell, 2001); (Cox & Lins, 1984).

In Ghana, currently the importers of fertilizers to the various sectors of food production and other uses are numerous with a growing interest in the fertilizer import business. Between 2004 and 2007, Ghana imported 674,000 metric tonnes of fertilizer (Yawson, Armah, Afrifa, & Dadzie, 2010). Fertilizer import data over a nine-year period from 1997 to 2001(60,000-80,000 metric tonnes) and from 2004 to 2007 (110,000-190,000 metric tonnes) presents a rising trend.

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The end users of fertilizers in the food production sector of Ghana, consists of a large number of small scale farmers in units of large households especially in the Northern, Brong-Ahafo and parts of the Ashanti region. With proper education, affordable price, timely availability and accessibility, demand for fertilizers in Ghana is enormous.

Carbon Dioxide Emissions from Agricultural Lands

Sources of soil carbon stock and CO2 emission

Carbon dioxide (CO_2) emissions contribute highest to agricultural emissions and are mainly attributed to soil and crop management practices that reduce soil organic carbon stocks. Forest activities impact on CO_2 emissions and deforestation mainly for cultivation negatively affects C storage, uptake and loss from woody biomass and soils.

Carbon dioxide 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 CO_2 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 (Conant, Easter, Paustian & Swan, 2007). Soil inorganic carbon (SIC) is comprised of primary carbonate minerals, such as calcite ($CaCO_3$) or dolomite ($CaMg (CO_3)_2$), or secondary minerals formed when carbonate (CO_3^{2-}),

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derived from soil CO_2, combines with base cations (e.g., Ca^{2+}, Mg^{2+}) and precipitates within the soil profile in arid and semi-arid ecosystems.

Soils can be described as a source of or sink for CO_2 depending on the current and historical land use and agricultural management practices. However, this behavior depends on the increase or decrease of soil organic carbon stock and is regulated by external factors.

Factors Regulating SOC Stock and CO2 Emission

The balance between soil organic carbon (SOC) losses induced by microbial decomposition of soil organic matter (SOM) and organic carbon (OC) inputs to soils as crop residues and manures (Halvorson, Del Grosso, & Reule, 2008). (Stewart, Paustian, Conant, Plante, & Six, 2009) are identified as the major regulator of the SOC stock in the soil. Therefore, when SOM decomposition is enhanced relative to the input of carbon, soils generally behave as net CO_2 sources with a decrease in SOC stocks as a result.

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 (Chapin, Matson, & Mooney, 2002).

Land use and management of agricultural systems have considerably changed SOC stocks in agricultural land through disparities in land use, tillage,

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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 (Conant et al., 2007). Soil organic C has been shown to decline significantly following even one tillage event (1–11% of soil C lost) (Conant et al.).

Management of CO2 losses in agricultural lands

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 (Paustian, Collins and Paul, 1997); (Smith, Powlson, Glendining & Smith, 1998); (West & Post, 2002); Ogle, Breidt, & Paustian, 2005) and as a consequence, is being promoted as an alternative management practice in mitigating GHG emissions from agricultural systems (Halvorson, Del Grosso, & Reule, 2008).

Management of C stock and CO_2 emissions can therefore be targeted on cropping system and crop management practices that influence CO_2 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 increasing C inputs

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to the soil include green manuring and organic manure application. Practices such as burning or removal of residues after harvest typically reduce C inputs to the soil.

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 (Halvorson, Del Grosso, & Reule, 2008). 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) (Skinner et al., 20014).

Nitrous Oxide Emissions from Agricultural Lands
Nitrous oxide emissions from application of nitrogenous fertilizer

Atmospheric N_2O concentrations have been increasing since the industrial revolution and currently account for 6 % of total anthropogenic radiative force. Microbial production in soils is the dominant N_2O source; this has increased with increasing use of N fertilizers (Davidson, 2009).

Nitrogenous fertilizers play an import role in increasing crop yields. Use of nitrogenous fertilizer, however, increases N_2O emissions from soil and water through nitrification and denitrification processes. The N cycle (Appendix 1)

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illustrates the mechanism for N_2O emissions. Nitrous oxide absorbs infrared radiation in the atmosphere, causing atmospheric warming, and can also combine with oxygen in the stratosphere to form NO, which reacts with ozone and decreases the ozone layer. Bouwman (1990), estimates the contribution of N_2O to global warming at approximately 5 % of the total radiative force.

The Intergovernmental Panel on Climate Change (2013), estimates total global nitrous oxide emissions at 10 to 17.5 million metric tons per year. Reliable estimates of the amount due to fertilizer application are not yet available. Anthropogenic factors that affect emissions from fertilizer use include the type and amount of fertilizer applied, application technique and timing, tillage practices, use of pesticides, irrigation practices, vegetation type, and soil residual N. Another contributing factor to the increasing level of N_2O emissions is leguminous crops that add N to the soil (Eichner, 1991).

Production of N_2O from agricultural lands

Nitrous oxide is emitted by both natural and human-related sources. Primary human-related sources of N_2O are agricultural soil management, animal manure management, and sewage treatment, mobile and stationary combustion of fossil fuel, adipic acid ($C_6H_{10}O_4$) production, and nitric acid production. Nitrous oxide is also emitted naturally from a wide variety of biological sources in soil and water, particularly from microbial sources in wet tropical forests

Nitrous oxide emission levels from a source can vary significantly from one country or region to another, depending on many factors such as industrial and

agricultural production characteristics, combustion technologies, waste management practices, and climate. For example, heavy utilization of synthetic N fertilizers in crop production typically results in significantly more N_2O emissions from agricultural soils than that occurring from less intensive, low-tillage techniques or from natural ecosystems. Also, the presence or absence of control devices on combustion sources, such as catalytic converters on automobiles, can have a positive significant effect on the level of N_2O emissions from these types of sources (Bernstein et al., 2007).

Agricultural soil management

Nitrous oxide is emitted naturally in soils through the microbial processes of denitrification and nitrification (Signor, Eduardo & Cerri, 2013). These natural emissions of N_2O can be increased by a variety of agricultural practices and activities, including the use of synthetic and organic fertilizers, production of nitrogen-fixing crops, cultivation of high organic content soils, and the application of livestock manure to croplands and pasture. All of these practices directly add additional nitrogen to soils, which can then be converted to N_2O. Indirect additions of nitrogen to soils can also result in N_2O emissions. Indirect additions include those processes by which applied fertilizer or manure nitrogen volatilizes as ammonia and oxides of nitrogen and then is ultimately re-deposited onto the soil in the form of particulate ammonium, nitric acid, and oxides of nitrogen. Surface run-off and leaching of applied nitrogen into ground water and surface waters can also result in indirect additions of nitrogen to the soil.

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Agricultural soils represent a very large, and growing, global source of N_2O. Current estimates for annual emissions from this source range from 2 to about 4 million tonnes of N_2O-N globally (IPCC, 2014). With a rapid increase in population growth, and the consequent need for more food production, both the area of agricultural soils and the intensity of their use are likely to continue to rise rapidly in coming decades. A major direct source of N_2O from agricultural soils is that of synthetic fertilizer use. Widespread increase in the use of such N based fertilizers has been driven by the need for greater crop yields, and by more intensive farming practices. Where large applications of fertilizer are combined with soil conditions favorable to denitrification and nitrification, large amounts of nitrous oxide can be emitted to the atmosphere.

Similarly, the widespread and often poorly controlled use of animal waste as fertilizer can lead to substantial emissions of N_2O from agricultural soils. Some additional N_2O is thought to be produced in agricultural soils by the process of nitrogen fixation (Mosier et al., 1998).

After fertilizer application or heavy rain, large amounts of N may leach from the soil into drainage ditches, streams, rivers and eventually estuaries. Also leaching to the groundwater can play an important role, at least in certain regions where conditions are suitable. Some of the N_2O emitted in agricultural soils is lost also in this way, being emitted to the atmosphere as soon as the drainage water is exposed to the air.

As with direct N_2O emission from agricultural soils, man takes full responsibility (although there are also natural direct and indirect N_2O emissions,

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especially from tropical wetlands) for indirect emissions. Not only do large quantities of leached N based fertilizer have a significant impact on indirect nitrous oxide emissions, they have also led to dangerously high nitrate concentrations in drinking water and to eutrophication in rivers and estuaries around the world. Increased food consumption and consequent increases in municipal sewage treatment have also inevitably led to increased indirect N_2O emissions from this source (Syakila, & Kroeze, 2011)).

Potential for control of N_2O emissions

Again, it is through properly informed land-management practice and fertilization campaigns that N_2O emissions can primarily be reduced. Much of the motivation for control of N based fertilizers has come from concern about high nitrate levels in drinking water supplies and the threat of eutrophication in estuaries and coastal waters. Individual governments have enacted changes in policy to bring about reductions in N leaching, with the creation of 'Nitrate Sensitive Zones' (NSZs) requiring particular attention in the UK. However, these interventions occur primarily in the developed countries (Bernstein et al., 2007).

Use of enhanced-efficiency N fertilizers is one of several possible management practices that can be effective in reducing environmental N losses and increasing N-use efficiency. Understanding the factors that influence N loss and the technical characteristics of the different enhanced-efficiency fertilizers is critical for determining their optimal use. In addition, quantification of the reductions in environmental N loss that can occur with use of these enhanced-efficiency N

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fertilizers under diverse cropping systems and environmental conditions would assist in the development of government-sponsored practice incentive programs designed to promote use of management practices that conserve and protect natural resources. A major limitation to use of many of these fertilizer products is their higher cost, limited availability and possible special handling procedures for transport, storage and application. Therefore, research which provides an economic evaluation of the costs and benefits of using the enhanced-efficiency fertilizers is important to assist growers in making informed decisions whether use of a particular fertilizer product is cost-effective for their specific site conditions.

Research in Missouri is exploring several management practices which may lower costs of using enhanced-efficiency fertilizers (Motavalli, Nelson, Kitchen, Anderson & Scharf, 2007). One approach is to mix controlled- or slow-release fertilizers with conventional urea or lower application rates of the enhanced-efficiency fertilizer because of its possible higher N-use efficiency. Another approach is to use a variable source N application strategy in which conventional urea fertilizer is applied to areas of a field which have a low risk of N loss and the enhanced-efficiency N fertilizer to the high risk areas of a field using a multi-bin spreader. Research conducted from 2005 through 2007 in a clay-pan soil in northeastern Missouri has shown a consistent 1.6 to 1.9 t ha^{-1} maize yield increase with use of PCU compared to urea in low-lying areas of a field but not on the side-slopes or summit positions of the field (Motavalli et al., 2007).

The rapid increase in the anthropogenic production of N fertilizers has been a major factor accounting for the growth in agricultural food production. Despite the overall benefits from use of reactive N, major environmental problems (e.g., soil and water acidification, contamination of surface and groundwater resources, increased ozone depletion and greenhouse gas levels, and loss of biodiversity) have developed due to the presence of excessive environmental N (Motavalli, Goyne & Udawatta , 2008).

Despite the unprecedented role synthetic N fertilizers have played in increasing agricultural crop and livestock production and meeting the nutritional requirements of a growing human population, strong evidence has emerged demonstrating the detrimental effects of the increasing amounts of reactive N in the environment (Howarth, 2004). Among the deleterious effects of excessive environmental N are acidification of soils and water resources, eutrophication of coastal marine ecosystems, loss of biodiversity in terrestrial and aquatic ecosystems and invasion of N-affine weeds, increased greenhouse gas levels due to emissions of N_2O, depletion of stratospheric ozone, increased ozone-induced injury to crop, forest and other ecosystems, and increased atmospheric haze and production of airborne particulate matter (Galloway & Cowling, 2002).

Processes of N_2O Losses

The primary mechanisms of N loss from agricultural fields are nitrate leaching, runoff and erosion, and gaseous losses from denitrification, nitrification

and ammonia volatilization (Follett, 2001). The relative magnitude of these N loss processes is affected by several factors, including variation in soil properties, climatic conditions, crop growth, and management practices (e.g., soil tillage method and the selection of the N source and its timing and method of application). Among the most important factors affecting N loss through soil processes, such as nitrate leaching and denitrification, are variations in soil water content and drainage either due to spatial differences in soil properties across agricultural fields or due to variation in precipitation during the growing season (Power, Wiese & Flowerday, 2001). For example, in the clay-pan region of the Midwestern United States, Bailey, Fansler, Smith and Bolton (2001) found relatively high rates of soil N_2O emissions that represented approximately 10 % of the fertilizer N applied to a corn field. These high rates of observed soil N_2O loss may be attributed to the relatively poor drainage of clay-pan soils that can cause high soil water content early in the growing season shortly after N fertilizer application. Research by Udawatta et al. (2002) in a paired watershed study in northeastern Missouri has shown agricultural watersheds in a common crop rotation in the Midwestern United States (i.e., corn and soybeans) are also vulnerable to N losses from both runoff and sediment loss, especially during large rainfall events, or after a sequence of closely-spaced small rainfall events.

Agricultural soils contribute significantly to CO_2 and N_2O emissions, and thus to global climate change, along with other factors such as climate, soil, and fertilizer use (Longoria-Ramírez, Mar-Morales & Ruiz-Suárez, 2007). This implies that N losses from agriculture represent an economic loss and an environmental

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impact. It is accepted that the emission of N_2O from soils is a result of the transformation of the nitrogen contained in the fertilizer by soil microorganisms where the principal process pathways are nitrification and denitrification. During denitrification of nitrate (NO_3^-) and nitrification of ammonium (NH_4^+), N_2O is emitted and so fertilizers or manure affect the availability of nitrate and/or ammonium in the soil.

Nitrous oxide emissions from fertilized agricultural soils are considered a complex process. In the nitrification and denitrification, nitrous oxide, nitric oxide and molecular nitrogen are emitted; also soil microorganisms can consume these gases. Wolf and Russow (2000) found that under water-saturated conditions the dominant process is the denitrification, but nitrification also occur to some extent. Under this condition N_2O and N_2 emissions were observed but nitric oxide (NO) was not detected. Speir, Townsend, More and Hill (1999) using the short-lived radioisotope ^{13}N, found that N_2O is emitted via denitrification in very low-fertility ecosystems. Flessa, Dorch, and Beese (1995) did not find extensive dependence between the N_2O emissions and soil temperature, soil water content and available NO_3^-. Veldkamp, Keller and Nuñez (1998) observed a great dependence between NO and N_2O emissions and soil water content, which is related to the supply of oxygen for nitrification and denitrification. They concluded that trace gas fluxes can be highly dependent on weather conditions at the time of sampling. In a previous publication, Veldkamp and Keller (1997) concluded that the most important factor on NO_x emissions from soils is related to the tillage level.

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Interaction of tillage level with fertilization practice has been observed. Maximum N_2O emissions were measured in corn fields with no-tilled systems and the emissions were greater when fertilizers were added (MacKenzie, Fan & Cadrin., 1998). This may be due to higher soil compaction which favors anaerobic conditions and denitrification. On the other hand, tillage favors aerobic conditions and nitrification. Adding fertilizers increases the available nitrogen to be processed on either way. The authors suggest, as a way to diminish N_2O emissions, to rotate crops (maize and forages), and to reduce fertilizer application and tillage intensity. Longoria-Ramírez (2007) have reported the relationship of the physical, chemical and biological soil properties, weather conditions and complex interactions among these factors. They attributed high variations in N_2O and N_2 fluxes due to the diverse combinations of these factors controlling gas fluxes. They concluded that the denitrification rates generally increased with increasing soil moisture content. They reported 10 to 20 times increased N_2O losses when the soil was subjected to anaerobic-aerobic cycles.

With a low soil C/N ratio, N can be mineralized creating favorable conditions for the generation of nitrous oxide. Denitrification had a positive correlation with pH, with an optimum in the range of 7.0 to 8.0, and below pH 6.0 the denitrification could be strongly inhibited. The $N_2:N_2O$ ratio strongly increased with soil pH. Regarding the temperature they found that nitrification increased between 25 and 35 °C, whereas denitrification was favored between 30 and 67 °C. Mogge, Kaiser and Munch (1999) also reported on N_2O emissions in soils amended with organic materials They found that the overall loss of N_2O represented 5.7% of

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the annual N-input (mineral nitrogen fertilizer plus organic nitrogen fertilizer); this percentage might reach values of 10 % of the applied fertilizer nitrogen and increase with soil moisture and the content of organic C available as electron donor.

Gaseous N_2O Losses Control Approach

On-going research is examining whether use of slow- and controlled-release N fertilizers could reduce N_2O emissions (Snyder, 2009). For example, research completed by Merchan (2006) in northeast Missouri showed that polymer coated urea (PCU) compared to urea can reduce efflux of N_2O from claypan soils under relatively wet climatic conditions caused by the absence of adequate tile drainage. Nash, Motavalli and Nelson (2012) also observed early season differences in soil N_2O flux among different N fertilizer sources across several landscape positions in a field in northeast Missouri.

Other researchers have also shown decreased N_2O emissions with use of slow- or controlled-release N fertilizers compared to conventional fertilizers, such as urea, under diverse crops and soil types (McTaggart & Tsuruta, 2003); (Shoji, Delgado, Mosier & Miura, 2001); (Vallejo, Diez,, López-Valdivia, Gascó & Jiménez, 2001). However, reduction of soil N_2O emissions due to use of slow- and controlled-release fertilizers has not always been consistent from year-to-year. For example, Merchan (2006), observed a decrease in N_2O emissions with use of PCU compared to urea in 2004 but not in 2005. These results are indicative of the complex soil, climatic and management factors that affect soil N_2O emissions, and the high variability in emissions of this gas that occurs within fields and over time.

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NOx Productions in Agricultural Soils

Nitrogen dioxide (NO_2) is derived from oxidation of NO, and is known as a precursor of nitric acid, which is a major component of acid rain. Agricultural soil is a major source of N_2O, accounting for 24% of the global annual emission (IPCC, 2014). NO from agricultural and non-agricultural soil is also considered to be a major source, accounting for 23% of the global annual emission (IPCC, 2014). Nitric oxide is produced naturally in the soil by microorganisms as a by-product of nitrification and denitrification that convert nitrogen from ammonium to nitrate. Recent estimates suggest that, globally, microorganisms may release similar amounts of NO, per year, as combustion sources (20 Tg of NO-N) (Rogers & Whitman, 1991); (Logan, 1983). The largest biogenic emissions of NO_x have been measured from systems that support rapid N cycling, high temperatures, and/or seasonally low moisture, including fertilized agriculture and seasonally dry tropical ecosystems (Hall, 1996).

Many researchers have found significant levels of NO from agricultural cropped lands. For instance, Kessel, Grieser, Wobrock and Jaeschke (1992), reported NO concentrations of 9,700 mmol m^{-3}, a value typically seen only in urban regions, measured near the ground in heavily fertilized agricultural regions of the Po Valley in Italy. However, given that Ghana's fertilizer use has increased dramatically (from approximately 60,000 metric tonnes in 1997 to 190,000 metric tonnes in 2007) and expected to rise above the current level of 7.3 kg ha^{-1} nutrients (Balu, Johnson, & Fuentes, 2012) the role of soil NO_x emissions in agricultural areas is likely to become more important in the future.

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In Northern Ghana, maize is planted in mid-June and is harvested at the end of October. Between October and May, the soil is left bare and exposed to maximum temperatures rendering most soil micro-organism inactive. At the end of the dry season, the soils are usually ploughed after the first rains which normally between 20 and 40 % water filled pore space. However, with considerable organic matter from previous crop residue even though in most cases they are removed or burned, the presence of soil moisture triggers nitrification. This is expected to result in the accumulation of nitrates in the soil during the short dry spell between the first rains which usually occurs in Early to late March and the actual beginning of the season's rainfall in June. Buresh and Datta (1991) reported a quick loss of nitrate through denitrification thereby emitting NO and N_2O in the process. With the soil not flooded, the N_2O in the soil remains active and is emitted into the atmosphere. More so, previous research on upland soils showed that emissions of N_2O occur over brief periods following rainfall events (Sexstone, Parkin & Tiedje, 1985) and relatively small changes in water status can greatly affect emissions positively (Denmead, 1979).

Modelling Greenhouse Gas Emissions

Models are estimates of real systems. Although, in theory, there is no limit to the refinement and detail of a mathematical model, with greater modification allowing more detailed depiction of the physical system, there is a practical limit in terms of the model outputs, which is, in part, defined by the intended end use. The

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range of models and approaches is often required to develop our understanding as a stakeholder community.

The value of a model should not be judged by its precision alone but also, it's utility. Mathematical models are powerful tools that are increasingly being used to examine the potential impacts of management and climate change in agriculture. Models can simulate the processes responsible for production, consumption and transport of N_2O (Williams, Hutchinson & Fehsenfeld, 1992). Models used to establish emissions under current management practices can also be used to compare alternative management scenarios intended to reduce emissions; this capability being more pertinent in a changing climate (Shepherd, Wu, Chadwick & Bol, 2011). Where measurements of emissions cannot easily be obtained, models may be used at the site-scale to interpolate and for nations to extrapolate measurement information, both spatially and temporally, for use in GHG inventories.

Quantifying current greenhouse emissions and anticipating their future evolution is an important analytical input to policymaking. However, accurate emissions monitoring and reporting are not simple, and processes are still being improved globally. Predicting the future yet more challenging; models that do so are heavily affected by assumptions to create scenarios of economic, social and policy change over time. As a result there is a wide array of visions of the future, the difference between which are important to understand. The DNDC (DeNitrification DeComposition) model was first described by Li and Frolking (1992) as a rain event-driven process-orientated simulation model for N_2O,

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CO_2 and N_2 emissions from agricultural soils in the U.S. The DNDC field scale model coupled decomposition and denitrification processes, as influenced by the soil environment, to predict carbon (C) and nitrogen (N) turnover in agricultural soils. During the past 20 years the original DNDC model, used by researchers throughout the world, has been modified and adapted to include different scenarios and other ecosystems, e.g. forests, wetlands, rice paddies.

Summary of Literature Review

Carbon dioxide emissions contribute to greatly to agricultural emissions and are mainly attributed to soil and crop management practices that reduce soil organic carbon stocks. 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 (Chapin, Matson, & Mooney, 2002). Soil organic C has been shown to decline significantly following even one tillage event (1–11% of soil C lost) (Conant et al., 2007).

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 (Halvorson, Del Grosso, & Reule, 2008). Microbial production in soils is the dominant N_2O source; this has increased with increasing use of N fertilizers (Davidson, 2009). Use of nitrogenous fertilizer,

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however, increases N_2O emissions from soil and water through nitrification and denitrification processes. Indirect additions of nitrogen to soils can also result in N_2O emissions.

Agricultural soils contribute significantly to CO_2 and N_2O emissions, and thus to global climate change, along with other factors such as climate, soil, and fertilizer use (Longoria et al., 2007). Nitrous oxide emissions from fertilized agricultural soils are considered a complex process. Flessa et al. (1995), did not find extensive dependence between the N_2O emissions and soil temperature, soil water content and available NO_3^-.

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CHAPTER THREE

MATERIALS AND METHODS

This chapter describes the methodology and provides information on experimental site and procedures used in this study. It describes procedures for each of the experiments conducted and the rationale for specific experimental procedures chosen. The chapter also presents what was done to answer the research questions and describes how it was done. Furthermore, the chapter states the experimental design used, describes the materials used in the study and explains how the materials were prepared. Finally, it explain how measurements were made and how the results were analyzed, calculations performed and statistical tests done to analyze the data.

Study Area

The study was carried out at Akukayilli, N 09^0 23' 38.2″ and W 001° 00' 18.4″ located in the Tolon District of the Northern region of Ghana. The region occupies 70,383 km^2 and is the largest region (i.e. 26 %) in Ghana in terms of land area. It shares boundaries with the Upper East and the Upper West Regions to the north, the Brong-Ahafo and the Volta Regions to the south, and two neighboring countries, the Republic of Togo to the east, and La Cote d' Ivoire to the west. The land is mostly low lying except in the north-eastern corner where the Gambaga escarpment rises along the western corridor. The experimental field was cultivated with cowpea in 2012.

Climate and Vegetation

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. The amount of rainfall recorded annually varies between 750 mm and 1050 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 temperature in the region, which may vary between 14 °C at night and 40 °C during the day. Humidity, which is very low at this time, mitigates the effect of the daytime heat (Kasei, 1996).

Vegetation cover ranges between Sudan and Guinea savannah. Farming forms the main occupation of about 70 % of the people in the region. Among the crops grown are maize (*Zea mays*), rice (*Oryza sativa*), sorghum (*Sorghum bicolor*), yams (*Dioscorea spp.*), tomatoes (*Lycopersicon esculentum*) and tree crops such as sheanut (*Vitellaria paradoxa*), cotton (*Gossypium spp.*) and kapok (*Ceiba pentandra*). The cultivation of rice and groundnut is mostly done as cash crops.

Soils at the Experimental Site

The soils at the experimental site is dominated by well to moderately drained sandy loams developed over Voltain clay. The top soils are characterized by strong brown with occasional iron and manganese concretions. It has an average

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depth of 90 cm. The soils are inherently low in fertility characterized by low levels of organic carbon, total nitrogen, available phosphorus and potassium, and cation exchange capacity. The soils are strongly acidic and classified as *Ferric Luvisols*. The experimental site was ploughed and harrowed at a depth of 30 cm.

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} y^{-1} plus NPK 15-15-15 at 60-40-40 kg N ha^{-1} y^{-1} and a control (plots without N fertilizer application) in a randomized complete block design with three replications was used. Triple superphosphate and muriate of potash each at the rate of 40 kg ha^{-1} y^{-1} of P$_2$O$_5$ and K$_2$O, respectively were applied together with the N fertilizer by dibbling. The NPK 60-40-40 is the recommended fertilizer for maize in Ghana (Safo, Kwakye & Bonsu, 1986). Plot size was 5 × 5 m was used. Each plot was separated by a path of 1 m which was left bare throughout the experimental period.

A maize cultivar, *Omankwa* was sown on 28th and 30th of July in years 2013 and 2014, respectively. Seven days after planting, plant population in the plots were adjusted, by either thinning or filling in, to reflect the average plant density in the field (6.25 plants m^{-2}), where plant germination was found to be uneven. Fifty per cent 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, in years 2013 and 2014 respectively as basal, the remaining 50 % of mineral N fertilizer was applied on August 28 and 30, in years 2013 and 2014, respectively. Weeding was

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done manually after crop had been established and whenever needed throughout the season.

An area (16 m²) within each plot was designated for measuring CO_2 and N_2O fluxes, while the remainder of the plot was used for plant sampling. Composite soil samples were collected using an auger at a depth of 10 cm within the 16 m² for the determination of soil moisture and forms of nitrogen (NH_4^+-N and NO_3^--N). For the determination of NH_4^+-N and NO_3^--N, composite soil samples (0-10 cm) were air-dried, inclusions removed, crushed and passed through a 2-mm sieve. Extraction was done immediately after sampling and were stored in air-tight plastic container in a refrigerator for analysis.

Data Collection

Chamber for measurements of N_2O and CO_2 fluxes

An improvised static chamber technique (Clayton et al., 1994) 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 (Appendix 2). 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 m², and used for CO_2 and N_2O flux. Collars were inserted into the soil permanently at a depth of 0.03 m, a week after planting in each experimental year.

Gas sampling began on 8 and 10 August in 2013 and 2014, respectively. 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 after start of sampling. Volume

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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 attain uniform air composition in the chamber. 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 m³ h⁻¹ and transported to the laboratory for analysis. Samples were analyzed for CO_2 and N_2O using a gas chromatography (Clarus 580, PerkinElmer, Rodgau, Germany), fitted with an electron capture detector (detection limit: N_2O < 1 ppbV / 1 nl l⁻¹ or lower) in Forschungszentrum Jülich GmbH, Institut für Bio- und Geowisschenschaften (IBG-3), Germany. Chamber closure and gas sampling were conducted between 09:00 and 16:00 h for each gas sampling. Flux rates were calculated according to equation 1:

$$FN_2O = \frac{b \times V_{ch} \times MWN_2O-N \times 10^6}{A_{ch} \times MV_{corr} \times 10^9} \dots \dots \dots \dots \dots \dots \dots \dots \dots .1$$

where F_{N_2O} = N_2O flux rate (µg N m⁻² h⁻¹), b = mixing ratio increase (ppb h⁻¹), V_{ch} represents chamber volume (m³), MWN_2O-N denotes molecular weight of N_2O-N (28 g mol⁻¹), A_{ch} represents base area of chamber (m²), MV_{corr} is the pressure and temperature-corrected mol volume of air (m³ mol⁻¹) as in equation 2:

$$MV_{corr} = 0.0224 \times \frac{273.15 + t}{273.15} \times \frac{P_a}{P_1} \dots \dots \dots \dots \dots \dots \dots .2$$

where t is the air temperature during measurements (˚C), P_0 represents standard atmospheric air pressure, P_1 represents air pressure during measurements. As CO_2 was analyzed from the same gas, molecular weight (MW_{CO_2-C}) of 12 g mol^{-1} was used in order to obtain mg CO_2-C m^{-2} h^{-1}. Annual cumulative N_2O and CO_2 fluxes were calculated by interpolating the N_2O and CO_2-C fluxes measured between sampling periods (Dong, Zhang, Qi, Chen & Geng, 2000).

Soil sampling and analysis

Plots were divided into five square cells. Soil cores were collected within the cell and were composited as one soil sample. Soils were sampled from plots at a depth of 0-10 cm after laying field before planting and were analyzed for pH, organic carbon, total nitrogen, exchangeable 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 determination of ammonium, nitrate and moisture content 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 ºC, Germany) while soil temperature at 10 cm depth was measured with a temperature probe inserted 10 cm below the soil surface.

Procedures used for determination of soil physical and chemical parameters are outlined in section 3.5 and 3.6. Different soil samples collected for soil moisture

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analysis were stored in and air-water tight plastic bags and transported to the laboratory for immediate analysis.

Soil physical analysis

Particle size distribution

The particle size analysis was done by the hydrometer method as outlined by Anderson and Ingram (1993). A 50 g air dry soil was weighed into a conical flask and a dispersing agent (sodium hexametaphosphate) added. After shaking using a reciprocal shaker at 400 rpm for 18 hours, the sample was transferred to 1 L sedimentation cylinder and made up to the mark with distilled water. A hydrometer was used to measure the density of the suspension of soil and water at various times. The different particles size fractions were calculated using the formula using equation 3:

% Sand = $100 - [H_1 + 0.2 (T_1 - 20) - 2]$ x 2

% Clay = $[H_2 + 0.2 (T_2 - 20) - 2]$ x 2

% Silt = $100 - (\% Sand + \% clay)$…………………………………..3

where:

W_T = total weight of air-dried soil used for analysis

H_1 = 1st hydrometer reading at 40 seconds

T_1 = 1st temperature reading at 40 seconds

H_2 = 2nd hydrometer reading at 3 hours

T_2 = 2nd temperature reading at 3 hours

− 2 = salt correction to be added to hydrometer reading

0.2 (T − 20) = temperature correction to be added to hydrometer reading, in degrees celsius.

Soil bulk density

A core sampler was driven into the soil with the aid of a mallet. Soil at both ends of the tube was trimmed and the end flushed with a straight − edged knife. The core sampler with its content was then dried in the oven at 105 °C to a constant weight. The volume of the core sampler was determined by measuring the height and radius of the core sampler. Bulk density was calculated using the formula using equation 4:

$$P_b = \frac{W_2 - W_1}{V} \dots\dots\dots\dots\dots\dots\dots\dots\dots 4$$

where:

P_b (g cm^{-3}) = dry bulk density

W_2 = weight of core cylinder + oven - dried soil

W_1 = weight of empty core cylinder

V = volume of core cylinder ($\pi r^2 h$), (π= 3.142)

r = radius of the core cylinder

h = height of the core cylinder

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Gravimetric moisture content (θm)

A moisture can with lid was oven–dried at 105 °C to a constant weight and the weight recorded (W_1). About 10 g of soil was weighed into the moisture can and the weight recorded (W_2). The can with soil and the lid was oven-dried at 105 °C for 24 hours to a constant weight (W_3). The soil moisture content was determined using equation 6.

$$\% \ \theta m = \frac{W_3 - W_1}{W_2 - W_1} \times 100 \ ....6$$

where:

θm = Gravimetric moisture content

W_1 = Weight of empty can + lid

W_2 = Weight of can + lid + fresh soil

W_3 = Weight of can + dried soil + lid

Upper limit (UL) and lower limit (LL) of available soil water, saturated hydraulic conductivity and degree of Saturation were estimated using the Decision Support System for Agro-Technology Transfer (DSSAT V 4.5, 1994) model.

Volumetric moisture content (θ$_v$)

Volumetric moisture content was calculated by using equation 5.

$$\theta v = \frac{\theta m}{Ps} \ x \ Pb ....5$$

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where

θm = Gravimetric moisture content

θ_v = Volumetric moisture content

P_b = bulk density (g cm^{-3})

P_s = particle density, with a value of 2.65 g cm^{-3}

Chemical Analysis of Soil

Determination of soil pH

A 10 g air- dried soil was weighed into a 100 ml beaker and 25 ml distilled water was added. The suspension was stirred vigorously for 20 minutes. The suspension was allowed to stand for about 30 minutes to allow the suspended clay to have settled from the suspension. The pH value was read using HT 9017 pH meter and the value recorded.

Soil Organic Carbon

Organic carbon was determined by the modified Walkley and Black procedure outlined by Nelson and Sommers (1982). Organic carbon was oxidized by potassium dichromate ($K_2Cr_2O_7$), and the reaction was facilitated by the heat generated by the addition of concentrated sulphuric acid (H_2SO_4) with 0.1667 M potassium dichromate ($K_2Cr_2O_7$) solution. The excess $Cr_2O_7^{2-}$ was determined by titrating with standard ferrous sulphate solution. The quantity of carbon oxidized was then calculated from the amount of $Cr_2O_7^{2-}$ reduced. Equations (7) and (8) gives a summary of the reactions involved.

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$$2Cr_2O_7^{2-} + 3C + 6H^+ \rightarrow 4Cr^{3+} + 3CO_2 + 8H_2O \quad \ldots\ldots\ldots\ldots\ldots 7$$

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O \ldots\ldots\ldots\ldots\ldots 8$$
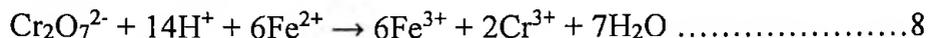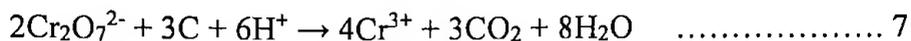
Two grams of soil sample was weighed into a 500 ml Erlenmeyer flask and 10 ml of 0.166 M $K_2Cr_2O_7$ solution added, followed by 20 ml of conc. H_2SO_4. About 200 ml of distilled water was added followed by 10 ml of 85 % orthorphosphoric acid (H_3PO_4).

The mixture was titrated with 0.5 M Ferrous Sulphate ($FeSO_4$) solution from blue-black colour to a permanent greenish colour. A blank reagent mixture was similarly treated. This was done to standardize the Ferrous Sulphate which is not a primary standard but oxidizes also gradually in the air. The percentage carbon was calculated with equation 9.

$$\% \, OC = \frac{M \times (V_{bl} - V_S) \times 0.39}{g} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 9$$

where:

M = molarity of the $FeSO_4$

V_{bl} = ml $FeSO_4$ of blank titration

V_s = ml $FeSO_4$ of soil sample titration

g = weight of soil in grams

mcf = moisture correction factor to oven dried weight (100 + moisture)/100

0.39 = 3 × 0.001 × 100 % × 1.3 where (3 is equivalent weight of C)

1.3 = a composition factor for the complete combustion of organic C.

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Total Nitrogen (N)

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 (Tel & Hegatey, 1984). Ten g of soil was weighed into a 250 ml Kjeldahl digestion flask and 10 ml of distilled water added to it. Ten millilitres of concentrated H_2SO_4 was added followed by one tablet of selenium and potassium sulphate mixture (99.9 % purity, 2-4 mm granules and was made in Equilibrium Equivalent Concentration (EEC), Electro Mechanical Brake (EMB) 45053 and 0.10 g salicylic acid.

The mixture was left to stand for 30 minutes and heated gently to convert any nitrates and nitrites into ammonium compounds. The mixture was then heated more strongly (300-350 °C) to digest the soil to a permanent clear colour. The digest was cooled and transferred to a 100 ml volumetric flask and made up to the mark with distilled water.

A 20 ml aliquot of the digest was transferred into a distillation flask and 10 ml of 40 % NaOH solution was added and steam from the tecator apparatus allowed to flow into the flask. The ammonium distilled was collected into 10 ml boric acid/ bromocresol green and methyl red indicator solution. The distillate was titrated with 0.01 M HCl solution. A blank digestion, distillation and titration were also carried out to check against traces of nitrogen in the reagents and water used. The percentage of N was estimated based on the equation 10.

$$\% \, N = \frac{(a - b) \times 1.4 \, M \times V}{s \times t} \dots \dots \dots \dots \dots \dots \dots .10$$

where:

a = ml HCl used for sample titration

b = ml HCl used for titration of blank

s = weight of soil taken for digestion in grams

M = molarity of HCl

1.4 = 1.4 10^{-3} × 100 % (14 = atomic weight of N)

V = total volume of digest

t = volume of aliquot taken for distillation

Exchangeable cations

The exchangeable base cations Ca^{2+}, Mg^{2+}, K^+ and Na^+ were extracted with 1.0 M neutral NH_4OAc solution (Black, 1965). The exchangeable acidic cations (Al^{3+} and H^+) were extracted with 1 M KCl solution as described by Page, Miller, and Keeney (1982).

After extraction, the Ca^{2+} and Mg^{2+} contents were determined using an atomic absorption spectrophotometer (AAnalyst 400, EN 55011-Class A Group 1, Perkin Elmer, Singapore) at wavelength of 422.7 nm and 285 nm, respectively and K^+ and Na^+ by flame photometer (PFP7, Jenway, Bibby Scientific Ltd, UK) at wavelengths of 766.5 nm and 589 nm, respectively. The exchangeable acidity was determined by titration of an aliquot of the KCl extract using 0.1 M NaOH and phenolphthalein indicator from a colourless solution to a permanent pink end point.

Exchangeable acidity, potassium and sodium were estimated using the equation 11 and 12, respectively.

Exchangeable acidity $(cmol_c kg^{-1}$ soil$) = \frac{V_S - V_b \times M}{g}$...................11

where:

V_b = ml of NaOH used to titrate blank

V_s = ml of NaOH used to titrate the sample extract

g = weight of air-dried soil

M = molarity of NaOH used for the titration

Cations (K and Na) were calculated with equation 12:

$$\chi = \frac{Conc. \times DF \times Ext.Vol}{y}$$ 12

where x is the amount of the cation (K or Na) in mg kg^{-1} soil, $Conc$ (mg L^{-1}) is the concentration of the cations in the solution, DF denotes the dilution factor used during measurement, and y the weight of soil sample used for the analysis.

The amount of cation (mg kg^{-1} soil) obtained was divided by the mole weight of the cation to obtain cmol$_c$ kg^{-1} soil. Similarly, Ca and Mg were calculated. The effective CEC was calculated by the summation of the basic and acidic cations.

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Available phosphorus (P)

The Bray 1 extraction solution procedure (Bray and Kurtz, 1945) was used for available P. Two grams of soil sample was extracted with 20 ml of Bray 1 solution (0.03 M NH$_4$F and 0.025 M HCl). The suspension was shaken by hand for one minute and immediately filtered through Whatman No. 42 filter paper. A standard series of 0, 1.2, 2.4, 3.6, 4.8 and 6.0 mg P L^{-1} was prepared by respectively measuring 0, 10, 20, 30, 40, 50 ml of 12.0 mg P L^{-1} into a 100 ml volumetric flask and made up to the mark with distilled water.

Phosphorus in the extract was determined on a spectrophotometer (Jenway spectrophotometer, model 7305, UK, Bibby Scientific Ltd) at a wavelength of 660 nm with blue ammonium molybdate as reducing agent. Available P was estimated using equation 13.

$$P \ (mg \ kg^{-1}) = \frac{(a-b) \times vs \times df}{g} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 13$$

where:

a = mg L^{-1} in sample extract

b = mg P L^{-1} in blank

vs = volume of extract

df = dilution factor

g = sample weight in grams

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Determination of NH_4^+-N

The Berthelot procedure as outlined by Kempers and Zweers (1986) was used. The procedure is based on the reaction in which a phenol derivative forms an azo-dye in the presence of ammonia and hypochlorite. In this method salicylic acid is used as the phenol source. The end product is an indophenol derivative, which in the presence of an alkaline medium is a greenish-blue colour, which can be measured at 660 nm wavelength on a visible wavelength range spectrophotometer. The quantity of ammonium ion or ammonia present depends on the intensity of the colour.

Working standards of 0, 5, 10, 15, 20, and 25 mg NH_4^+-N L^{-1} was prepared from a 1000 mg NH_4^+ - N L^{-1} stock standard. A solution called colour reagent 1 (R1) was prepared by dissolving 110 g salicylic acid in 10 M NaOH plus 100 ml of 0.5 % sodium nitroprusside and 5 ml of 4 % Na_2EDTA. Colour reagent 2 (R2) was prepared by weighing 0.2 g of sodium dichloroisocyanurate in 5 ml of distilled water and transferred into 200 ml volumetric flask. The solution was top up to the mark with di-sodium hydrogen phosphate ($Na_2HPO_4.12H_2O$) buffer solution of pH 12.3.

The buffer was made by dissolving 26.70 g of $Na_2HPO_4.12H_2O$ in a two litre volumetric flask and making up to the mark with distilled water after adjusting it to pH 12.3. One ml of sample and standard series were pipetted into a series of 5 ml volumetric flask and then 3 ml of R1 was added followed by 5 ml of R2 and distilled water added to the mark. These were left to stand for two hours for maximum colour development. The colour intensity of the solution was measured

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at 660 nm wavelength on spectrophotometer (Jenway spectrophotometer, model 7305, UK, Bibby Scientific Ltd). NH_4^+-N was estimated using equation 14:

$$NH_4^+\text{-N } \mu g^{-1} \text{ Soil}) = \frac{(a-b) \times V \times df}{g} \ldots\ldots\ldots\ldots\ldots\ldots..14$$

where:

a = NH_4^+-N L^{-1} of sample

b = NH_4^+-N L^{-1} blank

V = volume of extract

df = dilution factor

g = weight of soil used for the extraction

Determination of NO³⁻-N

The colorimetric method Cataldo, Haroon, Schrader and Youngs (1975) was used. Salicylic acid was reacted with the nitrite in the presence of NaOH to form a yellow colour. The intensity of the colour is a measure of the nitrite content in solution. A stock standard of 1000 mg NO_3^--N L^{-1} was prepared by dissolving 7.223 g of potassium nitrate in one litre volumetric flask with distilled water. A sub-standard solution of 50 mg NO_3^--N L^{-1} was prepared from the 1000 mg NO_3^- -N L^{-1} stock solution and from this a standard series of 0, 2, 5, and 10 mg NO_3^--N L^{-1} was prepared.

A 5 % salicylic solution was prepared by dissolving 5 g of salicylic acid in 95 ml of concentrated sulphuric acid and 4 M NaOH. One ml each of the standard

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series and sample extracts was pipetted into 25 ml volumetric flask, then 1 ml of salicylic solution was added and left to stand for 30 minutes. Ten ml of 4 M NaOH was then added and left to stand for 1 hour for full colour development. Colour intensity was measured at 410 nm wavelength on spectrophotometer (Jenway spectrophotometer, model 7305, UK, Bibby Scientific Ltd). NO_3 was estimated using equation 15:

$$\text{mg NO}_3^-\text{-N } kg^{-1} \text{ Soil} = \frac{(a - b) \times V \times df}{g} \dots\dots\dots\dots\dots\dots. 15$$

where:

a = NO_3^--N L^{-1} of sample

b = NO_3^--N L^{-1} blank

V = volume of extract

df = dilution factor

g = weight of soil used for the extraction

Measurement of N_2O, NO and NO_2 Emissions Following Dry Season Fallow

A laboratory study was conducted at the Forschungszentrum Jülich GmbH, Institut für Bio- und Geowisschenschaften (IBG), Germany between January and April 2015 to assess the effect of soil rewetting on N_2O and nitrogen oxide trace gasses (NO and NO_2). Soil samples used for this study were taken from experiment conducted in Ghana in 2013 and 2014 cropping seasons. Composite soil samples were taken from plots that had received N fertilizer and no fertilizer in the previous

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cropping seasons. Samples were taken from 0-20 cm depth 60 days after crop harvest when the soil had less than 1 % soil moisture (December 2014). Soil and air temperatures during soil sampling were between 35 and 40 °C.

Nitrous oxide flux measurement from soils after re-wetting

To study the formation of N_2O in soils previously fertilized with different N fertilizer types and quantities following six months of dry season, incubation experiments were conducted in the laboratory. Three g of soil (dry weight) was weighed into a 22-mL GC headspace vial (VWR International, Darmstadt, Germany), and the water content of the soil samples adjusted to 80 % water holding capacity (WHC) with deionized water.

Vials were closed gastight immediately afterward with butyl septa and aluminium crimp caps (VWR International). Each treatment was carried out in triplicate. The study was conducted with soil samples collected from the field 60 days after harvest and air dried. The incubation period in the gas chromatography was 7 hours, 35 minutes at room temperature (20 °C). The headspace of the sample vials was analyzed using a gas chromatograph (Clarus 580, PerkinElmer, Rodgau, Germany) equipped with an electron capture detector (ECD) for N_2O detection. The instrument was calibrated using three different standard gases with 250, 500, and 750 ppb N_2O balanced with N_2 (99.5 % purity, Linde, Munich, Germany).

Measurement of NO and NO₂ trace gases from soil after rewetting

Nitric oxide (NO) and Nitrogen dioxide (NO₂) emissions following dry season fallow were measured in the laboratory using chemoluminescence analyzer after re-wetting of soils sampled from plots 30 days after crop harvest. About 100 g of soil was weighed into a 300 ml flat bottom beaker and placed in gas tight chamber connected to a chemoluminescence analyzer. Samples were initially re-wetted with 60 % water holding capacity and then 80 % cumulatively after sample was detected to show no further NO_x emissions.

Dry soil was also used as a control. Prior to the measurement, the soil sample in the 300 ml beaker was pre-heated with infrared lamps to obtain an average soil temperature of 30 °C. It was then placed in a water-bath with temperature of 38 °C to maintain constant temperature within the chamber throughout the measurement period. Prior to the start of measurement, the analyzer was set to read the background emission and to calibrate the system. Measurement was then taken between 20 and 24 hours or until no further NO_x emissions was observed. Data was then extracted from the analyzer and NO and NO₂ emission was calculated using equation 16.

$$F_{NO} = \frac{\rho_a \times \gamma_a}{R \times T} \times t \times \beta_\alpha \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.16$$

where F_{NO} indicates the gas flux rate (NO and NO₂ nmol) of samples, pa is the pressure in the laser, $\gamma\alpha$ represents the volumetric flow rate (m³ m⁻³) in the flow-

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through chamber, in which samples were placed during gas measurement, R is the gas constant (pa m^3 k^{-1} mol^{-1}), T is temperature of the chamber during gas measurement, t is the period of gas measurement and $\beta\alpha$ is the average NO$_x$ mixing ratio. The amount of NO$_x$ in nano moles was calculated using equation 17:

$$(\mu_1-\mu_2) \times (t/1000000) \dots\dots\dots\dots 17$$

Where μ_1 and μ_2 represent amount of NO$_x$ in nmol s^{-1} for gas sample and background, respectively and t denotes period of measurement. The background gas flux rate was also calculated using equation 18:

$$y = \frac{pa \times Y}{\alpha \times T} \times t \times \beta \dots\dots\dots\dots\dots 18$$

where y represents the gas flux rate of background air, pa is chamber pressure, Y is the volumetric flow rate (m^3 m^{-1}) of background air, t was the period of measurement in seconds, β is the average NOx mixing ratio of the background air, α is the gas constant and T is the temperature in the chamber during measurement. Finally, gas flux rate per unit area and kg^{-1} dry soil were calculated using equation 19 and 20, respectively.

$$\gamma \times Vm^{-2} = \gamma m^{-2} \dots\dots\dots\dots\dots\dots 19$$

$$\gamma \times d = \gamma \ kg^{-1} \ \dots\dots\dots\dots\dots\dots\dots\dots 20$$

Where γ is gas flux rate, Vm^{-2} is volume of soil m^{-2} and γm^{-2} is the gas flux rate m^{-2}, d represents depth of soil and $\gamma \ kg^{-1}$ is the gas flux rate kg^{-1} dry soil.

Water holding capacity

Water holding capacity of the soil was determined in the laboratory by weighing 25 g soil of a thoroughly mixed sample of each of the three replicates representing each treatment plot. The soil samples were saturated with 35 ml water then were allowed to drain freely for one hour from the soil placed in a filter. It was then weighed and placed in an oven at 105 °C for 24 hours. Dry weight was recorded and the water holding capacity calculated by dividing the amount of water in the soil after free drainage by the dry weight and then multiplied by one hundred to obtain percent water holding capacity.

Soil N component analysis

Soil samples were analyzed for NH_4^+ and NO_3^- components at the Central Analytical Laboratory of Forschungszentrum Jülich. The total N content was determined using an elemental analyzer (vario EL Cube, Elementar Analysensysteme, Hanau, Germany). For measurements, 20 mg of soil, in triplicates, were analyzed. The Elemental Analyzer operates with the dynamic flash combustion of the sample. Samples are weighed in tin containers and introduced into the combustion reactor via the Thermo Scientific™ MAS™ 200R Auto-

sampler with the proper amount of oxygen. After the combustion, the gas produced are carried by Argon flow to a second reactor filled with copper, then they are swept through a H_2O trap, a GC column and finally detected by a thermal conductivity detector (TCD).

Nitrogen parameters measured included ammonium, nitrate and nitrite. Extraction was done by adding 25 ml of 1M KCl to 20 mg dry soil and shaken for one hour in a multi-shaker. It was then centrifuged at 3900 rpm for 5 minutes and then filtered using Whatman No. 42 filter paper. The filtrate was passed through 0.44 µm syringe filters after which 5 ml extract was used for the analysis. Extracts for NH_4^+ and NO_3^- were stored in a refrigerator prior to analysis in the event when analysis were to be delayed due to lack of space in the laboratory. Amount of NH_4^+ and NO_3^- were calculated as outlined in section 3.6.6.

Fate of Excess N Fertilizer in Soils

The fate of excess N fertilizer was determined in a laboratory experiment conducted at Forschungszentrum Jülich GmbH, Institut für Bio- und Geowisschenschaften (IBG-3), Germany. Soil samples used for this study were taken from the field plot experiments conducted in Akukayilli, Ghana in 2013 and 2014 cropping seasons. Soil samples were from the same plots as in the laboratory experiment for the determination of CO_2, N_2O, NO and NO_2 fluxes. Composite samples were taken from 0-20 cm depth 60 days after crop harvest when the soil had less than 1 % soil moisture. Soil and air temperature during soil sampling was between 35 and 40 ºC.

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For the determination of N_2O isotopic composition and ^{15}N isotopomer signatures, 15 g of soil that had passed through 2 mm sieve was weighed into 250 ml headspace vials (VWR International) treated with 60 and 120 kg ha^{-1} of sulphate of ammonia (SA) and urea (U) fertilizer solution and, 60-40-40 kg ha^{-1} of NPK fertilizer, respectively and incubated under gas tight conditions for 24 hours. Soil from plots that received no mineral N fertilizer was also treated with 2 ml deionized water. Five per cent of ^{15}N ammonium and ^{15}N Urea was added to treatments with sulphate of ammonia and urea fertilizer, respectively. The nitrate and ammonium composition of NPK was determined and its equivalent ^{15}N isotopes added accordingly.

After 24 h incubation time, the headspace of the vials was analyzed using an isotope ratio mass spectrometer (IRMS) (IsoPrime 100, Elementar Analysensysteme, Hanau, Germany) coupled to a pre-concentration unit (TraceGas, Elementar Analysensysteme) for online separation and purification of N_2O. With the IRMS, the mass-to-charge ratios (m/z) 44, 45, and 46 of the N_2O^+ ion and m/z 30 and 31 of the NO^+ fragment ion of N_2O were measured and used to determine the isotopologue and isotopomer signatures of N_2O (Toyoda and Yoshida, 1999). More specifically, $\delta^{15}N^{bulk}$ (i.e., the average $\delta^{15}N$ over the N_2O molecule), $\delta^{15}N^\alpha$ (i.e., $\delta^{15}N$ at the central position of the N_2O molecule), and $\delta^{18}O$ of N_2O were determined. The $\delta^{15}N$ at the terminal position of the N_2O molecule, $\delta^{15}N^\beta$, was calculated according to $\delta^{15}N^\beta = 2 \times \delta^{15}N^{bulk} - \delta^{15}N^\alpha$. The ^{15}N SP is then defined as $SP = \delta^{15}N^\alpha = \delta^{15}N^\beta$.

A correction for ^{17}O was performed, assuming a mass-dependent fractionation of ^{17}O and ^{18}O and using the calculations according to Kaiser, Rockmann and Brenninkmeijer (2003) with $^{17}R = 0.00937035 \times (^{18}R)^{0.516}$. Pure N_2O was used (99.999%, Linde, Munich, Germany) as working standard for isotope analysis, and $\delta^{15}N^{bulk}$, $\delta^{18}O$, and SP were calibrated against two reference gases (Ref 1: $\delta^{15}N^{\alpha}$: 15.70 ± 0.31‰, $\delta^{15}N^{\beta}$: -3.21 ± 0.37‰, $\delta15N^{bulk}$: 6.24 ± 0.11‰, SP: 18.92 ± 0.66‰, $\delta^{18}O$: 35.16 ± 0.35‰; Ref 2: $\delta^{15}N^{\alpha}$: 5.55 ± 0.21‰, $\delta^{15}N^{\beta}$: -12.87 ± 0.32‰, $\delta^{15}N^{bulk}$: -3.66 ± 0.13‰, SP: 18.42 ± 0.50‰, $\delta^{18}O$: 32.73 ± 0.21‰) provided by EMPA (Dübendorf, Switzerland) and as described in Mohn et al. (2014). Analytical precision, expressed as standard deviation, was 0.1‰, 0.2‰, and 0.2‰ for $\delta^{15}N$, $\delta^{18}O$, and SP, respectively. Isotope values are reported in the delta notation, with $\delta = (R_{sample}/R_{standard} - 1) \times 1000$, where R_{sample} and $R_{standard}$ are the ratio of heavy to light isotope ($^{15}N/^{14}N$ or $^{18}O/^{16}O$) in the sample and an international standard, i.e., atmospheric N_2 for nitrogen and Vienna Standard Mean Ocean Water (V-SMOW) for oxygen, respectively.

Modeling Greenhouse Gas Emissions with DNDC Model

A modified process-based biogeochemistry model, Denitrification-Decomposition Denitrification Decomposition (DNDC) model (Deng, et al., 2011) was used to predict the impact of N fertilizer source and rate on greenhouse gas emission with emphasis on N_2O. Compared to Forest-DNDC-Tropica which is regionalized for different areas of the world, DNDC can simulate the processes

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responsible for production, consumption and transport of nitrous oxide (N_2O) on farm scale.

Furthermore, it consists of six sub-models (soil climate, crop growth, decomposition, nitrification, denitrification, and fermentation) which interact and include fundamental factors and reactions, that integrate C and N cycles into a computing system. DNDC has been validated against numerous datasets observed worldwide has been independently tested by researchers in many countries and applied for their national C sequestration and N_2O inventory studies.

DeNitrification DeComposition model calibration and validation

Field data obtained from the 2013 field experiment at Akukayilli was used to calibrate and then independently validated the DNDC model. Calibration was performed to set the model input for *omankwa* maize crop parameters to ensure that the modeled crop growth had correct effects on the soil, climate and C and N dynamics in the Guinea Savanna agro-ecological zone of Ghana. No internal parameters in DNDC were calibrated leaving the biogeochemical processes embedded in DNDC unchanged.

Information including latitude of the experimental site, 2013 climate data (rainfall and temperature), soil properties (soil texture, bulk density, pH, soil organic carbon, field capacity, wilting point, clay fraction, saturation, conductivity) for top layer (<10 cm), maize variety *omankwa*'s planting/harvest dates, maximum yield, biomass partitions and C/N ratio, thermal degree days to maturity, water requirement, N fixation rate were collected and used for the validation. Again

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observed field management practices including tillage, fertilization were considered in the validation. When some of the required input information is missing in the DNDC, default data are used. This is characteristically the case for some of the soil properties such as field capacity, wilting point, clay fraction, saturation conductivity, and for the crop parameters such as biomass partitions and C/N ratio, water requirement and N fixation rate. Measured data used for the model calibration and validation include the crop phenology and yield, crop biomass, soil temperature, moisture and pH. Measured fluxes of CO_2 and N_2O from the soil-plant system in the 2013 growing season were also used.

The impact of different N fertilizer application rate and source on global warming potential was determined after model was calibrated and validated. Finally, the model was used to determine the effect of soil depth, N fertilizer application rate and source on nitrification and denitrification.

Data Analysis

Carbon dioxide and N_2O fluxes obtained from field experiment as well as delta N values from laboratory experiment were subjected to Analysis of Variance (ANOVA) using GenStat 9th edition. Igor Pro was used to analyze and plot graphs of N_2O and NOx results obtained from chemoluminescence analyzer. Means obtained was again subjected to ANOVA using GenStat 9th edition. Means comparisons were performed using Duncan's multiple range test and were separated using Least Significant Difference (LSD). Apart from course of NOx data all graphs were plotted using Sigma plot.

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CHAPTER FOUR

RESULTS AND DISCUSSION

Results obtained from the two years' field experiments are presented and discussed in this chapter. This chapter also presents and discusses results of the laboratory experiments conducted to determine the effect of rewetting on NOx emissions and the effect of excess N fertilization on N_2O emissions using isotopomer. Finally, the chapter concludes with a presentation and discussion on results of calibration, validation and simulation of the effect of N fertilization on greenhouse gas emissions using DNDC model.

Soil Physical and Chemical Properties

The initial soil physical and chemical properties of the experimental site are shown in Table 1 and 2, respectively. The soil is characterized by sandy loam texture, moderately drained with a bulk density of 1.3 g cm^{-3} (Table 1). These physical attributes would allow good air-moisture relationship that is conducive to easy root development, crop establishment and growth. The soil water properties were determined to access drainage and moisture conditions before imposing fertilizer treatments.

The soil physical properties of the experimental site 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 Bouwman, Boumans and Batjes (2002) showed that saturated water content and drained upper limit of available water influenced N_2O and CO_2 fluxes. Mean amount of stones determined

from a composite sample was 3 % ± 0.02 (Table 1). Again mean lower limit of available soil water, drained upper limit and saturation were 0.04 ± 0.01, 0.17± 0.01 and 0.46 ± 0.01 mm^3 mm^{-3} respectively (Table 1).

Similarly, soil chemical properties were analyzed before implementation of the experimental treatments. The results of chemical analysis (Table 2) 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 2). This is, however, expected to have a negative effect on the N_2O fluxes. Soil acidity can have a marked influence on denitrification since many of the bacteria responsible for denitrification are sensitive to low pH values (Tisdale, Nelson, Beatour, & Havlin, 1993). The results indicate that the soil at the experimental site is characterized by low inherent fertility typical of the West African Savannas.

The results 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$_c$ kg^{-1} soil in 2013 and 2014, respectively. This is consistent with characteristics of soils in northern Ghana as described by Benneh, Agyapong and Allotey (1990). The low organic carbon content suggests low CO_2 emissions. Furthermore, the low organic carbon and cation exchange capacity coupled with the low clay content point to the poor buffering capacity of the soil (Table 1).

Finally, the total N, available P, except exchangeable K are all below the critical crop nutrient required levels of 0.15 % N, 8.5 mg kg^{-1} P and 0.16 cmol$_c$ kg^{-1} K (Agboola & Ayodele, 1985). Again, the low clay content found in the top soil is an indicative of a typical Luvisols. Maximizing crop production on these soils will require integrated nutrient management comprising application of inorganic and organic fertilizers.

Table 1- *Physical Properties of Ferric Luvisols at Experimental Site (0-20 cm)*

Properties	Mean	Standard deviation
Stones (%)	3.42	± 0.02
Bulk density (g m^{-3})	1.31	± 0.02
Lower limit (mm^3 mm^{-3}) (SLL)	0.04	± 0.01
Upper limit (mm^3 mm^{-3}) (SDUL)	0.17	± 0.01
Upper limit, saturated (mm^3 mm^{-3}) (SSAT)	0.46	± 0.01
Sand (%)	64.89	± 3.65
Silt (%)	34.34	± 4.13
Clay (%)	0.77	± 4.54
Texture	Sandy Loam	

Table 2- *Mean Chemical Properties of Ferric Luvisols at the Experimental Site*

Properties	2013	Standard Deviation	2014	Standard Deviation
pH (1:2.5 water)	5.18	± 0.46	5.28	± 0.09
Organic Carbon (%)	0.57	± 0.04	0.59	± 0.02
Available P, Bray 1 (mg kg^{-1} soil)	5.86	± 1.36	6.86	± 0.88
Total nitrogen (%)	0.05	± 0.02	0.04	± 0.02
Al+H (cmol$_c$ kg^{-1} soil)	0.19	± 0.03	0.17	± 0.03
Ca (cmol$_c$ kg^{-1} soil)	1.97	± 0.11	1.87	± 0.09
Mg (cmol$_c$ kg^{-1} soil)	1.16	± 0.12	1.13	± 0.06
K (cmol$_c$ kg^{-1} soil)	0.54	± 0.08	0.41	± 0.06
Exchangeable Bases (cmol$_c$ kg^{-1} soil)	3.67	± 0.10	3.41	± 0.11
ECEC (cmol$_c$ kg^{-1} soil)	3.87	± 0.10	3.59	± 0.12
Base saturation (%)	94.81	± 0.59	95.59	±0.90

Climatic Elements 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 Figures 1 and 2, respectively.

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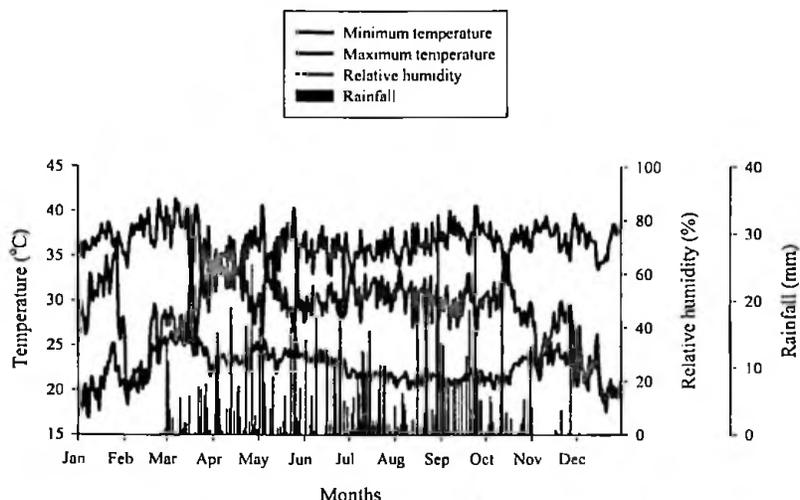
Figure 1: Daily maximum and minimum air temperatures, daily relative humidity and daily rainfall recorded in year 2013
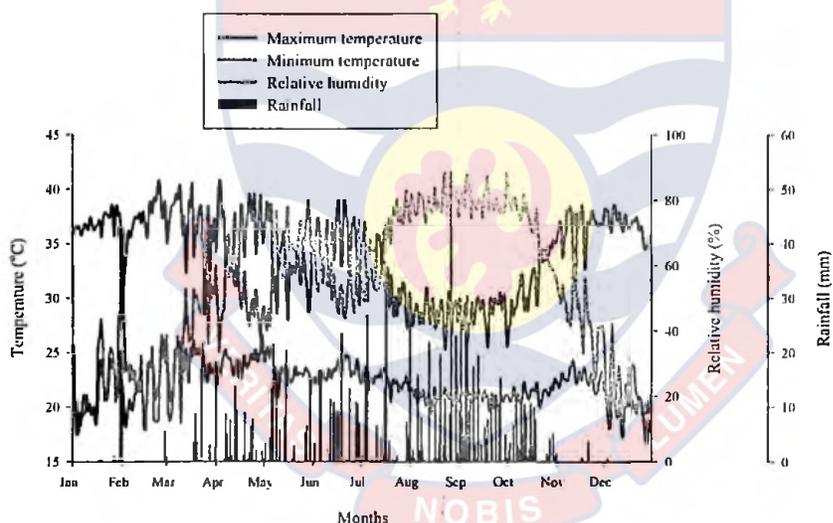
Figure 2: Daily maximum and minimum air temperatures, daily relative humidity and daily rainfall recorded in year 2014

Temperature

An annual average minimum and maximum air temperatures of 24 and 38 °C were recorded in both 2013 and 2014, respectively. Temperatures were, low in January and December. Highest temperatures were observed between February and late

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April prior to the beginning of the growing season in each year. Average minimum and maximum temperatures recorded during the 2013 growing seasons were 22 and 33 °C. Similar data were also recorded during the 2014 growing season. Average minimum and maximum temperatures were 21 and 32 °C, respectively.

Relative humidity

Relative humidity followed a similar pattern. Relative humidity was 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. 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 increase in daytime temperatures and reduced rainfall.

Rainfall

The rainfall pattern observed in 2013 was not different from 2014, although higher rainfall was recorded in 2014. Rainfall values recorded were 964 and 1168 mm for 2013 and 2014, respectively. There was an early start of rains in 2014 (Figure 2). 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. The total annual rainfall for the two years, rainfall values recorded during the 2013 and 2014 growing seasons were 601 and 862 mm, respectively. This indicates that 62

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and 73 % of the total annual rainfall occurred during the growing season between June and November in 2013 and 2014, respectively.

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 Figures 3 – 6 for both years. Minimum soil surface temperature observed during 2013 was 24 °C, with 33 °C as the maximum temperature. This occurred in late August and early September (Figure 3).
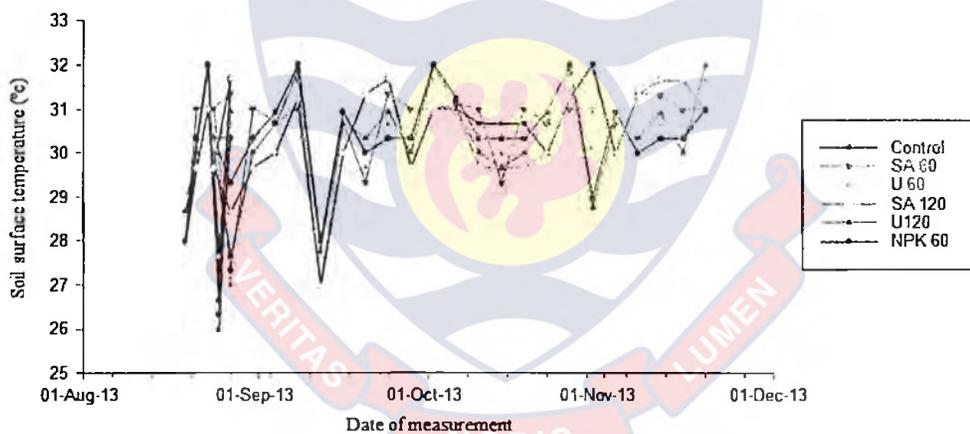
Figure 3: Soil surface temperature measured in 2013 growing season

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.

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Soil surface temperature stabilized at an average of 32 °C from end of October in year 2013 (Figure 3). Plots that received 120 kg N ha⁻¹ y⁻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 (Figure 4).
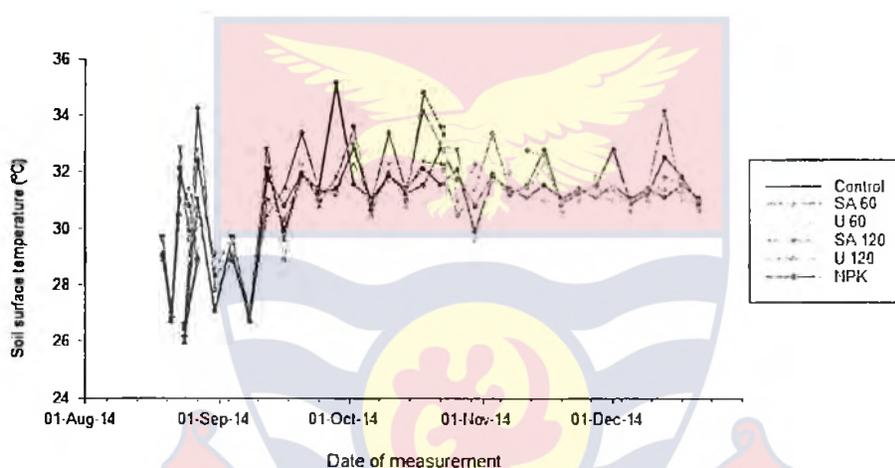
Figure 4: Soil surface temperature measured in 2014 growing season

In year 2014, plots that were treated with 60 kg N ha⁻¹ y⁻¹ showed a decline in soil surface temperature from September onwards. However, as recorded in 2013, the trend was not different from the other treatments. Measurement of soil surface temperature day(s) after heavy rainfall were however, affected.

Soil temperature measured at 10 cm depth showed similar trends in surface temperature. Plots that received 120 kg N ha⁻¹y⁻¹ had the lowest temperature from September to December in 2013 (Figure 5), although it was not statistically

different (p > 0.05) from the other plots. Plots that received 60 N kg ha^{-1} y^{-1} urea had 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 (Figure 6), respectively, could be attributed to higher biomass establishment that provided lush canopy protecting the soil surface from direct heating. These results, however, suggest that nitrification and denitrification have dominated N loss processes when temperatures were between 20 and 30 °C with adequate soil moisture in most periods of the growing season.
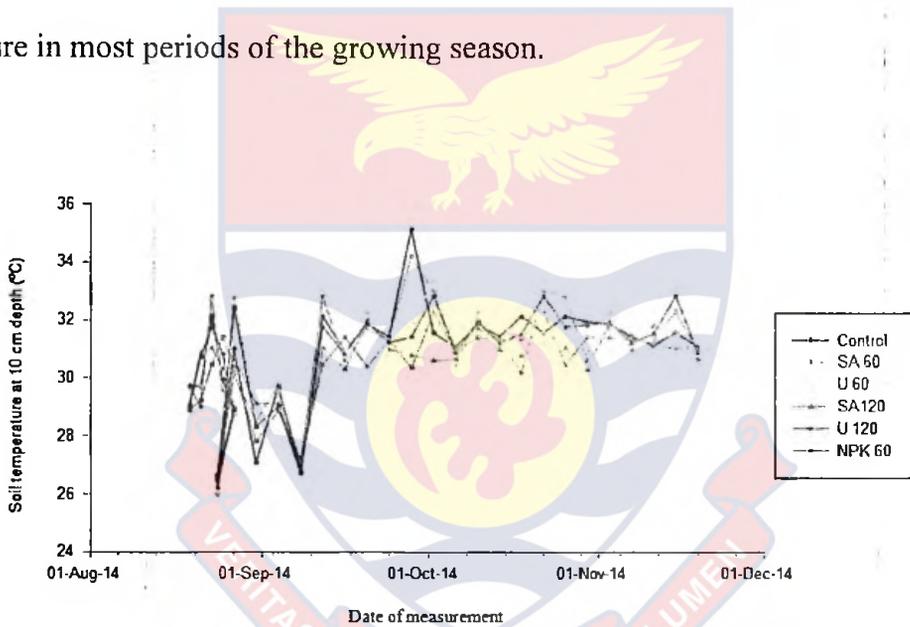
Figure 5: Soil temperature at 10 cm depth measured in 2013 growing season
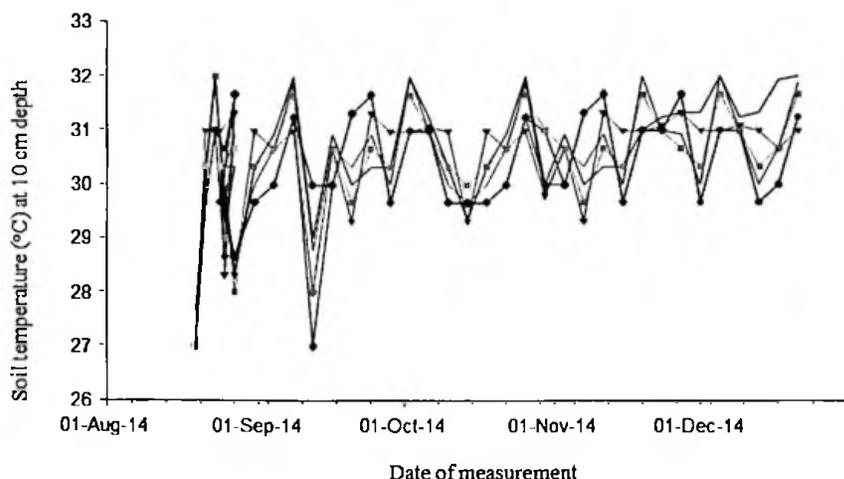
Figure 6: Soil temperature at 10 cm depth measured in 2014 growing season

Soil Moisture Properties

Soil moisture is the most critical environmental factor for the occurrence of aerobic and anaerobic conditions. Denitrification takes place under anaerobic conditions whereas nitrification occurs under aerobic conditions. Under anaerobic conditions, oxygen is depleted and therefore microbes use NO_3^- as an electron acceptor in the absence of O_2 leading to the formation of N_2O gas. Several factors are responsible for exclusion of oxygen from the soil, prominent among them is soil moisture. Different parameters are used to assess the oxygen-moisture content in the soil. For this experiment water filled pore space (WFPS) and volumetric water content (VWC) were used.

Results of water filled porosity measured during gas sampling in 2013 and 2014 are presented in Figures 7 and 8, respectively.

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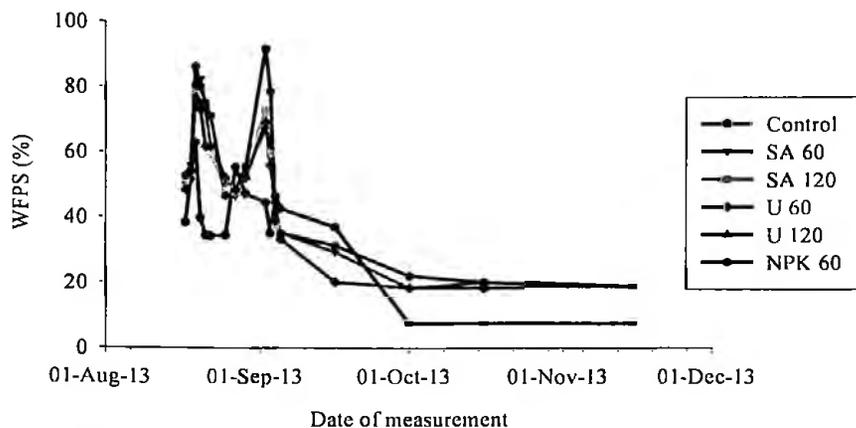
Figure 7: Water filled pore space measured in 2013 growing season
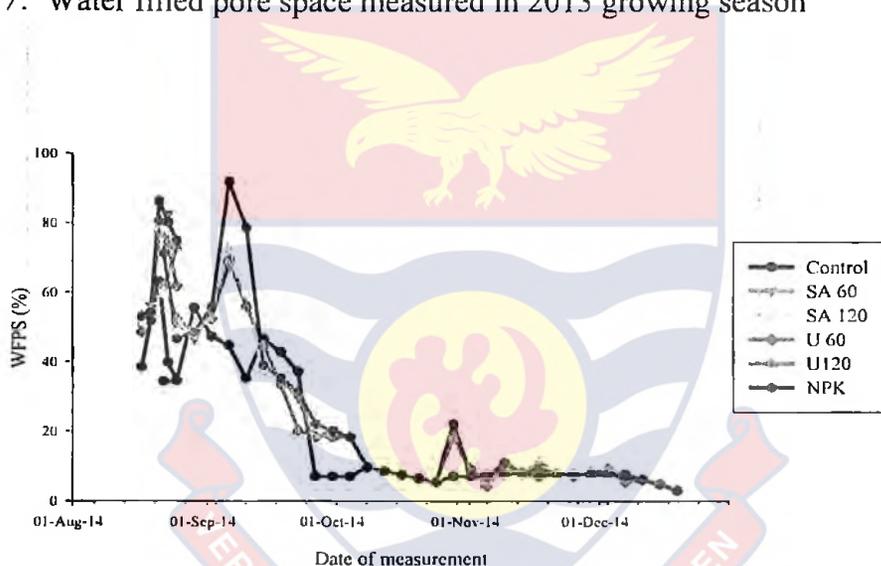
Figure 8: Water filled pore space measured in 2014 growing season

Mean maximum WFPS of 90 % occurred on plots that received NPK 60-40-40 kg ha^{-1} y^{-1} between August and September 2013 (Figure 7). In decreasing order, the WFPS were SA 120 > U 120 > U 60 > SA 60 kg N ha^{-1} y^{-1} in that order. On the contrary, control plots recorded low WFPS at the same period. The results showed that WFPS from plots of NPK 60-40-40 and SA 120 were higher than from plots that received no mineral N fertilizer but were not different from each other as well as the other plots.

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Water filled pore space showed a similar pattern in 2014, but only plots of NPK 60-40-40 kg ha^{-1} y^{-1} were greater than values obtained from the control plots. In both years, the control plots consistently showed lower WFPS except towards the end of September when the U 120 plots had the lowest WFPS. This result indicated that WFPS was high in middle of August and peaked in September where rainfall was also high. It declined with decreasing rainfall towards the end of the year. The low WFPS recorded on the control plots could be attributed to higher evapotranspiration throughout the growing season.

The results further imply that application of N fertilizer affected WFPS by enhancing conditions that promoted the formation of denser crop canopy, and more roots that possibly provided larger pore space for water infiltration and retention and hence reduced runoff (Maidl & Fischbeck, 1988).

The results of VWC measurement during gas sampling days are presented in Figures 9 and 10 for 2013 and 2014, respectively. The results showed a similar pattern to that of the WFPS in both years. The controlled plots exhibited the lowest VWC in most cases between August and early September in both years. Mean maximum VWC of 0.20 mm^3 mm^{-3} was recorded on plots treated with NPK 60-40-40 in 2013. This was, followed by plots where SA 120, U 120, U 60 and SA 60 were applied (Figure 9).
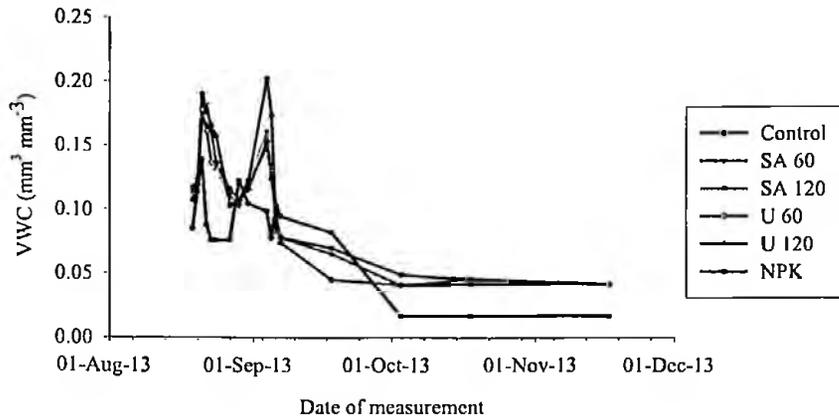
Figure 9: Volumetric water content measured in 2013 growing season
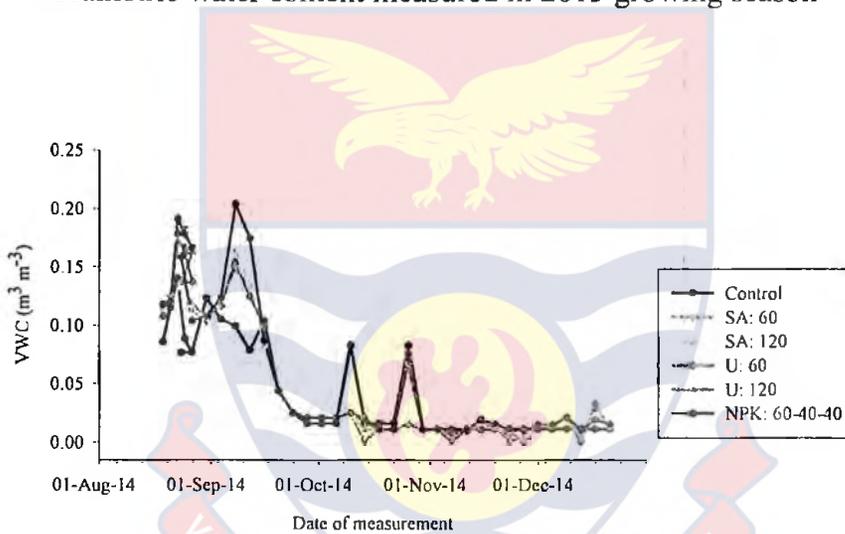
Figure 10: Volumetric water content measured in 2014 growing season

Although application of NPK 60-40-40 consistently produced the highest VWC through most part of the study period compared to the controlled neither the N source nor increasing rate of application significantly increased the VWC. Although there were not differences in VWC among the N fertilized plots for both WFPS and VWC, the results seemed enough to enhance soil-crop processes including fertilizer dissolution and transport through plant tissues, nitrification and

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denitrification that are affected by the presence of soil moisture. Presumably, high evaporation from control plots might have accounted for the low VWC recorded in both years. Crops on these plots showed stunted and poor growth with poor canopy throughout the growing season thereby exposing the soil to direct heat and further enhancing evaporation. Furthermore, with declined WFPS of soil from the control plots, the low VWC could be attributed to increased runoff.

Ammonium (NH_4^+-N) and Nitrate (NO_3^--N) Losses

The concentrations of NH_4^+-N and NO_3^--N determined during gas sampling days are presented in Figures 11 and 12 for 2013 and 2014, respectively. In 2013, the highest values of NH_4^+-N were found in the soil treated with U 60, followed by SA 60, U 120 and SA 120 and NPK 60-40-40 in decreasing order. Plots that received no N fertilizer had the lowest ammonium concentration in the soil throughout the sampling period (Figure 11).
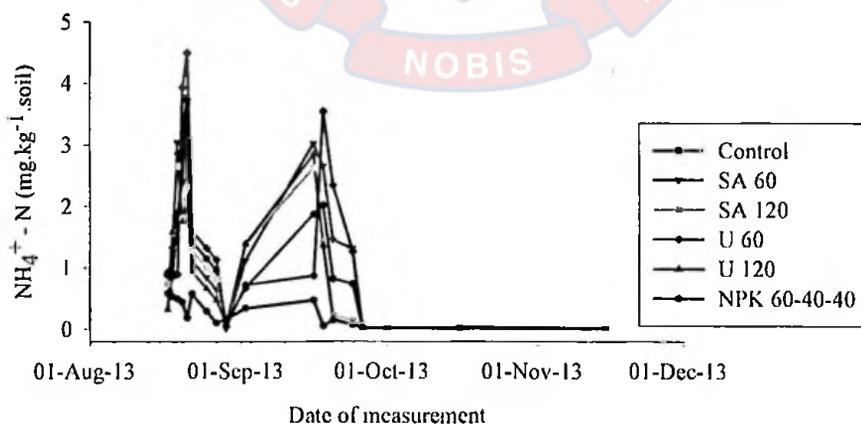
Figure 11: Ammonium N content of the soil in 2013 growing season

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Although plots that were treated with N fertilizer showed higher amounts of NH_4^+-N compared with plots without N fertilization, only plots where U 60 and SA 60 were applied yielded consistently higher values than the control plots. Similarly, in 2014, the NH_4^+-N content of plots treated with SA 120, U 60 and SA 60 were all consistently higher than from the control plots (Figure 12).

Figure 12: Ammonium N content of the soil in 2014 growing season

The same treatments mentioned above were significantly superior to plots that received NPK 60-40-40 in the release of NH_4^+-N but not from the other plots. In both years, NH_4^+-N was highest from two to twelve days after fertilizer application (12th and 14th August for basal fertilizer application, 28th and 30th August for top dressing in 2013 and 2014, respectively), after which the concentration declined. This observation suggests that N mineralization was influenced by the application of the N fertilizer as a substrate. The N application might have narrowed the C:N ratio of the soil environment that favoured the release of NH_4^+-N. However, with the decline in N content as a result of possible

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immobilization, volatilization, leaching and other N losses, caused by plant uptake, higher environmental temperatures and higher rainfall intensities between August and October, ammonium concentration constantly decreased from October till the end of the year. The decrease in soil moisture content from the end of October (See Figures 7, 8, 9 and 10) coupled with increased soil temperature (See Figures 3, 4, 5 and 6) that could have led to a reduction in microbial activities involved in mineralization. This might have resulted in decline of NH_4^+-N concentration in the soil between October and December in both years.

The results of NO_3^--N determined during gas sampling days in 2013 and 2014 are presented in Figures 13 and 14, respectively.
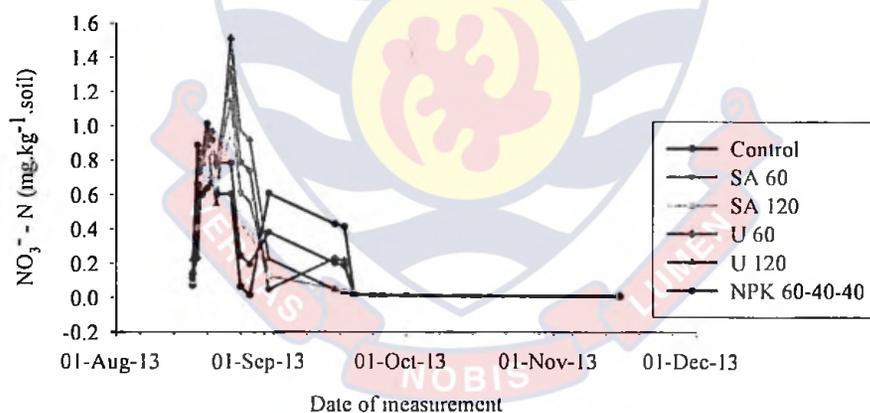
Figure 13: Nitrate content of the soil in 2013 growing season

In 2013 a maximum of 1.5 mg kg^{-1} soil NO_3^--N was measured for U 120 in late August, followed by plots treated with U 60, SA 60, and SA 120 in decreasing order over the same period of time. The results further indicated that only the U 60 plots produced consistently higher amounts of NO_3^--N than the amount obtained from

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the control plots. This did not present a clear pattern of nitrate concentration in the soil with respect to the amount of N fertilizer applied. The observation could be explained by poor N mineralization as a result of ten days drought that followed N fertilizer application

In 2014 the results further showed that U 120 plots contained the maximum amount of NO_3^- -N content (1.5 mg kg^{-1} soil) in the soil following the application of N in August, followed by plots of U 60, SA 60, SA 120 and NPK 60-40-40 in descending order (Figure 14).
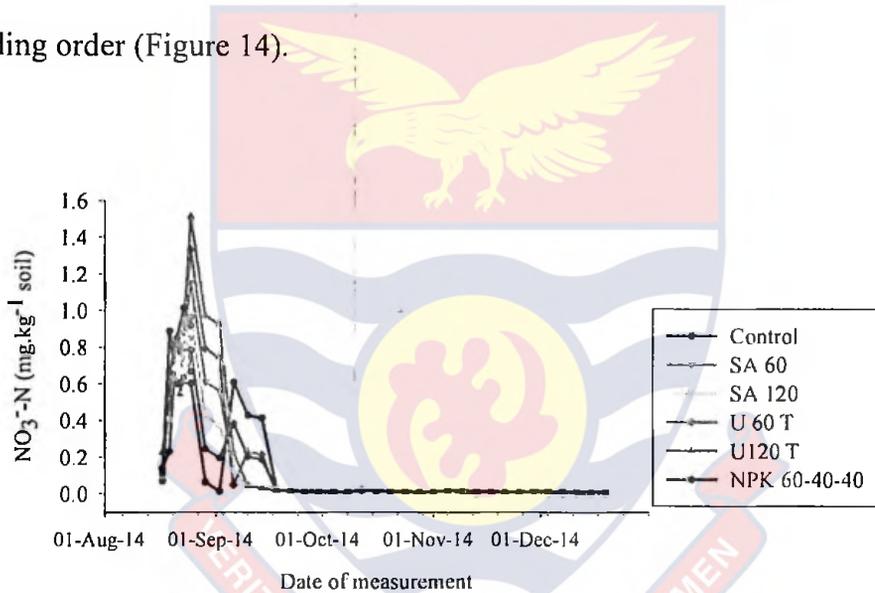
Figure 14: Nitrate content of the soil in 2014 growing season

Nitrate content of plots that received N fertilizer contained higher NO_3^--N than plots that received no N fertilizer. The results further indicated that plots of U 120 had a significantly higher NO_3^- N content than the other plots except for U 60. Furthermore, NO_3^--N content of SA 120 was also not significantly different. However, in both years, ANOVA showed that ammonium and nitrate N

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concentration from fertilized plots were only significantly different from the control plots between 2 and 10 days after fertilization (Appendix 3).

The two year results suggest that climatic conditions such as temperature and moisture as well as mineral N fertilizer application may have greatly affected the process of nitrification. Since N is required by plants in the large quantities and is most frequently the limiting factor in crop productivity in soils of northern Ghana, proper management of N input is important to maintain soil NO_3^--N before and immediately after fertilizer application. It is therefore, important for farmers to direct attention towards tillage operations that maintain and enhance efficient use of applied N in the soil, than to the climatic factors, which cannot entirely be controlled by farming operations.

Soil CO_2 Flux from Fertilized and Unfertilized Plots

The CO_2-C fluxes measured in 2013 and 2014 over data collection period are presented in Figures 15 and 16, respectively. In 2013, plots of NPK 60-40-40, SA 120 and U 60 had a higher CO_2 flux than the plots that received no N fertilizer until mid of October (Figure 15).
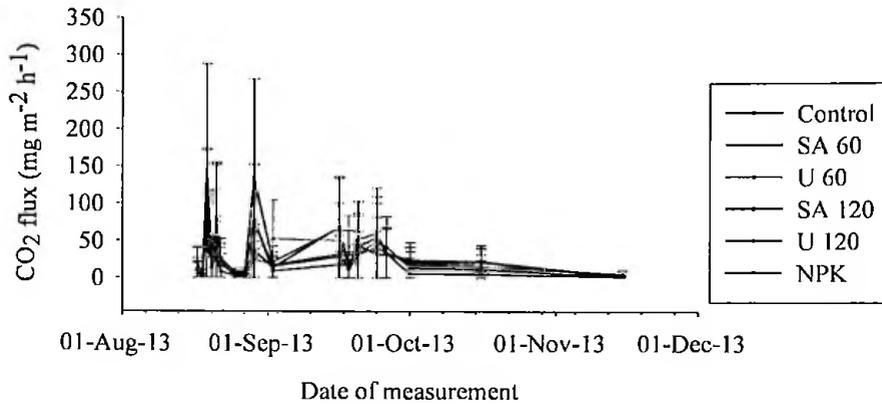
Figure 15: CO_2 flux (mg m^{-2} h^{-1}) in the 2013 growing season (error bars represent standard deviation)

Thereafter CO_2 fluxes from N fertilized plots were lower than from the control plots, except, plots that received SA 120 and U 60. Mean CO_2 fluxes recorded ranged between 1 and 140 mg m^{-2} h^{-1}. Maximum CO_2 (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. These were significantly higher (p < 0.001; LSD = 18.730) than emissions from SA 60 and NPK 60-40-40 as well as control plots throughout 2013. In 2014, CO_2 emissions followed similar trend as 2013. However, in 2014, higher CO_2 fluxes occurred later between September and October, compared to year 2013 (Figure 16).

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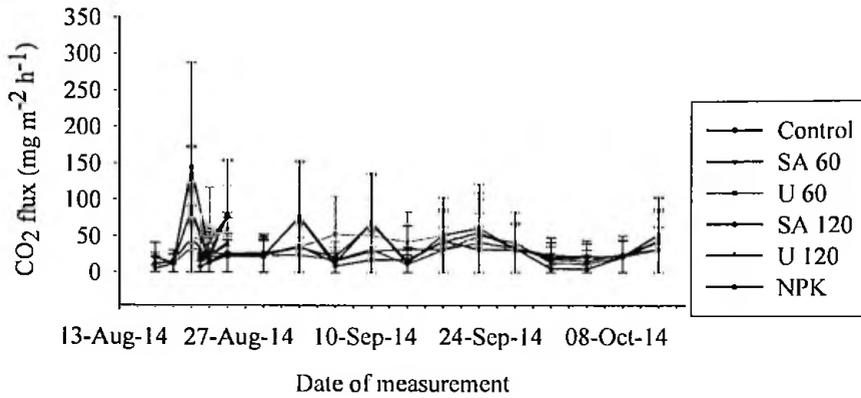
Figure 16: CO_2 flux (mg m^{-2} h^{-1}) in the 2014 growing season (error bars represent standard deviation)

Furthermore, the peaks of CO_2 fluxes occurred in September on the control plots. These results are in agreement with findings of Al-Kaisi, Kruse and Sawyer (2008) who reported higher CO_2 fluxes without mineral N fertilizer under tropical conditions.

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 CO_2 flux after N fertilization could be attributed to higher CO_2 sequestration from the atmosphere by the plants to meet their photosynthetic needs. This indicates that CO_2 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 CO_2 release because it was later consumed in the process of photosynthesis by the plants. This shows that CO_2 uptake could

potentially provide a strong negative feedback on changing CO_2 concentrations in the atmosphere by adopting agronomic practices that enhance higher biomass production.

The CO_2 contained in plant biomass through photosynthesis can be stored in the soil as organic carbon by converting plant residue into soil organic matter after the residue is returned to the soil. Management practices, such as tillage also increased CO_2 emission from the soil by disrupting soil aggregates, increasing aeration, incorporating plant residue, and oxidizing soil organic C (Reicoscky & Lindstrom, 1993); (Beare, Cabrera, Hendrix & Coleman, 1994); (Jastrow, Boulton, & Miller, 1996). Respiration by plant roots and soil micro-flora and fauna also contribute a major portion of CO_2 emission from the soil (Rochette & Flanagan (1997); (Curtin, Wang, Selles, McConkey, & Campbell, 2000).

Also, the marginal increase in CO_2 emission could be attributed to increase 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 CO_2 flux. However, other factors such as pH of the soil might have influenced the decline of CO_2 with increased application of N fertilizer to a certain threshold. The results also indicate that microbial respiration, may have significantly enhanced when 120 kg ha^{-1}y^{-1} sulphate of ammonia was applied, giving rise to an increase in the soil CO_2 flux (Rochette & Flanagan, 1997); (Curtin et al., 2000). On the contrary application of 120 kg ha^{-1} y^{-1} urea resulted in CO_2

fluxes that were not significantly different from applying the lower rates of the N fertilizer and control. This observation might be attributed to high N volatilization from urea compared with sulphate of ammonia.

The cumulative CO_2 fluxes for the growing seasons of 2013 and 2014 are presented in Figures 17 and 18, respectively. The cumulative flux illustrates total CO_2 flux emitted since the beginning of the growing season taking into account the time interval between measurements. Cumulative CO_2 fluxes for year 2013 ranged between 0.2 and 0.4 kg C m^{-2} (Figure 17).
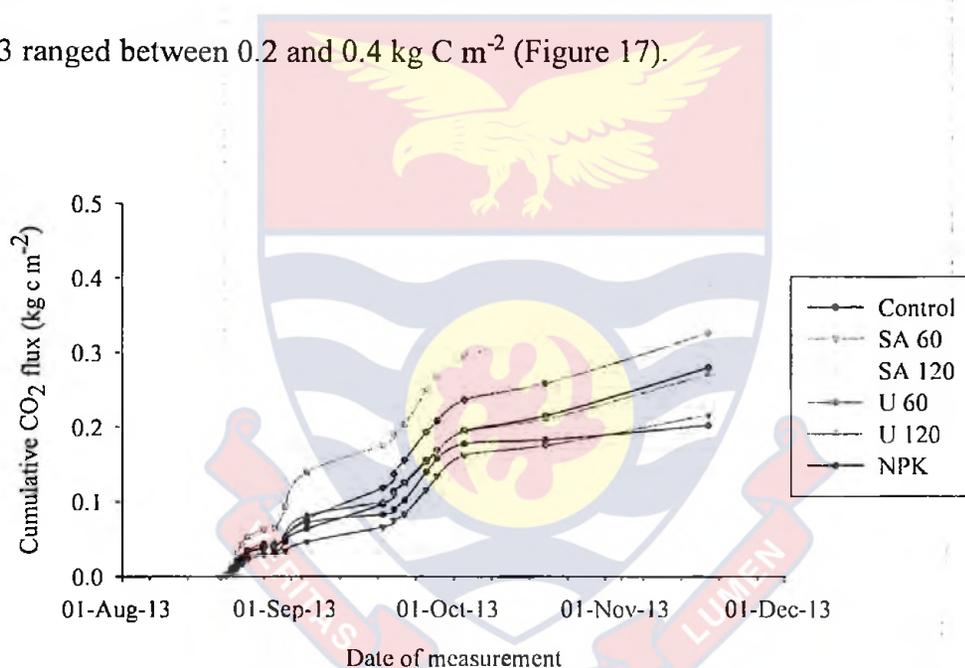
Figure 17: Cumulative CO_2 flux (kg C m^{-2}) in the 2013 growing season

Cumulative CO_2 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 CO_2 fluxes that were higher than SA 60, NPK 60-40-40 as well as control plots. However, the latter was not significantly different from the application of 60 kg ha^{-1}y^{-1} as urea.

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Cumulative CO_2 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 CO_2 flux ranged between 0.15 and 0.25 kg C m^{-2} (Figure 18). Similar to 2013, the cumulative CO_2 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.
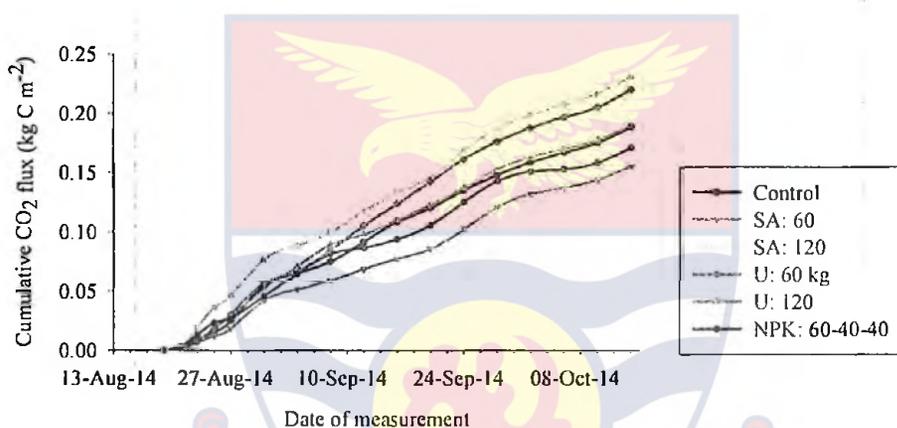
Figure 18: Cumulative CO_2 flux (kg C m^{-2}) in the 2014 growing season

The results further showed that cumulative CO_2 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 CO_2 uptake that resulted in the decline in CO_2-C emission. Furthermore, the differences in gas flux that existed between fertilized and unfertilized plots as well as the time of measurements showed that a significant amount of CO_2 flux could have been lost when fluxes were taken in 0, 20, 40 and 60 minutes.

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Quantification of Soil N₂O Flux from Fertilized and Unfertilized Plots

Nitrous oxide fluxes measured in 2013 and 2014 growing seasons are presented in Figures 19 and 20, respectively. In year 2013, mean N_2O fluxes measured throughout the growing season ranged between 0.1 and 17 μg m^{-2} h^{-1}. (Figure 19).
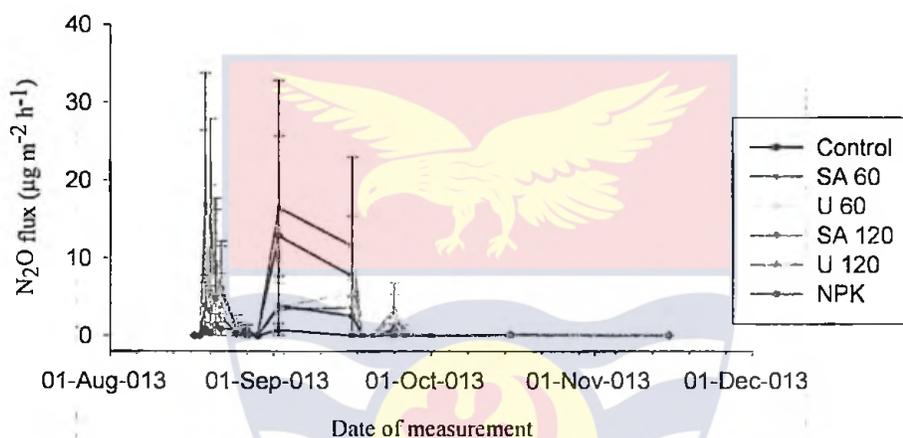
Figure 19: N₂O flux (μg N₂O-N m^{-2} h^{-1}) in the 2013 growing season (error bars represent standard deviation)

Higher N_2O fluxes was obtained between two and ten days after fertilizer application. However, N_2O fluxes measured after topdressing were found to be lower than fluxes measured after basal fertilizer application, which was done approximately two weeks after planting. Maximum N_2O flux of 17 μg m^{-2} h^{-1} was observed from plots that received 120 kg N ha^{-1} y^{-1} urea between two and ten days after fertilizer application in 2013. This was followed by SA 120, U 60 and SA 60 kg N $ha^{-1}y^{-1}$. Meanwhile, plots that received no N fertilizer consistently showed low N_2O fluxes throughout the growing season of 2013.

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Mean N_2O flux at U 120 kg N $ha^{-1}y^{-1}$ was significantly higher (p < 0.001) than SA 60 kg and NPK 60-40-40, as well as plots that received no N fertilizer, but was not significantly different (p > 0.05) from plots of SA 120. Also, N_2O fluxes from plots of SA 60 and U 60 was found not significantly different (p > 0.05) from each other as well as flux from plots that received no N fertilizer.

Nitrous oxide fluxes in 2014 showed a similar pattern as in year 2013. Mean maximum N_2O flux of 17 ± 2.1 and 13 ± 2.2 μg m^2 h^{-1} were observed at U 120 and SA 120 kg N ha^{-1} y^{-1} (Figure 20).
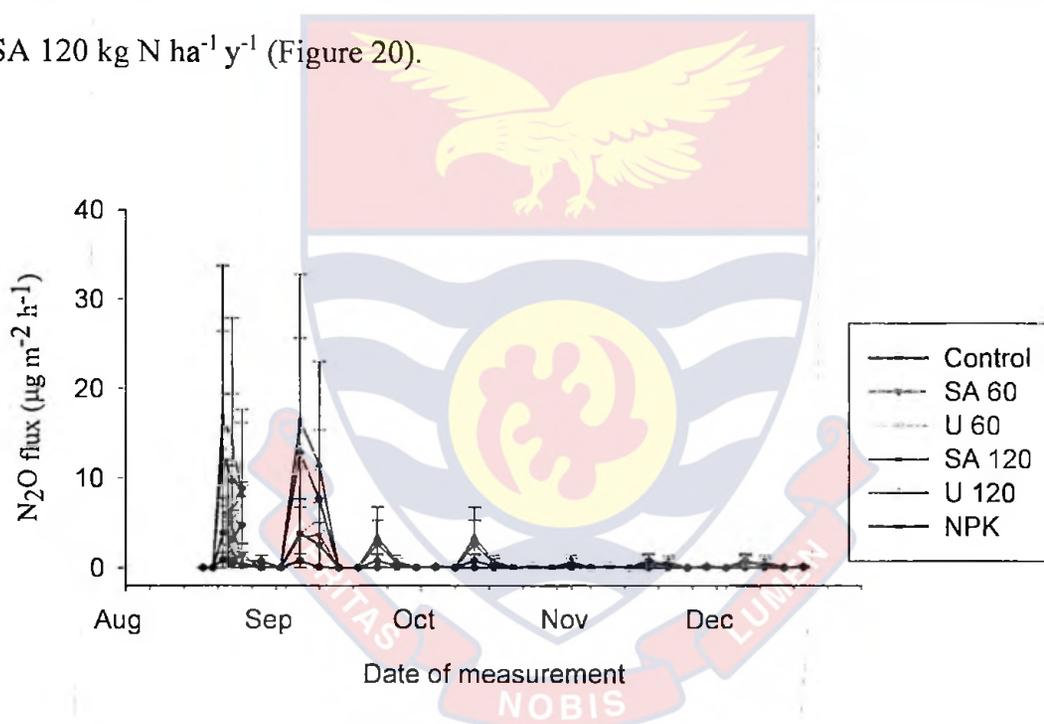
Figure 20: N_2O flux (μg N_2O-N m^{-2} h^{-1}) in the 2014 growing season

In year 2014 plots that received no N fertilizer consistently showed low N_2O flux throughout the measurement period in the growing season with N_2O fluxes of less than 1 μg m^2 h^{-1}. Although fluxes measured in 2014 showed a similar trend as the previous year, statistical analysis showed highly significant differences among

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fluxes measured from different plots. Mean N_2O flux measured from U 120 was found to be significantly higher ($p < 0.001$) than from SA 60, SA 120 and U 60. It was also found to be significantly different from plots that NPK 60-40-40 kg N ha^{-1}y^{-1} as well as plots that received no N fertilizer. Also, mean fluxes measured from plots that received NPK 60-40-40 kg N ha^{-1}y^{-1} were significantly higher than the control plot. However, flux measured from the latter was found not to be significantly different ($p > 0.05$) from U 60 and SA 120. Similarly, mean N_2O flux of SA 120 was also found to be significantly higher ($p < 0.001$) than SA 60 as well as plots that received no fertilizer but significantly not different ($p > 0.05$) from U 60.

N_2O in both years remained relatively high between two and ten days after fertilizer application. However, comparatively higher fluxes were also recorded in the last week of October in 2013 as well as middle of October in 2014 following the last heavy rains of the growing season in both years. Also, in both years relatively high N_2O fluxes were found immediately following heavy rains. This results are consistent with findings of Dick, Cheng and Wang (2000) who reported N_2O fluxes of up to 2000 µg m^{-2} h^{-1} after heavy rainfall in Ugandan soils. In both years of flux measurements, application of N at 120 kg ha^{-1} y^{-1} led to an increase in N_2O fluxes. The application of urea stimulated N_2O fluxes more than sulphate of ammonia, even though in some cases this was not significant for application at a rate of 60 kg ha^{-1} y^{-1}. The results imply that the different levels and forms of N addition to soil had strong effects on N_2O emissions in the period of August and December in each year in the study area. The significant N_2O emissions within 2-

10 days after fertilizer application is consistent with findings of Liu, Mosier, Halvorson and Zhang (2005 and 2006) and Schils et al. (2008) who reported highest N_2O fluxes occurring in the first or second week after application of N fertilizers to the soil. This demonstrates that N_2O production was strongly limited by the availability of inorganic N substrate during the growing seasons. The short surges in N_2O emission in this experiment after each N fertilizer application are characteristic and consistent with other studies. For instance, Bergstrom, Tenuta and Beauchamp (2001) and Hyde et al. (2006) reported similar results of N_2O emissions on N fertilized grasslands.

The relatively low N_2O fluxes measured after October in both years could be attributed to the low soil water content (WFPS < 30 %) on most sampling days (See Figures 7 and 8) in 2013 and 2014, respectively. A WFPS primarily below 30 % might have slowed down microbial metabolism, microbial movement, and the diffusion of metabolic substrates (including ammonium and nitrate) to the site of consumption (Weitz, Linder, Frolking, Crill & Keller, 2001) as the optimal soil water content is generally about 60 % WFPS for nitrification and greater than 80% WFPS for denitrification (Davidson & Schimel, 1995). More so, Zhang and Han (2008) found that the effect of fertilization disappears approximately two months after the application of N leading to reduced N_2O fluxes.

Annual cumulative N_2O fluxes were calculated for each treatment (Figure 21 and 22) for   2013 and 2014, respectively. In both years, the cumulative N_2O emissions for the growing season were in the order of U120 > SA 120 > U 60 > SA 60 > NPK 60-40-40 > Control. Cumulative flux from U 120 was higher than from

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the other treatments, especially from plots that received no N fertilizer, except for SA 120 in both years. Similarly, cumulative flux for plots treated with SA 120 kg ha^{-1} y^{-1} was also consistently higher than the other treatments. However, cumulative fluxes from NPK 60-40-40 was not different from SA 60, U 60 as well as plots that received no N fertilizer. This indicated that application of N at 120 kg ha^{-1} y^{-1} using urea or sulphate of ammonia increased N_2O emissions significantly ($p < 0.05$) in both years.
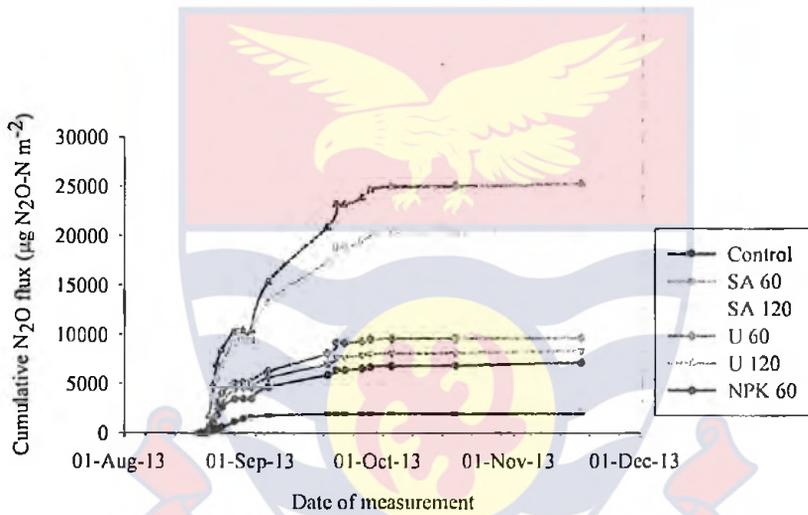
Figure 21: Cumulative N_2O flux (µg N_2O-N) measured in the 2013 growing season
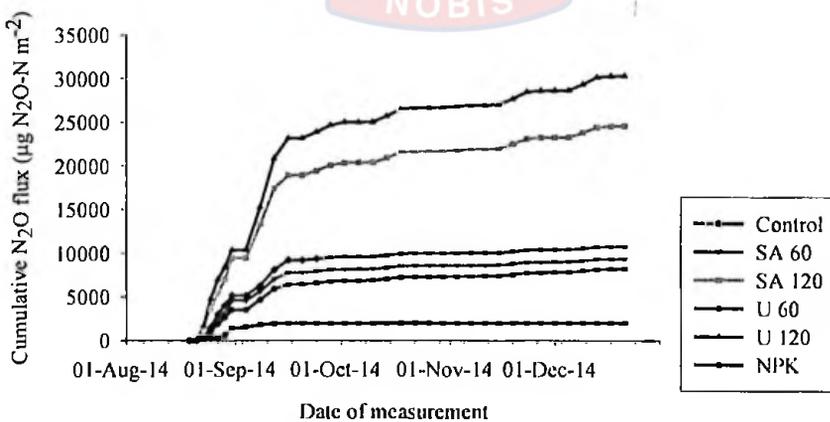
Figure 22: Cumulative N_2O flux (µg N_2O-N m^{-2}) in the 2014 growing season

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Based on the two-year flux measurement, it can be deduced that N_2O emission increased with increasing N application rates but also affected by the N fertilizer type. However, the application of 60 kg N ha^{-1} y^{-1} can be considered an approximation of the threshold N level for the increase of N_2O emissions because a considerable increase of N_2O emissions was induced by application of 120 kg N ha^{-1} y^{-1} only. These results are supported by the findings of Malhi, Lemke, Wang, Farrell and Chhabra (2006) who observed a significant increase in N_2O flux only when fertilized N levels exceeded 80 kg N ha^{-1} y^{-1} in a cropping season. Similarly, Kachanoski, O'Halloran and Rochette (2003) found that N_2O emissions began to increase significantly with fertilized N levels above 100 kg N ha^{-1} in an irrigated corn field.

The situation of N_2O fluxes demonstrating a threshold response to N level exists because N_2O releasing paths compete for N with assimilatory N immobilization by both micro-organisms and plants. Therefore, it is only when N applied to soil exceeds microbial immobilization and plant N demand can N_2O emissions increase (Velthof, Brader & Oenema, 1996); (McSwiney & Robertson, 2005); (Hodge, Robinson & Fitter (2000). Results of grain yield (See Table 3, page 125) showed that plots treated with N fertilizer produced significantly higher grain yield than the control plots. This indicated that N supplied were higher than demanded, therefore, microbial and crop N demand were met. The results from this study, therefore, agrees with findings of Velthof et al. (1996) McSwiney and Robertson (2005) Hodge et al. (2000) who also found significant N_2O flux from plots treated with N fertilizer than non-fertilized plots.

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Relationship between Soil Temperature, CO_2 and N_2O Fluxes from Fertilized and Unfertilized Fields

Relationship between soil temperature, CO_2 fluxes from fertilized and unfertilized fields

The results of relationship between CO_2 flux and soil temperature are presented in Figures 23-28. The results showed no correlation ($p > 0.05$) and r^2 ranges between 0.002 and 0.0684 (Figures 23-28) between CO_2 flux and soil surface temperature for the non-fertilized and fertilized plots, respectively. In spite of the non-correlation, plots that received N fertilization showed better correlation with soil surface temperature than the non-fertilized plots (Figures 24–Figures 28).
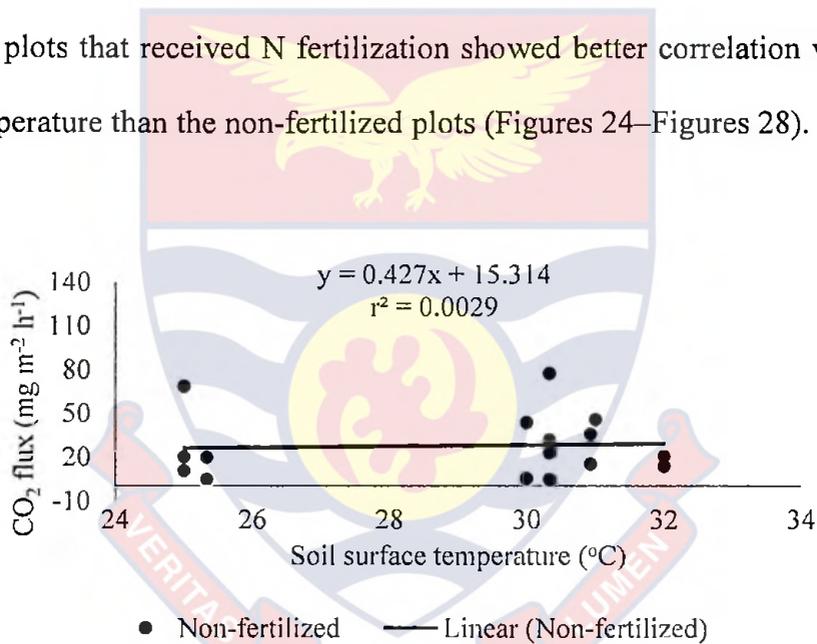
Figures 23: CO_2 flux (mg m^{-2} h^{-1}) from non-N fertilized plots as a function of soil surface temperature (^oC)

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$y = 3.3134x - 71.701$
$r^2 = 0.1244$
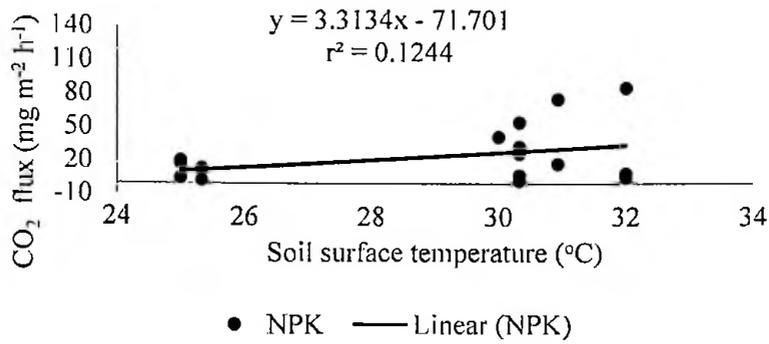
Figures 24: CO_2 flux (mg m^{-2} h^{-1}) from plots treated with NPK 60-40-40 kg ha^{-1} as a function of soil surface temperature (^{o}C)

$y = 5.4087x - 113.77$
$r^2 = 0.1126$
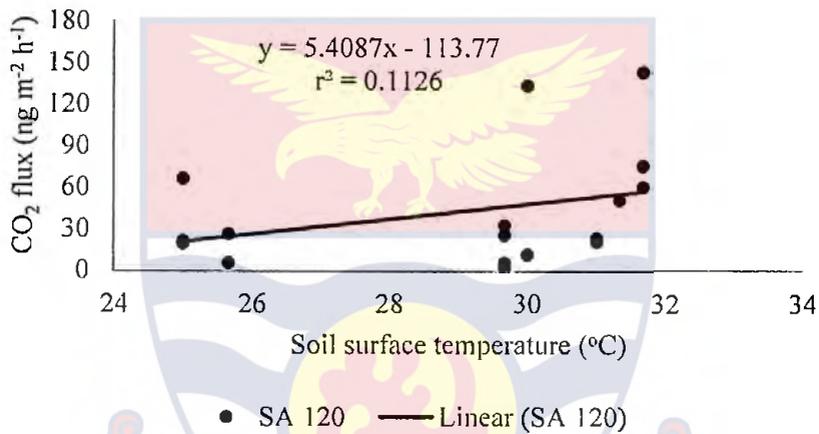
Figures 25: CO_2 flux (mg m^{-2} h^{-1}) from plots treated with 120 kg N ha^{-1} sulphate of ammonia as a function of soil surface temperature (^{o}C)

$y = 1.2867x - 15.934$
$r^2 = 0.0684$
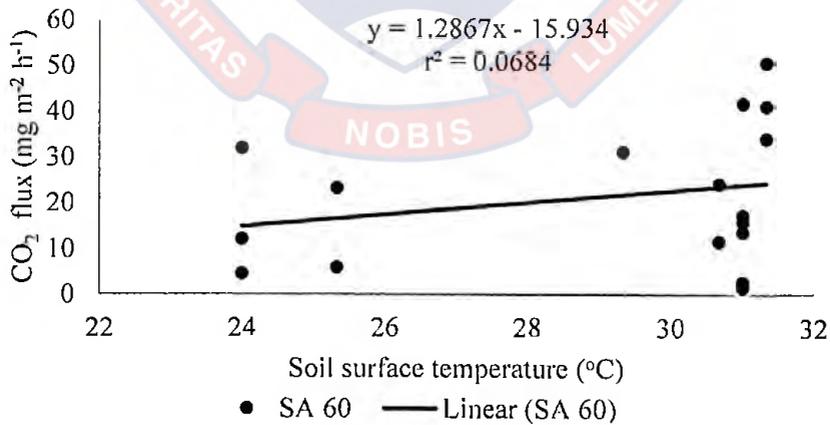
Figures 26: CO_2 flux (mg m^{-2} h^{-1}) from plots treated with 60 kg N ha^{-1} sulphate of ammonia as a function of soil surface temperature (^{o}C)

96
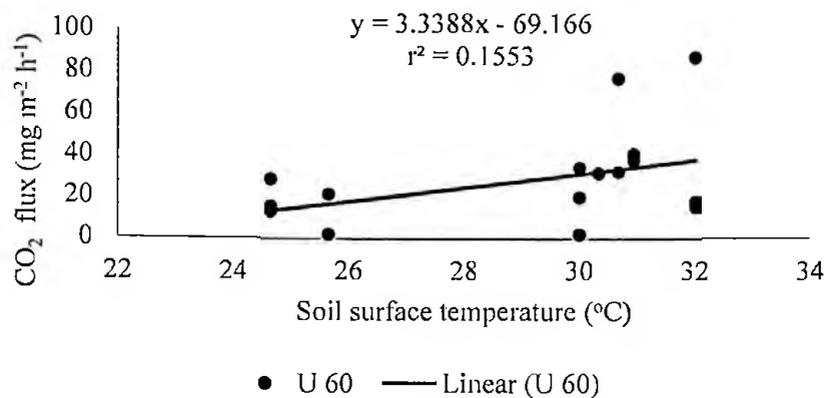
Figures 27: CO_2 flux (mg m^{-2} h^{-1}) from plots treated with 60 kg N ha^{-1} urea as a function of soil surface temperature ($^{\circ}$C)
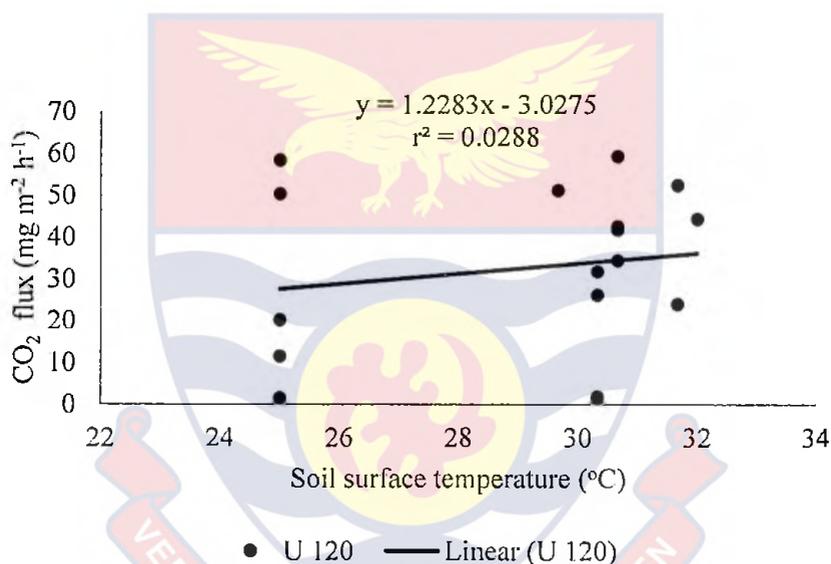
Figures 28: CO_2 flux (mg m^{-2} h^{-1}) from plots treated with 120 kg N ha^{-1} urea as a function of soil surface temperature ($^{\circ}$C)

Similar results were obtained for CO_2 flux and soil temperature measured at 10 cm depth which even showed no correlation. The order of correlation found although not significant ($p > 0.05$) was U 120 > NPK > SA 120 > SA 60 > U 60 > non-N fertilized plots (Figures 29-34).

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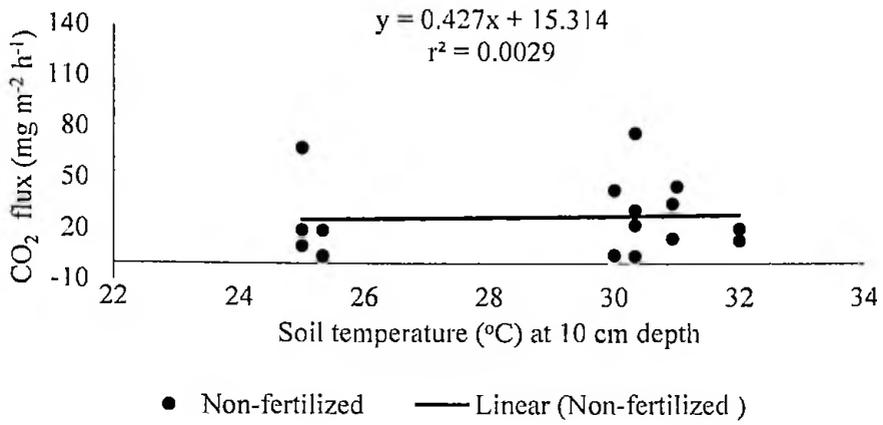
Figure 29: CO_2 flux (mg m^{-2} h^{-1}) from non-N fertilized plots as a function of soil temperature ($^{\circ}$C) at 10 cm depth
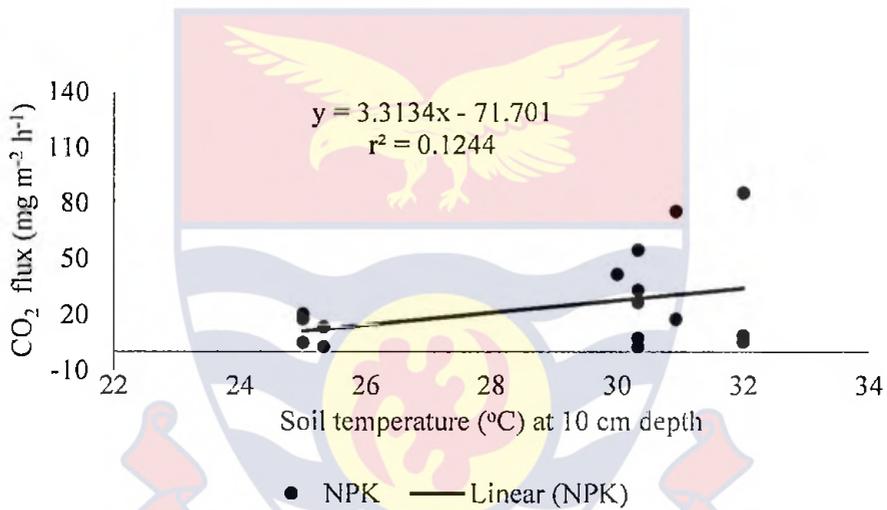
Figure 30: CO_2 flux (mg m^{-2} h^{-1}) from plots treated with NPK 60-40-40 kg ha^{-1} as a function of soil temperature ($^{\circ}$C) at 10 cm depth

$$y = 5.4087x - 113.77$$
$$r^2 = 0.1126$$
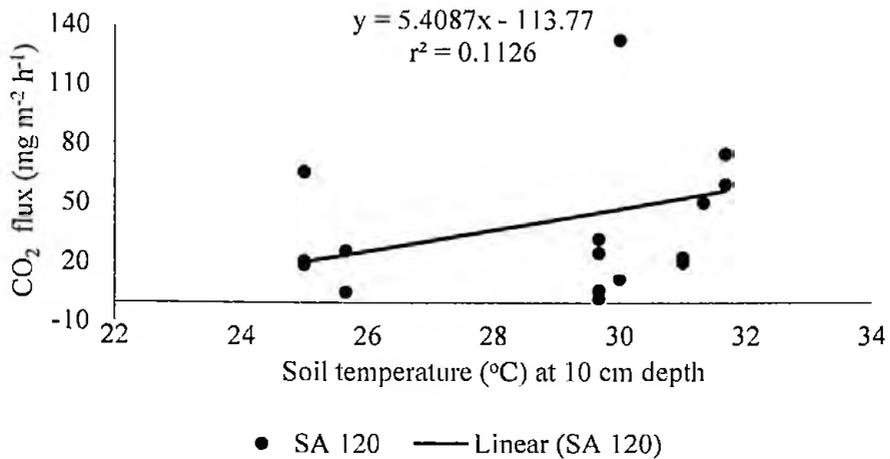
Figure 31: CO_2 flux (mg m^{-2} h^{-1}) from plots treated with 120 kg N ha^{-1} sulphate of ammonia as a function of soil temperature (°C) at 10 cm depth

$$y = 1.2867x - 15.934$$
$$r^2 = 0.0684$$
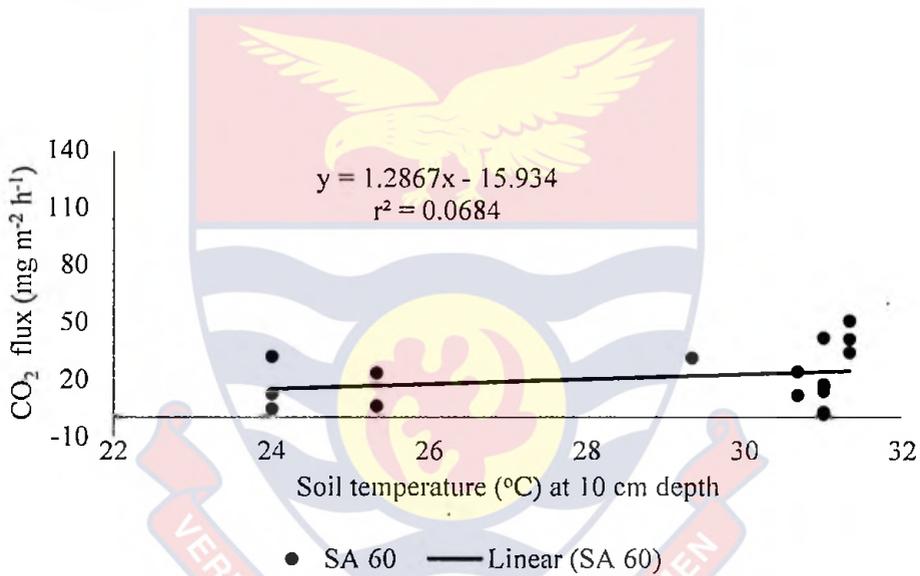
Figure 32: CO_2 flux (mg m^{-2} h^{-1}) from plots treated with 60 kg N ha^{-1} sulphate of ammonia as a function of soil temperature (°C) at 10 cm depth

$y = 3.3388x - 69.166$
$r^2 = 0.1553$

U 120 ——Linear (U 120)
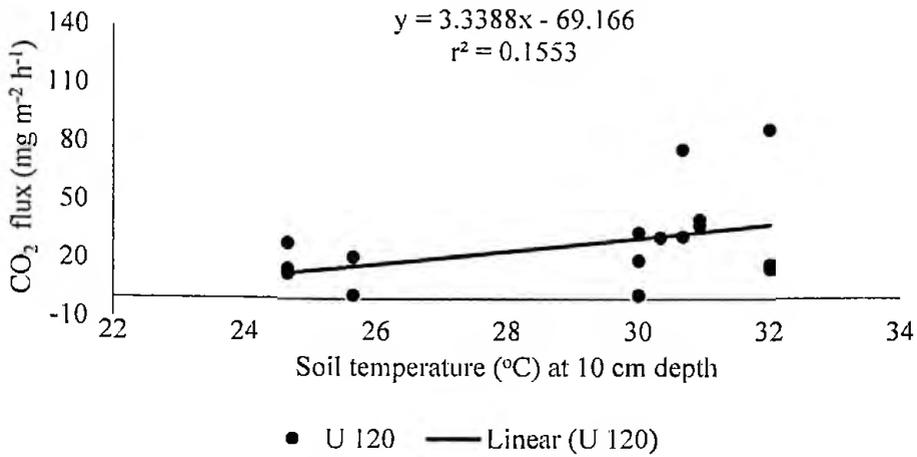
Figure 33: CO_2 flux (mg m^{-2} h^{-1}) from plots treated with 120 kg N ha^{-1} urea as a function of soil temperature (^{o}C) at 10 cm depth

$y = 1.2283x - 3.0275$
$r^2 = 0.0288$

U 60 ——Linear (U 60)
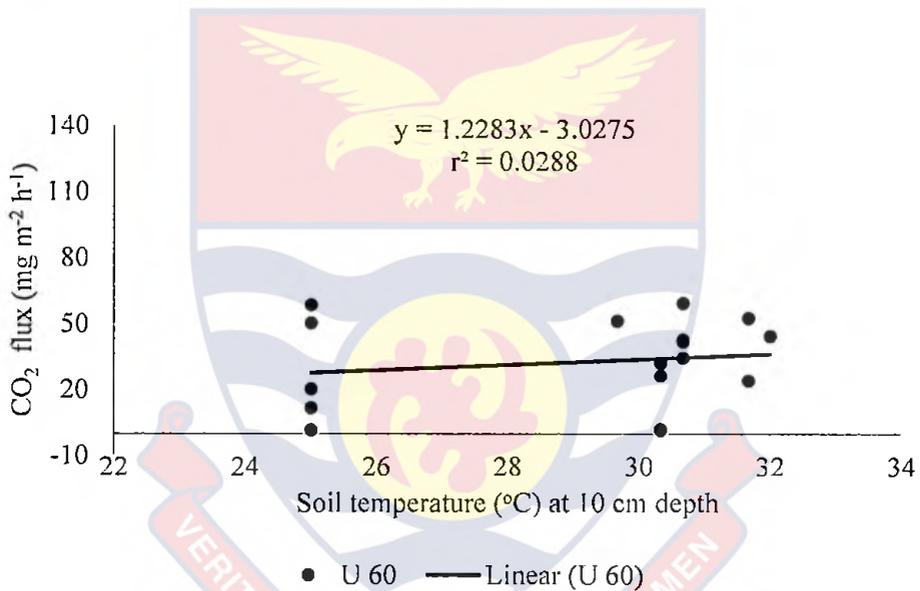
Figure 34: CO_2 flux (mg m^{-2} h^{-1}) from plots treated with 60 kg N ha^{-1} urea as a function of soil temperature (^{o}C) at 10 cm depth

Again, the correlation between CO_2 flux and soil temperature was better with N fertilized plots than the non N fertilized plots although not significant (Figures 30-34). Application of N fertilizer or otherwise did not affect soil temperature both at the surface and at 10 cm depth. Therefore, temperature at the

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study site did not influence CO_2 fluxes. This result suggests a water limited microbial activity in most periods of the flux measurement hence the lack correlation (See Figures 7, 8, 9 and 10). Microbial activities are expected to be elevated with increased soil temperature thereby increasing CO_2 emission by soil respiration and contributing to global warming as reported by Allison, Wallenstein and Bradford (2010). However, in this study, soil temperatures within sampling period were not significantly different among different times of the day. For instance, soil surface temperatures measured in the first 14 days when maximum CO_2 flux was observed ranged between 24 and 26 °C (See Figures 3, 4, 5 and 6). Also, soil temperatures between September and October ranged constant between 30 and 32 °C.

The rise in temperature from an average of 24 °C in the first 14 days of flux to an average maximum of 32 °C from September to November in both years should have been associated with an increase in CO_2 emissions but was found otherwise in this study. The lack of response of CO_2 emission to temperature change in this study could be attributed to the agronomic management such tillage, sole cropping system, reduced microbial respiration due to unfavourable soil temperatures. This is also consistent with reports that suggest that increase in respiration may not necessarily persist as temperatures continue to rise. Again, field management practices also probably affected soil temperature and water content (Curtin, Wang, Selles, McConkey, & Campbell, 2000); Al-Kaisi and Yin (2005) which could directly influence CO_2 emission rates (Bajracharya, Lal, & Kimble, 2000); (Parkin & Kaspar, 2003); (Amos, Arkebauer, & Doran, 2005). For instance, tillage can dry

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the soil but no-till can increase soil water content and reduce soil temperature because of residue accumulation at the soil surface (Curtin et al., 2000); (Calderon & Jackson 2002); (Al-Kaisi & Yin 2005). Similarly, cropping system can reduce soil temperature by providing shade with increased biomass growth but can reduce soil water content due to increased evapotranspiration (Amos et al., 2005).

Relationship between soil temperature and N_2O fluxes from fertilized and unfertilized fields

Both soil surface temperature and soil temperature measured at 10 cm depth produced similar positive but weak correlations $r^2 < 0.218$; $r^2 < 0.218$) (Figures 35-40 and 41-46), with N_2O flux respectively. The marginal increase in N_2O flux with increasing soil temperature could be attributed to enhanced microbial activity, unlike CO_2 flux, both surface temperature and temperature at 10 cm depth might have favoured microbes responsible for nitrification and denitrification. This result is in agreement with other findings. For instance, Firestone and Davidson (1989) reported that production of NO and N_2O in soils is primarily driven by microbial processes such as nitrification and denitrification, and soil temperature is a key variable affecting microbes and thereby the emission rates of both gases even though the flow of nitrogen and soil water content are the main drivers of the magnitude of NO and N_2O fluxes.

Furthermore, Pilegaard et al. (2006) also reported a short term relationship between soil temperature and N_2O fluxes which is also consistent with the results of this study. Several investigations including Slemr and Seiler (1984); Skiba et al.

(1998); Smith, Powlson, Glendining and Smith (1998) also reported emissions of both NO and N_2O increase with increasing soil temperature due to the fact that rates of enzymatic processes generally increase with temperature as long as other factors including substrate and moisture are not limiting. In this study, significant N_2O flux was measured when WFPS was above 40% and mineral N as substrate was highly available between two and ten days after fertilizer application.

Figure 35: N_2O flux (μg m^{-2} h^{-1}) from non-N fertilized plots as a function of soil surface temperature (°C)

Figure 36: N_2O flux (μg m^{-2} h^{-1}) from plots treated with NPK 60-40-40 kg ha^{-1} as a function of soil surface temperature (°C)

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Figure 37: N_2O flux ($\mu g\ m^{-2}\ h^{-1}$) from plots treated with 120 kg N ha^{-1} sulphate of ammonia as a function of soil surface temperature ($^{\circ}C$)
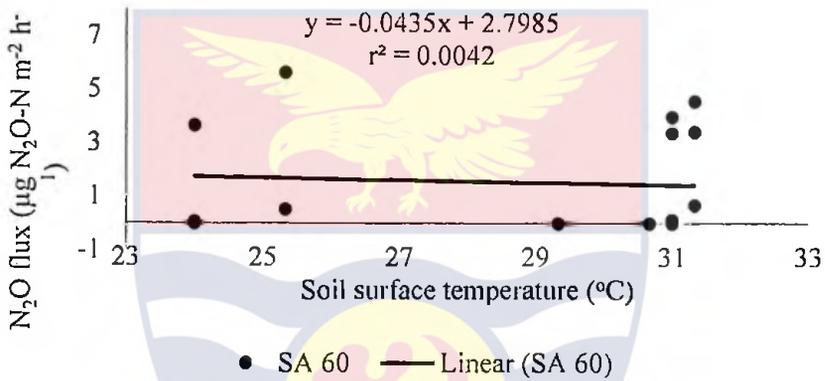
Figure 38: N_2O flux ($\mu g\ m^{-2}\ h^{-1}$) from plots treated with 60 kg N ha^{-1} sulphate of ammonia as a function of soil surface temperature ($^{\circ}C$)
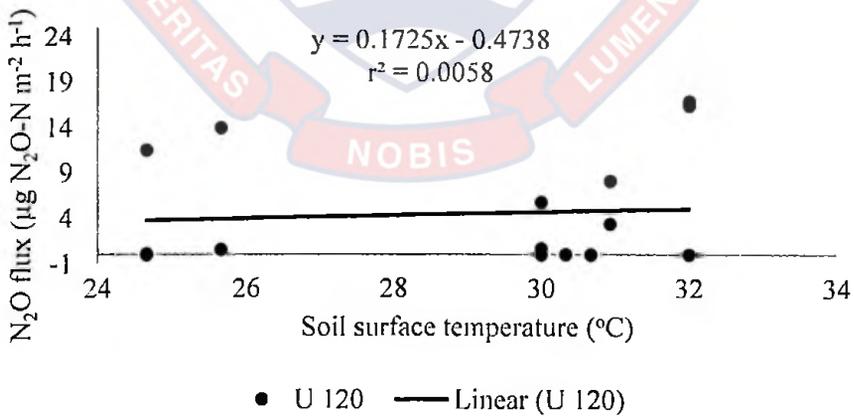
Figure 39: N_2O flux ($\mu g\ m^{-2}\ h^{-1}$) from plots treated with 120 kg N ha^{-1} urea as a function of soil surface temperature ($^{\circ}C$)

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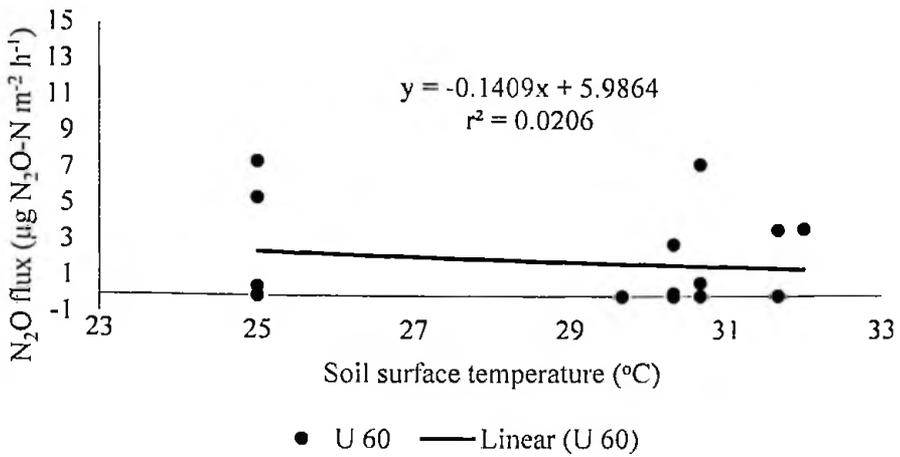
Figure 40: N2O flux (μg m^{-2} h^{-1}) from plots treated with 60 kg N ha^{-1} urea as a function of soil surface temperature (°C)

Figure 41: N2O flux (μg m^{-2} h^{-1}) from non-N fertilized plots as a function of soil temperature (°C) at 10 cm depth

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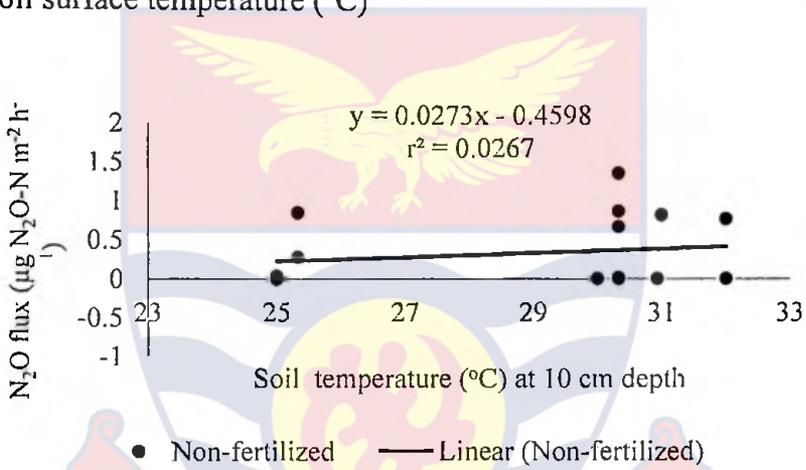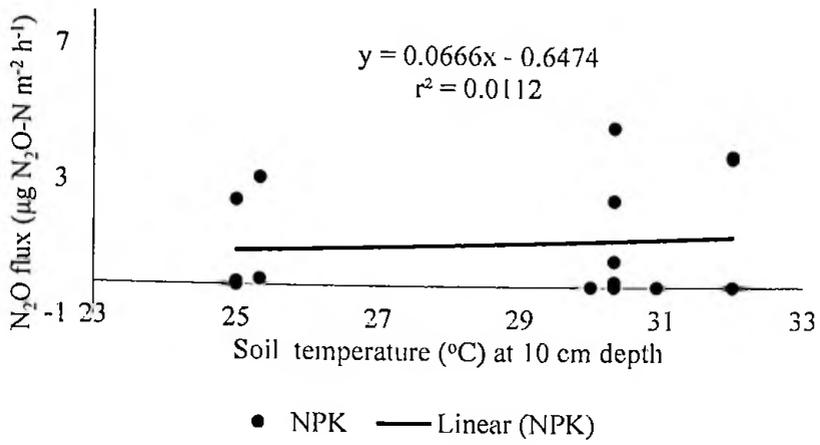
Figure 42: N_2O flux (μg m^{-2} h^{-1}) from plots treated with NPK 60-40-40 kg ha^{-1} as a function of soil temperature (^{o}C) at 10 cm depth

Figure 43: N_2O flux (μg m^{-2} h^{-1}) from plots treated with 120 kg N ha^{-1} sulphate of ammonia as a function of soil temperature (^{o}C) at 10 cm depth

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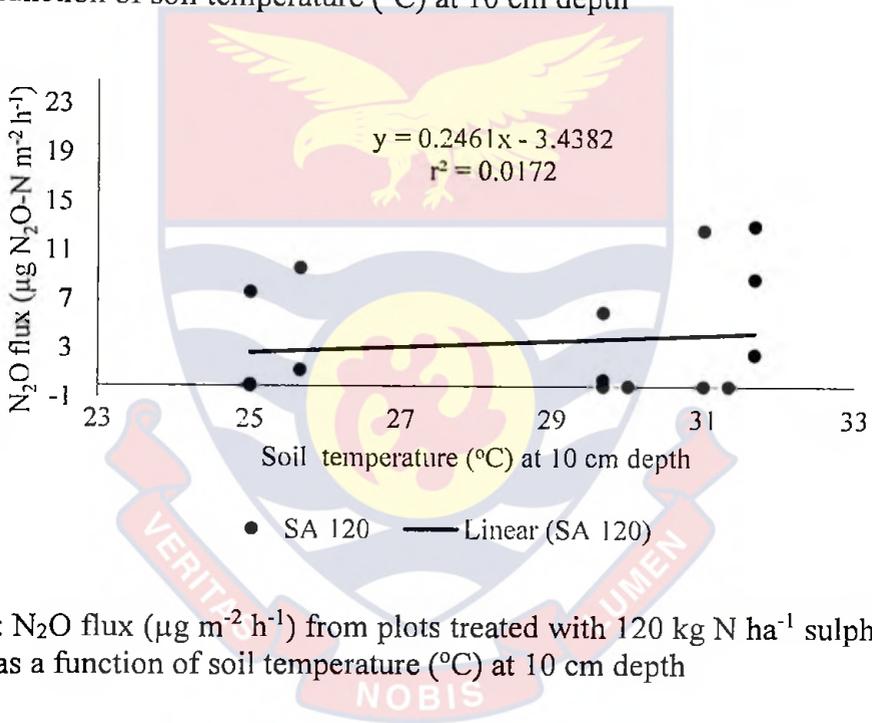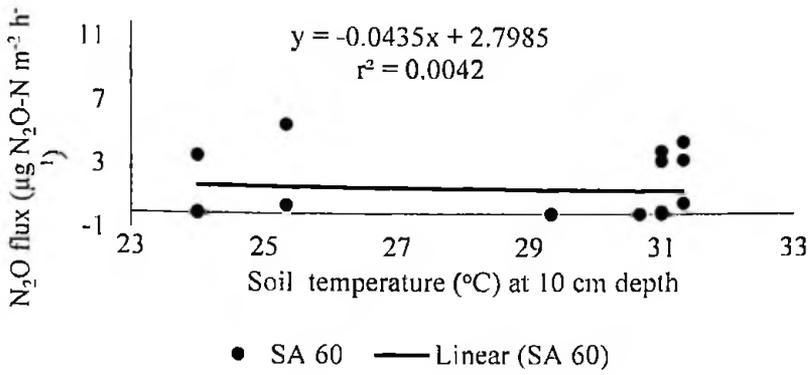
Figure 44: N₂O flux ($\mu g\ m^{-2}\ h^{-1}$) from plots treated with 60 kg N ha^{-1} sulphate of ammonia as a function of soil temperature (°C) at 10 cm depth
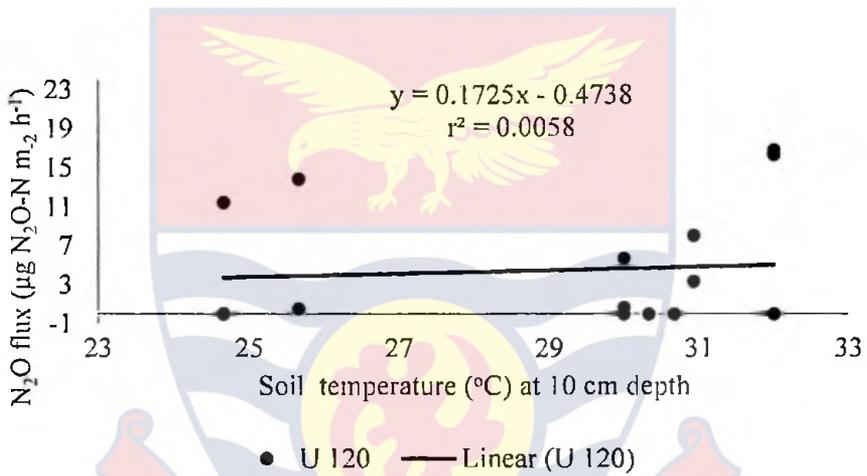
Figure 45: N₂O flux ($\mu g\ m^{-2}\ h^{-1}$) from plots treated with 120 kg N ha^{-1} urea as a function of soil temperature (°C) at 10 cm depth
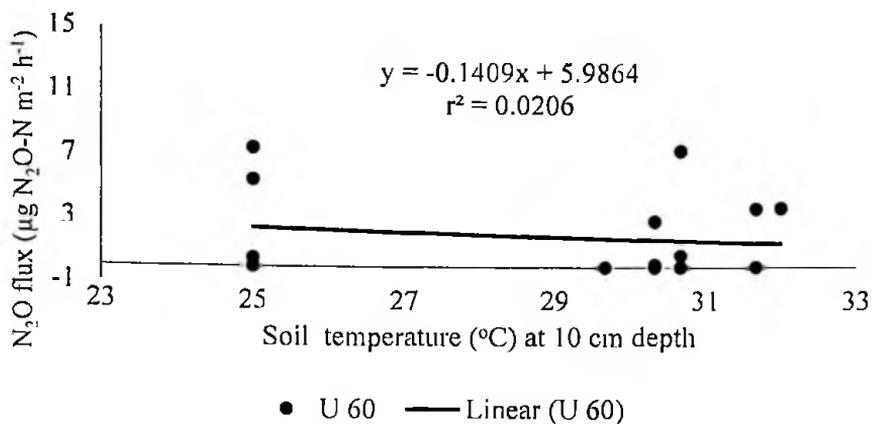
Figure 46: N_2O flux (μg m^{-2} h^{-1}) from plots treated with 60 kg N ha^{-1} urea as a function of soil temperature (^{o}C) at 10 cm depth

Relationship between WFPS, CO_2 and N_2O Fluxes from Fertilized and Unfertilized Fields

Relationship between WFPS and CO_2 fluxes from fertilized and unfertilized fields

The relationship between CO_2 fluxes and WFPS was computed using a linear regression function. No significant correlation ($p > 0.05$) was found between WFPS and CO_2 fluxes. From both N fertilized and non-fertilized plots, $r^2 < 0.15$. Although not significant, the influence of WFPS on CO_2 emission from soils are slightly higher on plots treated with 120 kg N ha^{-1} (Figures 47 and 48) compared to 60 kg N ha^{-1} (Figures 49, 50 and 51) and non-N fertilized soils (Figure 52). Previous studies of CO_2 production and moisture relationships have shown several contradictory results. Some studies have found a parabolic relationship between moisture and CO_2 production (Douglas & Tedrow, 1959); (Linn & Doran, 1984). Other investigators have found either positive (Froment, 1972); (Pal & Broadbent,

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1975); (Orchard & Cook, 1983); (Schlentner & van Cleve, 1985); (Coxson & Parkinson, 1987) (Kucera & Kirkham, 1971); (DeSanto, Alfani & Sapio, 1976); (Kowalenko, Ivarson & Cameron, 1978) relationships between these factors.
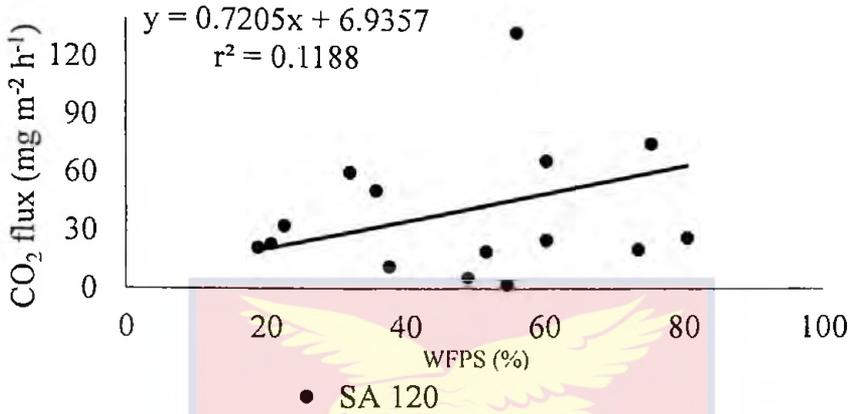
Figure 47: CO_2 flux (mg m^{-2} h^{-1}) from plots treated with 120 kg N ha^{-1} sulphate of ammonia as a function of WFPS
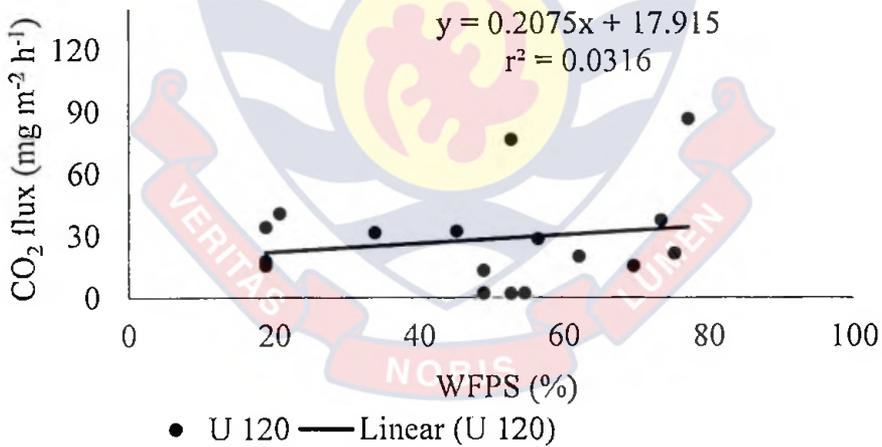
Figure 48: CO_2 flux (mg m^{-2} h^{-1}) from plots treated with 120 kg N ha^{-1} urea as a function of WFPS

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$$y = 0.1337x + 17.688$$
$$r^2 = 0.0152$$
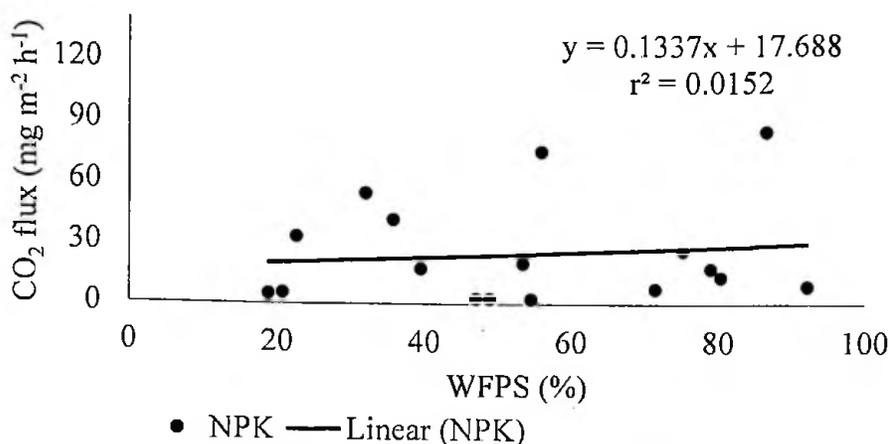
Figure 49: CO_2 flux (mg m^{-2} h^{-1}) from plots treated with NPK 60-40-40 kg ha^{-1} as a function of WFPS

$$y = 0.0016x + 21.325$$
$$r^2 = 0.0012$$
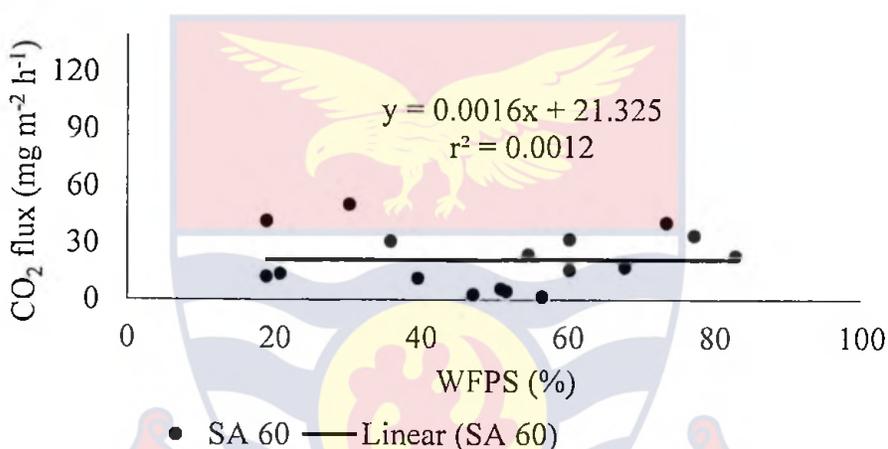
Figure 50: CO_2 flux (mg m^{-2} h^{-1}) from plots treated with 60 kg N ha^{-1} sulphate of ammonia as a function of WFPS

$$y = 0.2558x + 20.354$$
$$r^2 = 0.0642$$
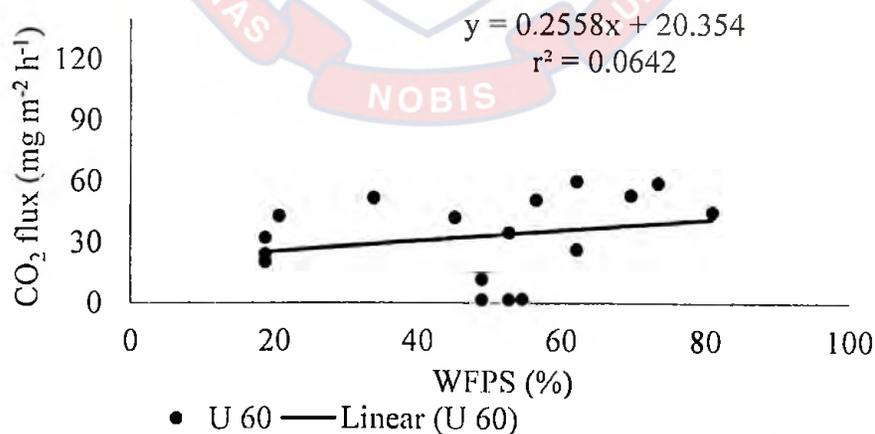
Figure 51: CO_2 flux (mg m^{-2} h^{-1}) from plots treated with 60 kg N ha^{-1} urea as a function of WFPS

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The plot shows CO$_2$ flux (mg m^{-2} h^{-1}) on the y-axis (0 to 120) versus WFPS (%) on the x-axis (0 to 80), with the regression equation:

$$y = -0.044x + 29.369$$
$$r^2 = 0.0011$$

● Non-fertilized ——Linear (Non-fertilized)
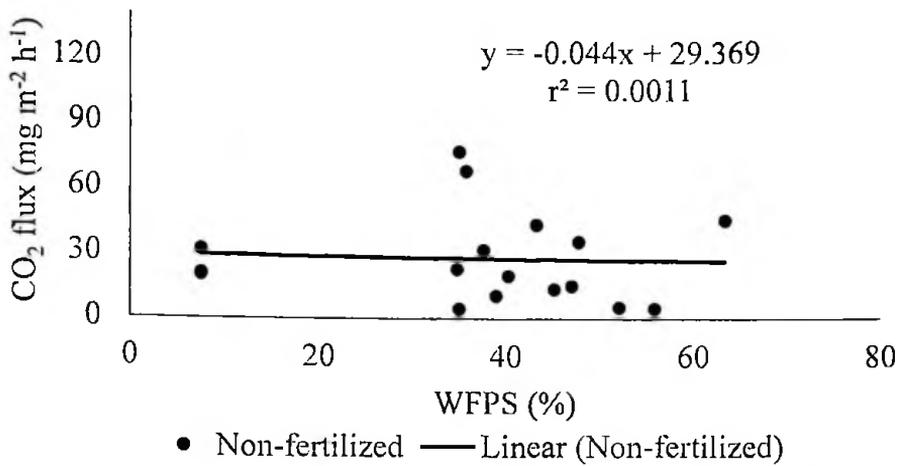
Figure 52: CO$_2$ flux (mg m^{-2} h^{-1}) from non-N fertilized plots as a function of WFPS

Other investigators have also found variable or non-significant relationships between soil moisture and CO$_2$ production (Miller & Johnson, 1964); (Reiners, 1968). Furthermore, Schlentner and van Cleve (1985); Coxson and Parkinson (1987) reported that wet forest soils tend to exhibit high CO$_2$ production at moisture contents near or above saturation, possibly due to the development of microbial populations tolerant to low aeration status. However, in this study, WFPS measured during CO$_2$ flux sampling days was not saturated throughout the growing season and more so in most cases from October to December WFPS measured was below 30 % pointing towards water limitation, this might have resulted in low soil microbial respiration (See Figures 7 and 8). Therefore, moisture limiting microbial activity conditions at the experimental field was probably a factor in this study as it is reasonable to expect microbial populations in wet soils to be more active under wet conditions. Also, Groffman and James (1991) reported that soils of intermediate moisture content showed no significant moisture-CO$_2$ production

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relationship. Meanwhile, soil respiration in this study was mostly moisture-limited accounting for restricted diffusion of dissolved organic carbon.

Relationship between WFPS and N₂O fluxes from fertilized and unfertilized fields

The linear relationship between N_2O flux and WFPS is presented in Figures 53-58. There was no correlation between N_2O fluxes from the control plots and WFPS (Figure 53). A positive and significant ($p < 0.05$, $r^2 > 0.6$) correlation was found between N_2O flux and WFPS from plots that received N fertilization. The correlation was more prominent on soils treated with sulphate of ammonia than urea. A higher correlation was found from plots treated with NPK 60-40-40 kg ha⁻¹ y⁻¹ (Figure 54) which was higher than the correlation from plots that received 120 kg N ha⁻¹ sulphate of ammonia (Figure 55).
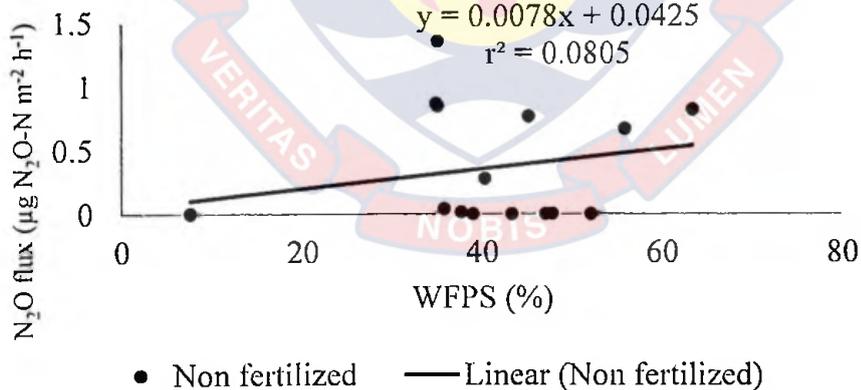
Figure 53: N₂O flux (μg N₂O-N m⁻² h⁻¹) from non-N fertilized plots as a function WFPS (%)

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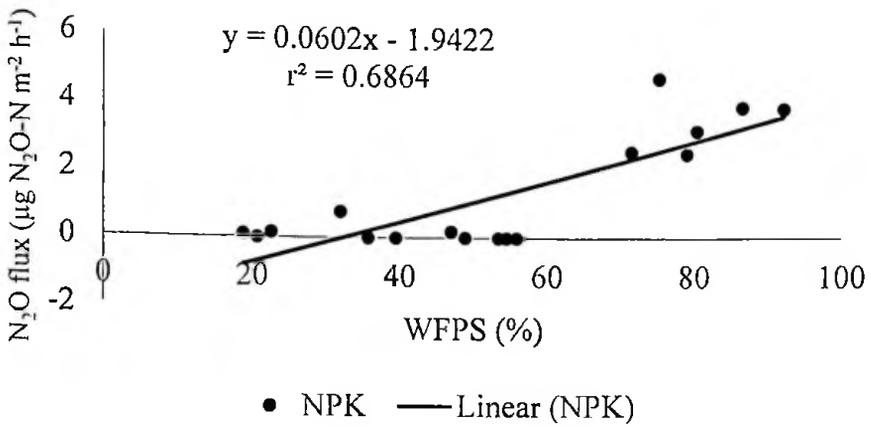
Figure 54: N₂O flux (μg N₂O-N m⁻² h⁻¹) from plots treated with NPK 60-40-40 kg ha⁻¹ as a function WFPS (%)
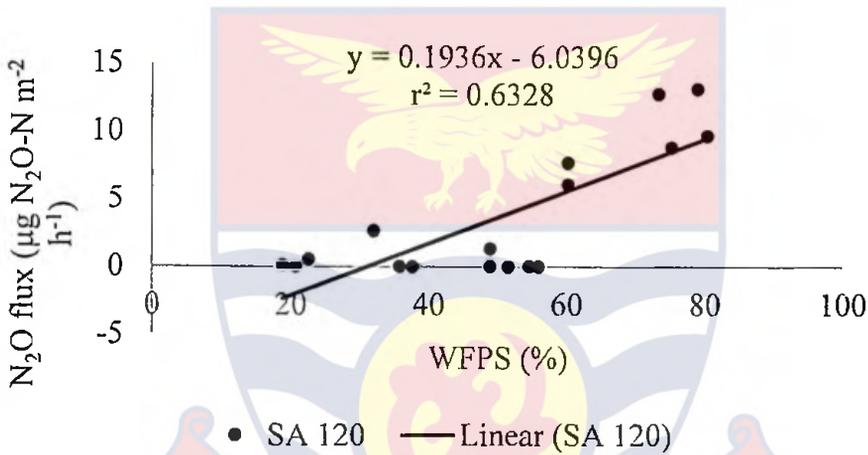
Figure 55: N₂O flux (μg N₂O-N m⁻² h⁻¹) from plots treated with 120 kg N ha⁻¹ sulphate of ammonia as a function WFPS (%)

Plots treated with sulphate of ammonia at 60 kg N ha⁻¹ showed the highest positive correlation ($r^2 = 0.7094$) (Figure 56) which was contrary to correlation between WFPS and N₂O flux from soils treated with 60 kg ha⁻¹ urea (Figure 57). When urea was applied at 120 kg N ha⁻¹ the correlation was not better ($r^2 = 0.5622$) than observed when 120 kg N was applied as sulphate of ammonia (Figure 58).

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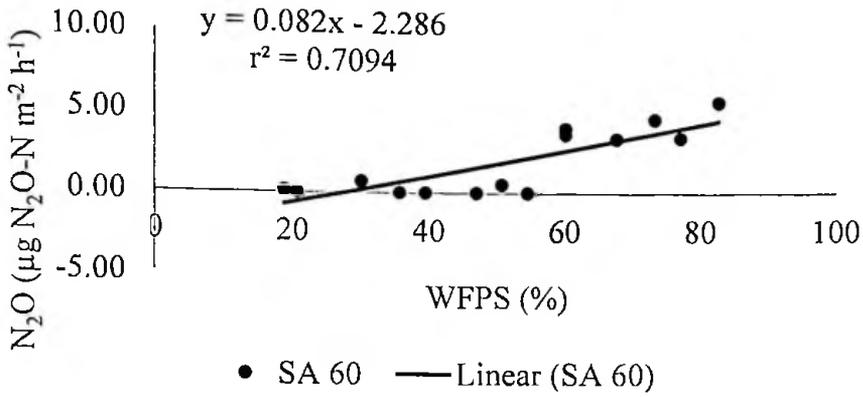
Figure 56: N₂O flux (μg N₂O-N m⁻² h⁻¹) from plots treated with 60 kg N ha⁻¹ sulphate of ammonia as a function WFPS (%)
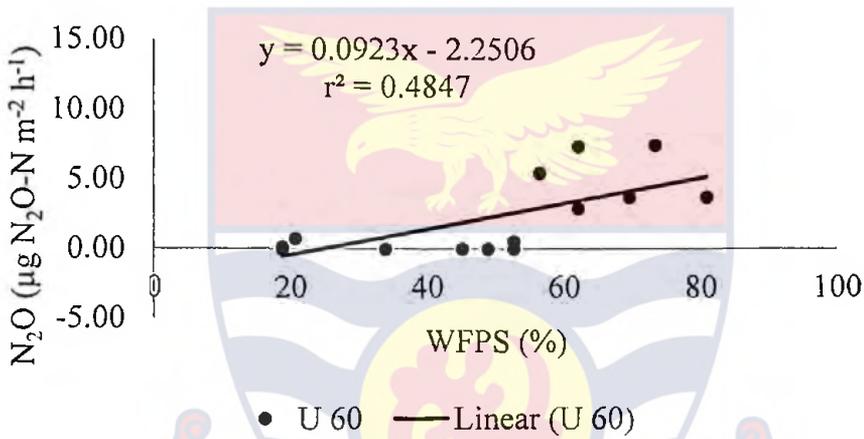
Figure 57: N₂O flux (μg N₂O-N m⁻² h⁻¹) from plots treated with 60 kg N ha⁻¹ urea as a function WFPS (%)

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$y = 0.2264x - 5.7729$
$r^2 = 0.5622$

● U 120   ——Linear (U 120)
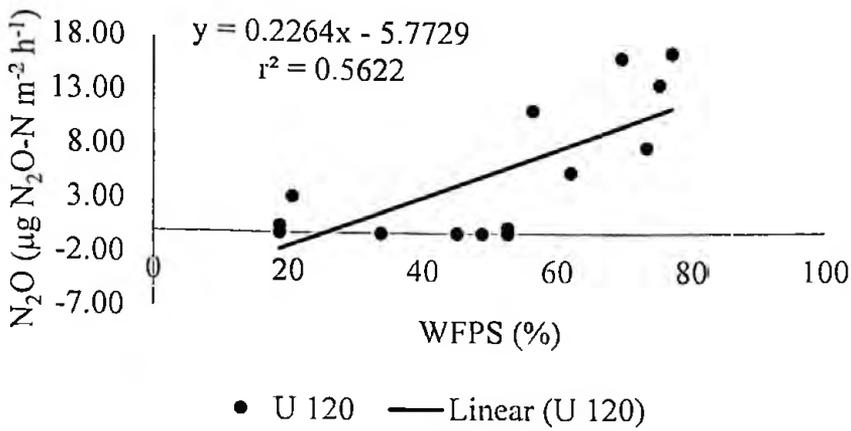
Figure 58: N$_2$O flux (μg N$_2$O-N m^{-2} h^{-1}) from plots treated with 120 kg N ha^{-1} urea as a function WFPS (%)

These results support the findings of Firestone and Davidson (1989), who reported that production of N$_2$O in soils is primarily driven by microbial processes such as nitrification and denitrification, therefore soil moisture is an integral factor in the presence of optimum temperature for enhanced microbial activities including soil respiration. The results of this study also agree with the findings of other researchers, (Skiba et al., 1998) and Smith et al. (1998), who reported that, soil water, thus, acts as a transport medium for NO$_3$-N and NH$_4^+$-N and influences the rate of oxygen supply, therefore controls whether aerobic processes such as nitrification or anaerobic processes such as denitrification dominate within the soil. Furthermore, Wolf and Russow (2000), Papen and Butterbach-Bahl (1999) also reported that N$_2$O emissions are known to increase at higher water contents through larger losses from denitrification. In this study, soil moisture was relatively high when significant N$_2$O fluxes were measured between August and middle of October.

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Relationship between N₂O Flux, Soil Ammonium-N and Nitrate-N

The correlation between N_2O Flux, Soil Ammonium-N and Nitrate-N was computed using linear regression from field data. Plots that received no N fertilization showed a positive but weaker correlation ($r^2 = 0.2497$) between measured NH_4^+-N and N_2O flux (Figure 59). Correlation between N_2O fluxes and ammonium (NH_4^+-N) from plots treated with NPK 60-40-40 kg ha^{-1} significant (Figures 60). The large variations in NH_4^+-N observed on plots that received 60 kg N ha^{-1} urea might have accounted for the weaker positive correlation ($r^2 = 0.3396$) found between N_2O fluxes and NH_4^+-N (Figure 61).
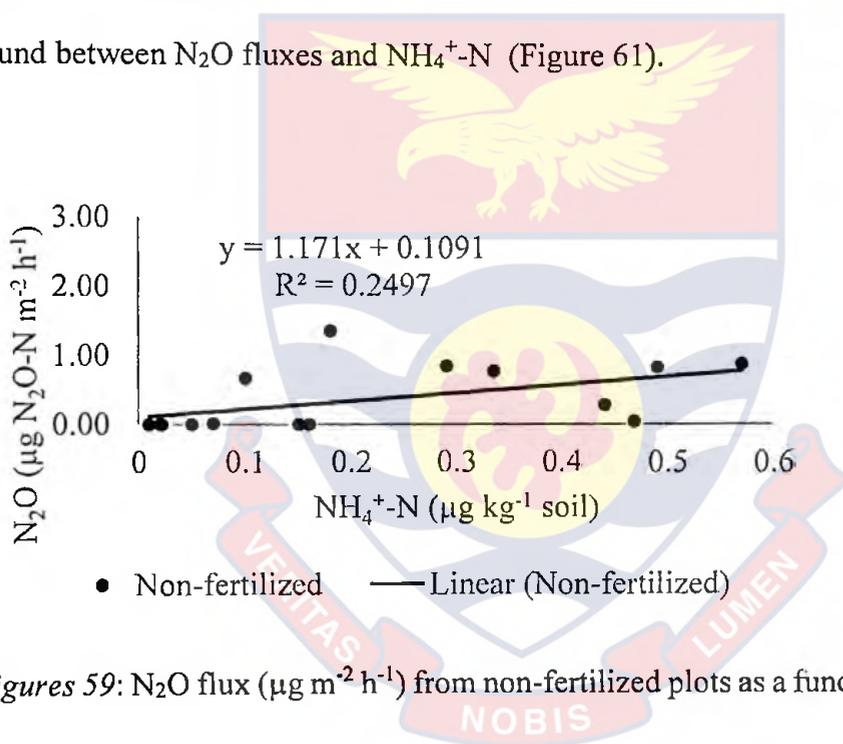
Figures 59: N₂O flux (μg m^{-2} h^{-1}) from non-fertilized plots as a function ammonium N

$y = 3.3838x + 0.1773$

$r^2 = 0.5376$
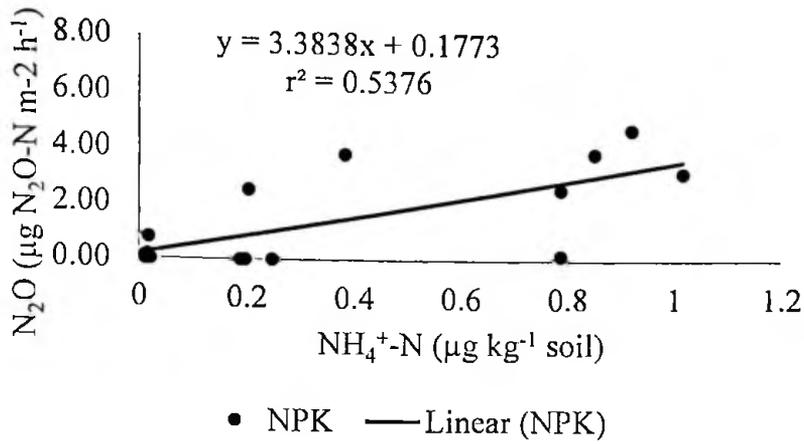
Figures 60: N_2O flux ($\mu g\ m^{-2}\ h^{-1}$) from plots treated with NPK 60-40-40 kg ha^{-1} as a function ammonium N

$y = 1.0966x + 0.4892$

$r^2 = 0.3396$
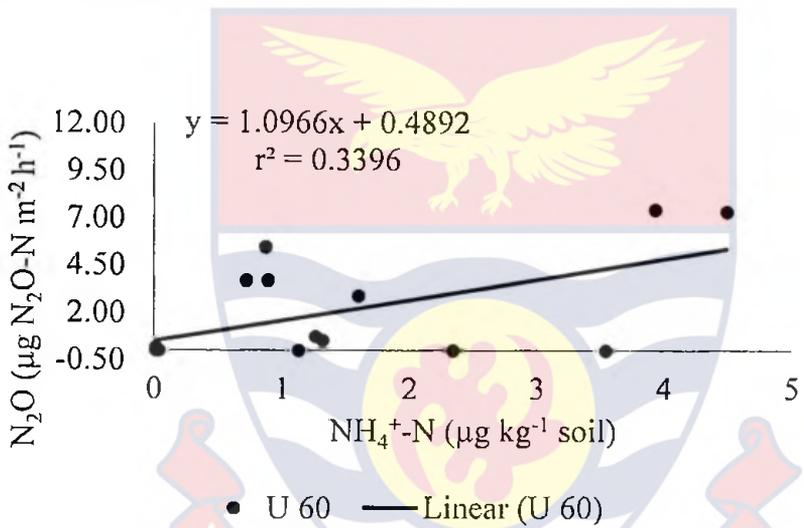
Figures 61: N_2O flux ($\mu g\ m^{-2}\ h^{-1}$) from plots treated with 60 kg N ha^{-1} urea as a function ammonium N

A higher and positive linear correlation was found when either urea or sulphate of ammonia was applied at 120 kg N ha^{-1} (Figures 62 and 63). Although not significantly positive the correlation was more prominent when urea was applied at 120 kg N ha^{-1} than compared with same rate as sulphate of ammonia. However,

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application of 60 kg N ha^{-1} y^{-1} sulphate of ammonia showed a better correlation (r^2 = 0.5288); (Figure 64) compared with when 60 kg N ha^{-1} y^{-1} was applied.
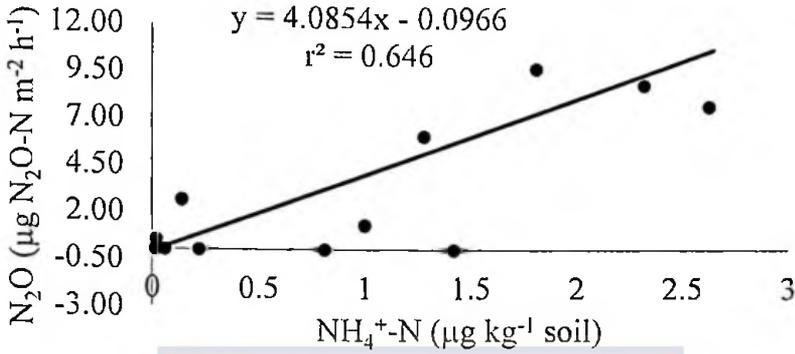
Figures 62: N$_2$O flux (μg m^{-2} h^{-1}) from plots treated with 120 kg N ha^{-1} sulphate of ammonia as a function ammonium N
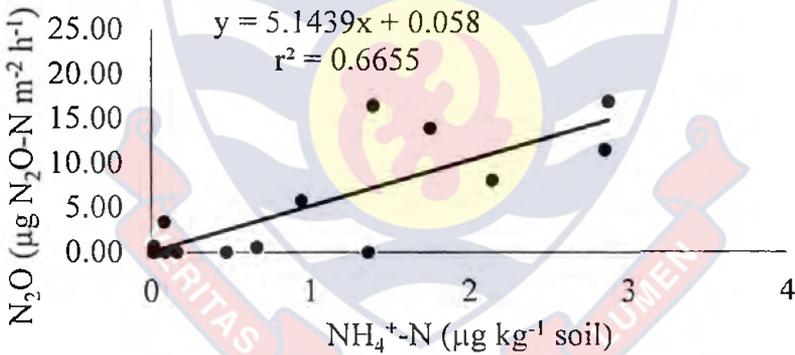
Figures 63: N$_2$O flux (μg m^{-2} h^{-1}) from plots treated with 120 kg N ha^{-1} urea as a function ammonium N

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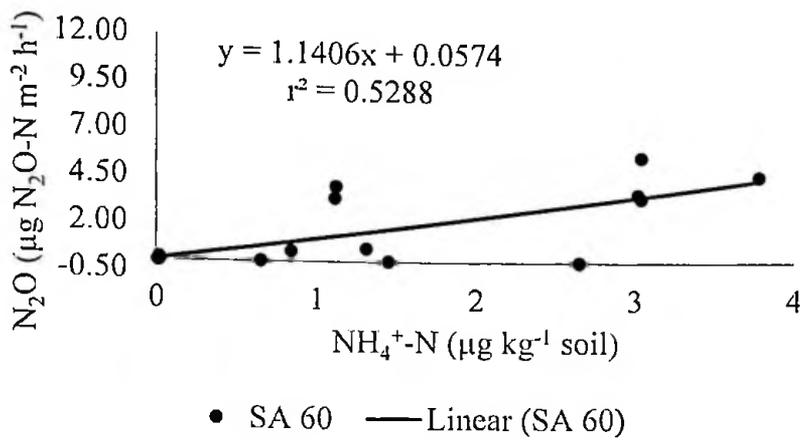
Figures 64: N_2O flux (μg m^{-2} h^{-1}) from plots treated with 60 kg N ha^{-1} sulphate of ammonia as a function ammonium N

This result suggests that the presence of adequate NH_4^+-N as a substrate influences microbial activities involved in nitrification leading to the production of higher levels of N_2O fluxes. This result is also supported by the fact that higher N_2O fluxes were observed between two and ten days after the application of the N fertilizer. Furthermore, the presence of labile organic matter from weeds and crop residues could also have promoted microbial respiration, thereby inducing the creation of anaerobic microsites in which nitrification could take place as reported by Tiedje, Sexstone, Parkin, Revsbech and Shelton (1984) and Smith (1997). The above observation might be the possible reason for the significant correlation between N_2O flux and NH_4^+-N in this study.

On the contrary, the control plots showed the highest correlation between N_2O flux and NO_3^--N ($r^2 = 0.5444$) (Figure 65). This was followed by plots treated with NPK at 60-40-40 kg ha^{-1} ($r^2 = 0.5376$) (Figure 66)

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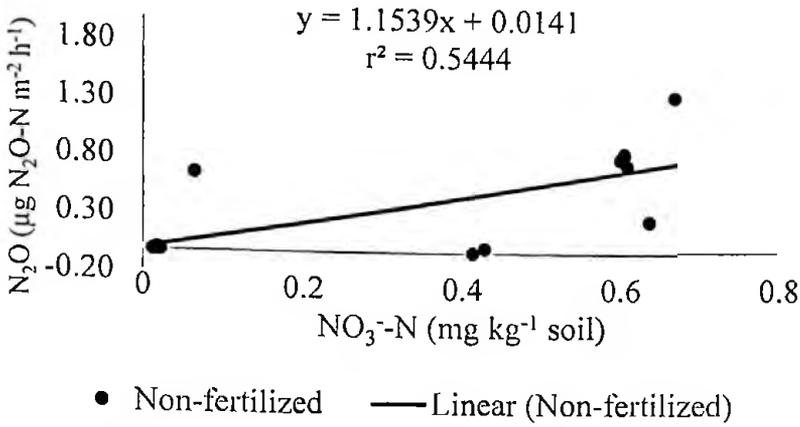
Figure 65: N2O flux (μg m^{-2} h^{-1}) from non-N fertilized plots as a function of nitrate N
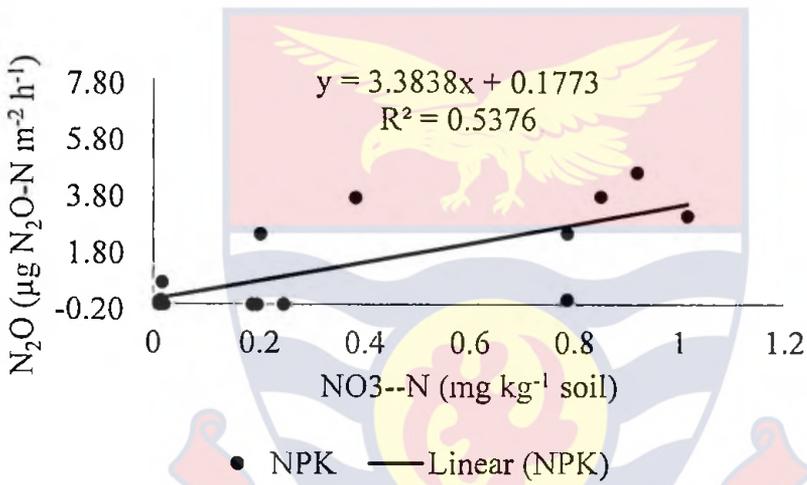
Figure 66: N2O flux (μg m^{-2} h^{-1}) from plots treated with NPK 60-40-40 (kg ha^{-1}) as a function of nitrate N

Application of 120 kg N ha^{-1} as sulphate of ammonia or urea showed no significant correlation ($r^2 = 0.0.1994$) (Figure 67) and ($r^2 = 0.2542$) (Figure 68) between N2O flux and NO3$^-$-N. However, the correlation was improved although not significant ($p > 0.05$) between N2O flux and NO3$^-$-N from plots treated with 60 and 120 kg N ha^{-1} sulphate of ammonia or urea (Figure 69 and 70). The non-significant relationship between N2O fluxes and nitrate could be attributed to increased

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nitrification leading to higher consumption of nitrate in the soil. The higher consumption could have been as a result of inadequate NO_3^--N to satisfy microbial and crop demands, rapid absorption of NO_3^--N by plants and high leaching losses. Furthermore, temperatures above 30 °C are also expected to increase nitrate loss.
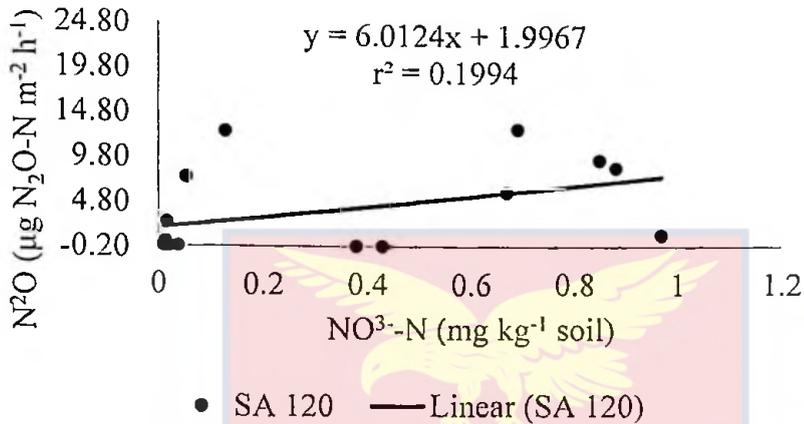
Figure 67: N$_2$O flux (μg m^{-2} h^{-1}) from plots treated with 120 kg N ha^{-1} sulphate of ammonia as a function of nitrate N
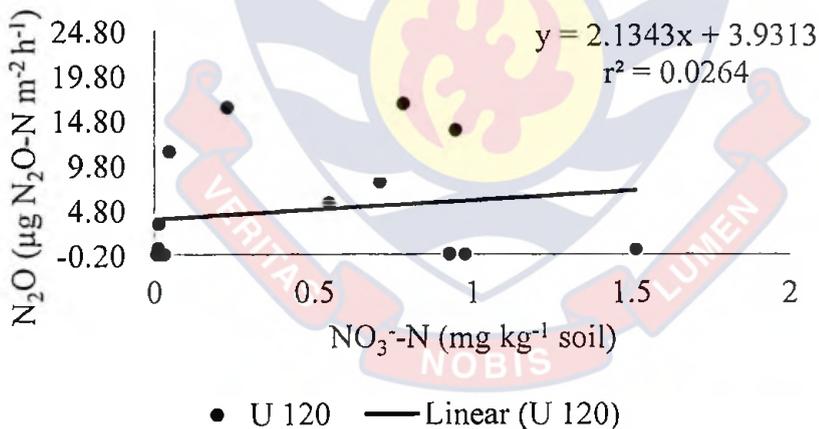
Figure 68: N$_2$O flux (μg m^{-2} h^{-1}) from plots treated with 120 kg N ha^{-1} urea as a function of nitrate N
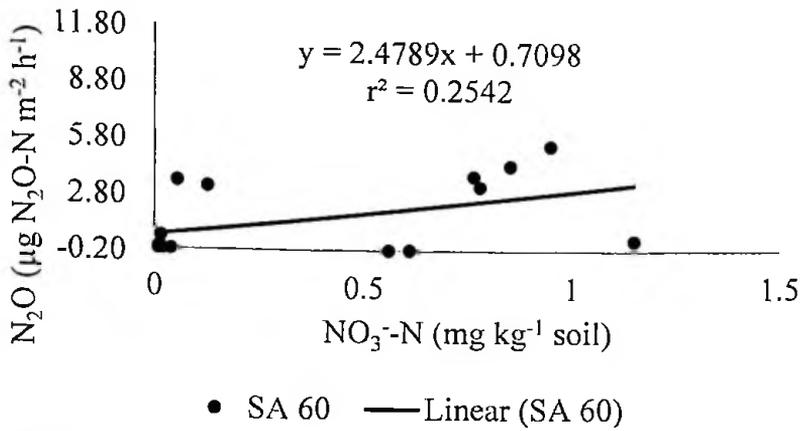
Figure 69: N_2O flux ($\mu g\ m^{-2}\ h^{-1}$) from plots treated with 60 kg N ha^{-1} sulphate of ammonia as a function of nitrate N
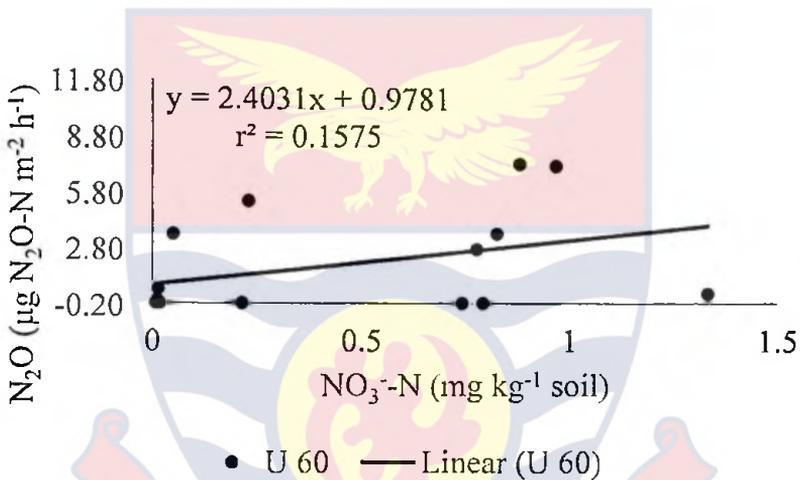
Figure 70: N_2O flux ($\mu g\ m^{-2}\ h^{-1}$) from plots treated with 60 kg N ha^{-1} urea as a function of nitrate N

In this study, soil temperatures measured, both surface and at 10 cm depth were between 30 and 32 °C (See Figures 3, 4, 5 and 6) and this could have also enhanced the decline of NO_3^--N. Linn and Doran (1984), reported similar results indicating no significant relationship between NO_3^--N levels and N_2O emissions. However, other studies have found contradictory results on the relationship between NO_3^--N and N_2O fluxes. For instance, Bowman and Focht (1974) found

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denitrification rates to be dependent upon NO_3^--N concentration. Therefore, the results of this study suggest that the availability of NH_4^+-N influences potential N_2O fluxes whereas N_2O emission may not be strongly dependent on the presence of $NO_3^-- N$. The latter could be attributed to the fact that $NO_3^-- N$ in the soil resulting from mineral N application did not probably exceed crop demand and leaching losses to elevate N_2O emissions. However, in crop production, application of N fertilizer is the main source of N and crop take it up in the form of NH_4^+-N and NO_3^--N. This, therefore would be a regulating factor in N_2O emissions from cropped lands. Therefore, an increase in N availability exceeding crop and microbial demand, and also leaching losses would likely increase N_2O emissions.

Considering the non-significant relationship between NO_3^--N and N_2O in this study, it can be deduced that nitrification was the major source of N_2O in the soils. However, this may not always be the case when other factors such as optimum temperature and soil moisture are limiting.

Cumulative N_2O Emission in Relation to N Fertilizer Input

The emission factor (EF) was calculated as the percentage of N_2O-N emitted, from the amount of the fertilizer N applied. The observation-based EF was calculated from individual fertilization treatments in each year according to the formula of Flechard et al. (2007) as in equation 15.

$$EF\ (\%) = 100 \times \frac{N_2O_{fert} - N_2O_{zero-N}}{k \times N_{fert}} \dots\dots\dots\dots\dots\dots\dots\dots..15$$

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where N_2O_{fert} represents the cumulative N_2O flux (kg N ha^{-1} y^{-1}) in the fertilized plots, and N_2O_{zero-N} is the cumulative flux in the zero-N treatment. N_{fert} denotes the amount of applied N (kg N ha^{-1}). k is 0.9 using the Intergovernmental Panel on Climate Change method (IPCC, 2001).

The average N-induced N_2O emission factors range between 0.10 % and 0.22 % (Figure 71), with an overall EF value of 0.15 %. Maximum EFs obtained from N fertilizer application following the order U 120 > SA120 > U 60 > SA 60 > NPK 60-40-40 (Figure 71).

This EF value obtained from this experiment is by far less than the default mean EF of 1.25 % or 1 % proposed by the IPCC (Bouwman, 1996); (IPCC, 1997 and 2006). However, regional-specific EFs have not been obtained for the Guinea Savanna agro-ecological zone of Ghana so far, therefore, a default value of 1.25 % is still being used for calculating N_2O emissions from soils due to fertilizer application in this area for estimating national EF. This method will probably overestimate the GHG emission inventory in the Guinea Savanna agro-ecological zone of Ghana. Certainly, considering the relatively small experimental plot and only a two-year observation period in this study, the EFs obtained may be considered rough approximation of N_2O losses from the Guinea Savanna agro-ecological zone of Ghana.
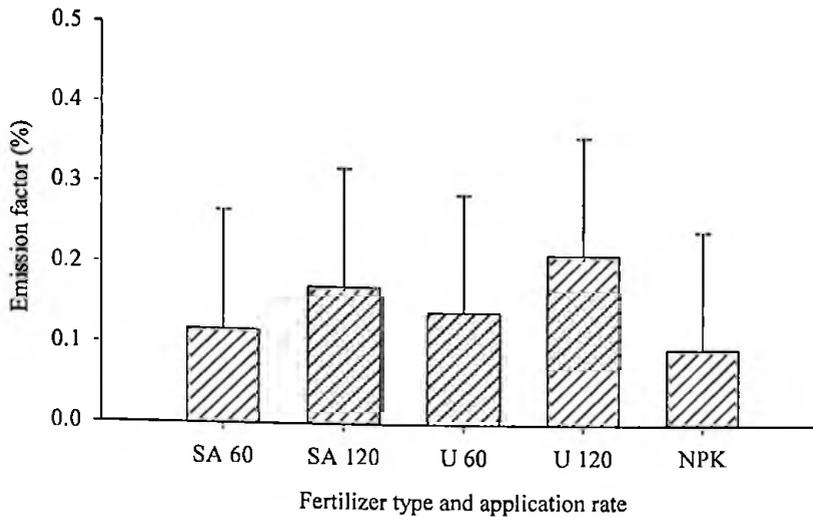
Figure 71: Emission factors (kg N ha y^{-1}) in relation to N fertilizer rate and type (Error bars represent standard deviation)

Response of Grain and Stover Yields to N Fertilizer Application

Results of mean grain and stover yields obtained from this study are presented in Table 3. Grain and stover yields were significantly increased by N fertilization in both years ($p < 0.05$ for both years). In both years maximum grain yields of 2246 and 2446 kg ha^{-1} were obtained from plots that were treated with U 120 kg ha^{-1}. In both years, maize grain yields from N fertilized plots were not significantly different (LSD = 748.7 and 628.7 for years 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 4829 and 5917 kg ha^{-1} respectively. Also, application of N fertilizer produced stover biomasses that were significantly higher ($p < 0.05$) than without N fertilization in both years.

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Table 3- *Mean Grain and Stover Yield*

Treatment	2013		(kg ha⁻¹) 2014		Stover-grain ratio	
Kg ha⁻¹ y⁻¹	Grain	Stover	Grain	Stover	2013	2014
Control	387	2292	420	2591	5.92	6.17
SA: 60	2000	4229	2110	4129	2.11	1.96
SA: 120	2171	5917	2381	5927	2.73	2.49
U: 60	2146	4938	2216	4958	2.30	2.24
U: 120	2246	4542	2446	5142	2.02	2.10
NPK: 60 -40-40	2008	4829	2118	5989	2.40	2.83
LSD	748.7	685.9	628.7	615.9		
CV%	1.2	11.2	1.6	11.2		
p	<0.001	0.022	<0.001	0.021		

Although statistical analysis showed no significant difference (p > 0.05) between grain yields produced in both years among treatments, grain yields in year 2014 were found to be higher than the previous year. Lower rainfall and poor distribution pattern might have accounted for the differences in yields obtained. Again, the relatively short drought spell that occurred following fertilizer application might have affected dissolution of the N fertilizer and it subsequent transport to the plant roots making it unavailable for plant use, resulting in a delay in crop physiological activity at silking and/ or tasseling that caused 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 when crops were tasseling whereas 690 mm of rainfall was recorded in 2014 at the same period.

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The non-linear increase in grain yield with increasing mineral N application from 60 to 120 kg N ha^{-1}y^{-1} could be explained by higher N loss from plots that received 120 kg ha^{-1} y^{-1} N irrespective of the N source. Analysis of agronomic N use efficiency indicated higher N use efficiencies when 60 kg ha^{-1} N was applied irrespective of the N source. Average agronomic N use efficiencies of 29.63, 27.66, 27.50, 16.19 and 15.60 kg kg^{-1} was found from the treatments in the order U 60 > NPK 60-40-40 > SA 60 > U 120 > SA 120, respectively (Table 4).

Table-4 *Agronomic N Use Efficiency Observed on Fertilization*

Treatments (kg ha^{-1} y^{-1})	kg kg^{-1}
U 60	29.63
NPK 60-40-40	27.66
SA 60	27.5
U 120	16.19
SA 120	15.6

Agronomic N use efficiency was calculated using a modified procedure of Hashemi-Dezifooli et al. (1998). This result showed that high amount of N fertilizer reduces N use efficiency. This result supports the findings of Jamaati-e-Somarin et al. (2010) who also reported decline in agronomic N use efficiency with increasing N application from 60–180 kg ha^{-1}.

In both years, the type and rate of N application affected maize grain yield but not significantly. The application of urea was better compared to sulphate of ammonia in its effect on grain yield of the crop. Doubling the rate of N applied (i.e. 120 kg ha^{-1} y^{-1}) as sulphate of ammonia and urea resulted in grain yield increase of

8.6 % and 4.7 % respectively in 2013, and 12.8 % and 10.4 % in 2014. The influence of the two N sources on maize grain yield in both years was superior to the N in the compound fertilizer although not significantly.

Nitrogen fertilization promoted higher grain yield at the expense of vegetative growth. Without N application, stover-grain ratio was 5.92 and 6.17 in 2013 and 2014, respectively. The ratios drastically reduced by using the different source and amount of N application ranging from 2.1 to 2.7 in 2013 and 2.0 to 2.8 in 2014 (See Table 3, page 125). Redistribution of assimilates as a consequence of N fertilization could probably explain the trend observed.

Cumulative Gas Fluxes from Experimental Fields

The application of 120 kg N ha^{-1} SA yielded a total of 4000 kg ha^{-1} CO_2-C at the end of the growing season. This was followed by U 120 with 3000 kg ha^{-1} CO_2-C. Total cumulative CO_2-C from the different treatments is in the order SA 120 > U 120 > U 60 > Control > SA 60 > NPK 60-40-40 (Figure 72). Application of SA 120 significantly ($p < 0.05$) emitted higher cumulative CO_2-C than the other treatments except the U 120.

The highest cumulative N_2O flux at the end of the growing season was by the application of 120 kg N ha^{-1} as urea. This was followed by SA 120. Among the treatments, application of NPK 60-40-40 and SA 60 exhibited the least N_2O flux (Figure 73).

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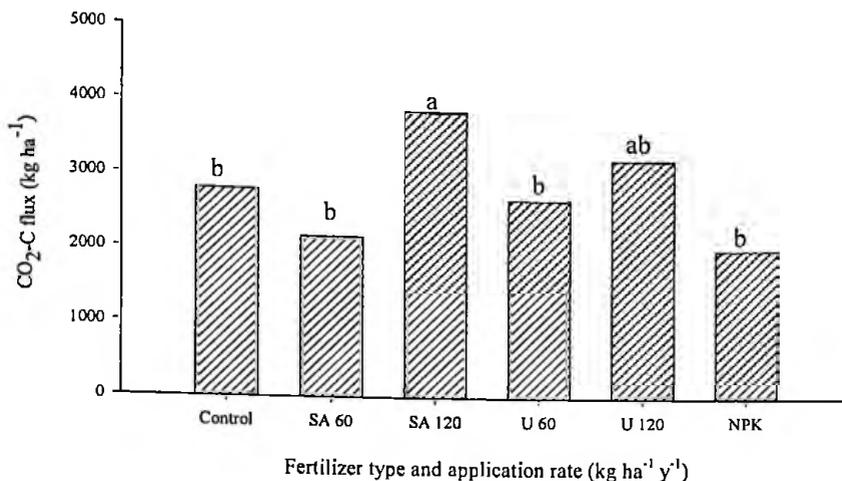
Figure 72: Cumulative CO_2 flux (kg ha^{-1}) of fertilized and unfertilized maize field (Bars with the same letters are not significantly different ($p > 0.05$) from each other)
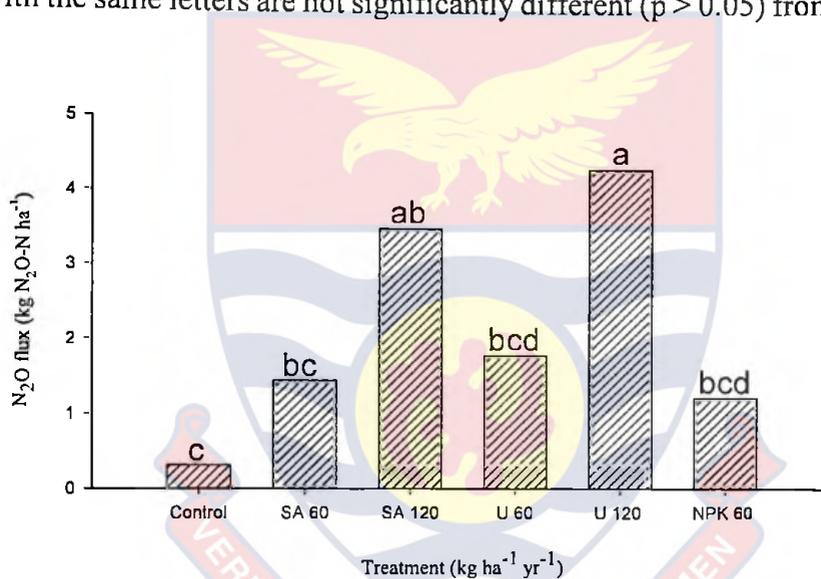
Figure 73: Cumulative N_2O flux (kg ha^{-1}) of fertilized and unfertilized maize field (Bars with the same letters are not significantly different ($p > 0.05$) from each other)

The influence of N fertilizer on the total cumulative N_2O fluxes observed was in the order U 120 > SA 120 > U60 > SA 60 > NPK 60-40-40 > Control. Using 298 as the conversion factor to convert N_2O to CO_2 equivalent as reported by IPCC (2013) the treatments SA 120 and U 120 emitted N_2O-CO_2eq that were 2.5 and 4 times higher than that of plots that were treated with either 60 kg N ha^{-1} y^{-1} sulphate

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of ammonia or urea. Furthermore, NPK 60-40-40, SA 60 and U 60 emitted N_2O-$CO_2 eq$ that were 1.5, 2 and 2 times higher than the control plots, respectively. For instance, Nan Ha et al. (2015) reported 399.4 kg CO_2eq of N_2O was emitted from N fertilized fields when one t ha^{-1} summer maize grain was produced. However, without N fertilization, the emitted N_2O-CO_2 equivalent was 3 times less than that of N_2O-CO_2eq emitted by soils from fertilized plots. Considering the demand for increased food production in Ghana due to increasing population coupled with poor soil fertility in the Guinea Savanna agro-ecological zone, production of crops, especially maize, without N fertilization should be discouraged. Therefore, the use of optimum N fertilizer rates that increases crop productivity with minimum N_2O and CO_2 emissions with less NO_3^--N losses should be considered. Results from this study showed that application of any of the treatments NPK 60-40-40, SA 60 and U 60 that produces an average grain yield of 2 t ha^{-1} with less cumulative N_2O emission and comparatively higher nitrogen use efficiency can be recommended as a good practice. Other studies have reported similar results.

Furthermore, when cumulative CO_2 fluxes emitted were related to grain yield produced, the unfertilized fields emitted the highest CO_2 per grain yield (7.6 kg kg^{-1}) (Figure 74). Although application of SA 120 or U 120 resulted in the highest amount of CO_2 emitted per hectare of cropped field, which was comparatively higher than the CO_2 emitted without N fertilization, CO_2 emitted per kg grain produced was lower. Contrary to the cumulative CO_2 fluxes, which were not significantly different among the treatments (See Figure 72, page 128), grain-

yield-related cumulative CO_2 fluxes were significantly lower in NPK, U60 and U120 as compared to the non-fertilized plots.
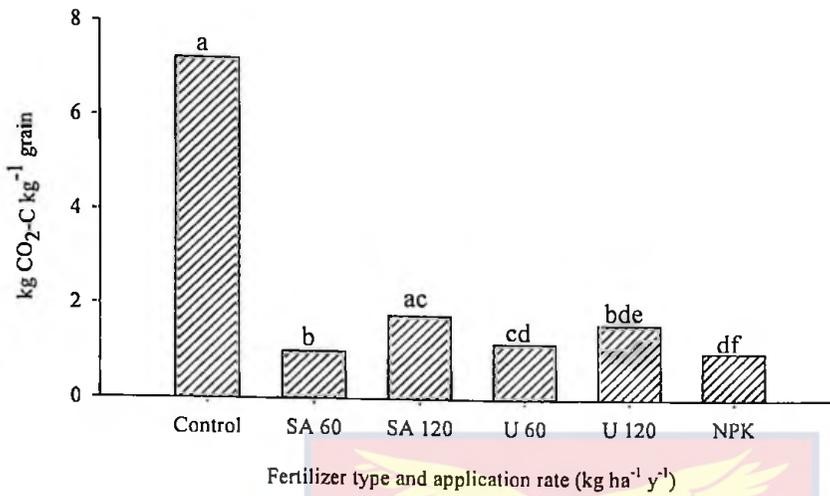
Figure 74: Yield-scaled cumulative CO_2 emissions (kg CO_2-C.kg^{-1} grain) (Bars with the same letters are not significantly different ($p > 0.05$) from each other)

Although studies by Greef, Hansen, Pasda and Diepenbrock (1993) reported that crop production caused GHG emissions and at the same time the crops fixed about 1.6 t of CO_2 per t of biomass produced, the results of this study cannot be related to this phenomenon because CO_2 emission was measured from the soil and also when crop biomass were less.

In U 120 and SA 120 treatments 1.24 and 1.04 g N_2O were emitted per kg grain produced respectively. Meanwhile, the control treatment as well U 60, SA 60, NPK 60-40-40 emitted an average of 0.46 g N_2O kg^{-1} grain (Figure 75). The higher N_2O emitted from U 120 and SA 120 in this study can be attributed to lower nitrogen use efficiency. Although N_2O emitted kg^{-1} grain from plots without N fertilization was low, it however, cannot be regarded as an alternative because it resulted in lower grain yield (See Table 3, page 125).

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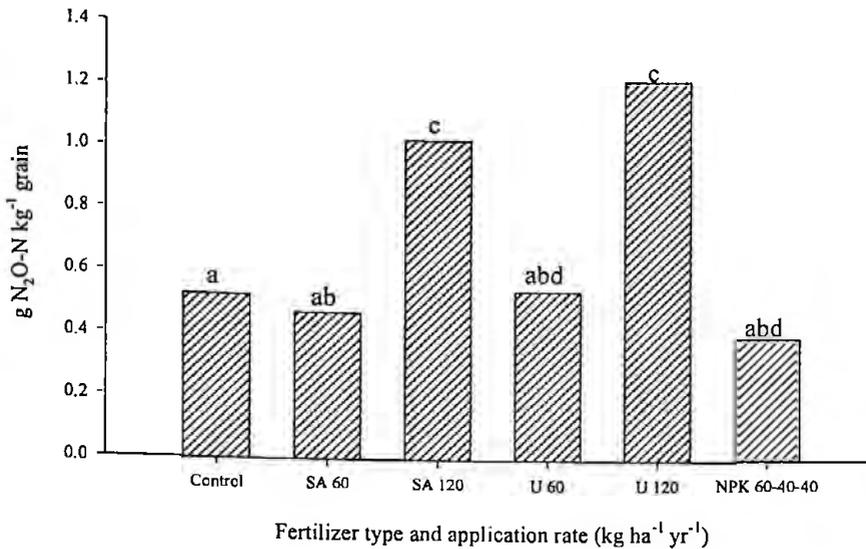
Figure 75: Yield-scaled N_2O emissions (g N_2O-N kg^{-1} grain) (Bars with the same letters are not significantly different ($p > 0.05$) from each other)

The results, therefore, suggest that N application above the economic optimum rate should be avoided. This will improve N uptake by crops compared with N inputs thereby reducing N_2O losses. Furthermore, 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 land such as forest reserves from being converted into agricultural land because intensive crop production allows for high yields per hectare and also increased CO_2 sequestration.

Nitrous Oxide Emissions after Rewetting of Previously Dry Fertilized Ferric Luvisols

Nitrous oxide emissions measured were found to be linear during the incubation period, with standard deviation mainly below 10-15 % of emission

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means. ANOVA showed significant difference within seven hours of incubation period and among treatments. The highest emissions were recorded after seven hours of incubation and were significantly higher ($p < 0.001$) from emission recorded less than one hour of incubation (Figure 76).
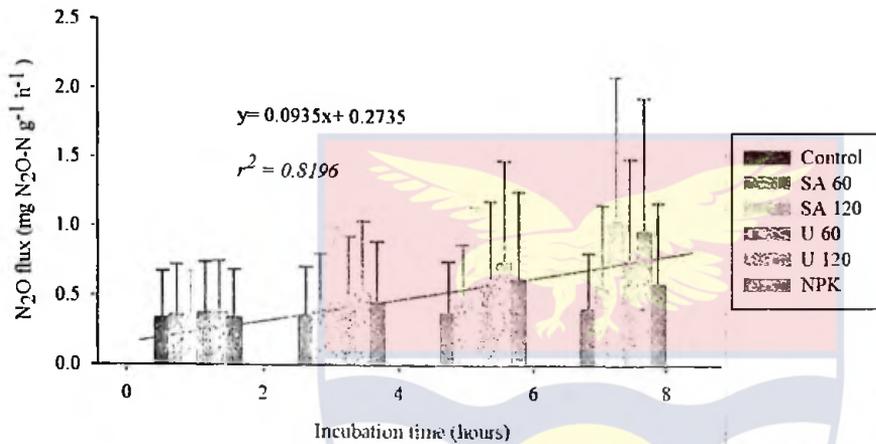
Figure 76: Residual effect of fertilizer treatment on N_2O emission after re-wetting of dry *Ferric Luvisols* (error bars represent standard deviations).

Also, emissions from the application of SA 60 and NPK 60-40-40 were not significantly higher than applying U 60 but were significantly higher than fertilizing with U 120 and SA 120. Emissions from the latter were however not significantly different from each other. Throughout the incubation periods, treatment U 120 showed higher emission rate than the other treatments except at 7 hours of incubation where treatments of SA 120 had the highest emission rate.

The results further showed highly significant differences ($p < 0.001$) among treatment means of all plots. Highest N_2O-N flux per kg dry soil was recorded from plots that received SA 120 kg N ha^{-1} y^{-1} and lowest from plots that received no N

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fertilizer. Mean values of N_2O-N flux per kg dry soil h^{-1} recorded were between 0.00236 ± 0.001168 and 0.00026 ± 0.000173 µg NO_2-N kg^{-1} dry soil h^{-1} (Figure 77). ANOVA analysis showed highly significant effect ($p < 0.001$; Appendix 4) of N fertilizer application on N_2O-N fluxes kg^{-1} dry soil h^{-1}. N_2O-N flux rate increased from 0.03 ± 0.003 without fertilizer application to 0.31 ± 0.019 µg kg^{-1} dry soil h^{-1} with the application of SA 120 (Figure 78).
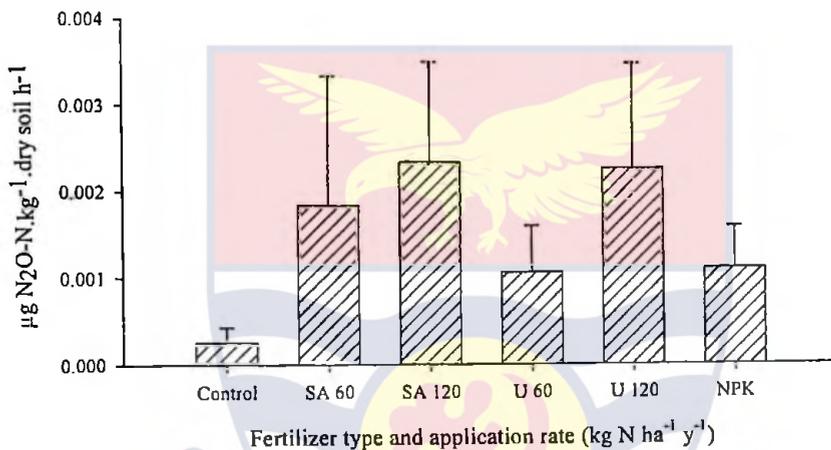
Figure 77: Mean N_2O flux (µg N_2O-N kg^{-1} dry soil) following re-wetting of previously fertilized dry *Ferric Luvisols* at 80 % water holding (error bars represent standard deviations).

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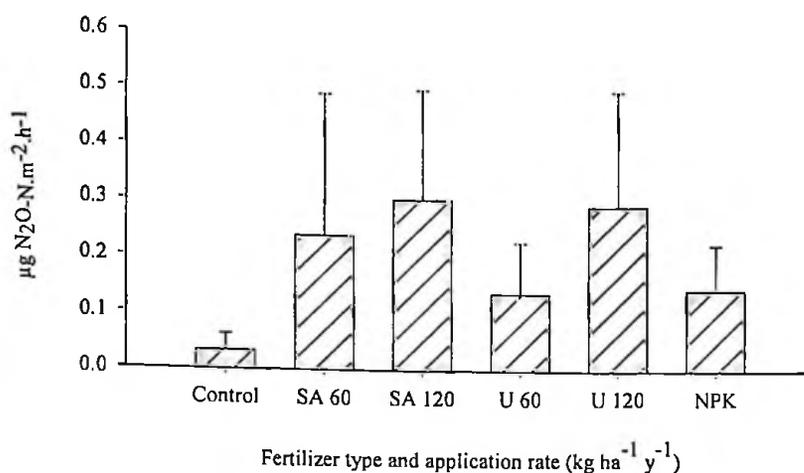
Figure 78: Mean N₂O flux (μg N₂O-N m⁻²) following re-wetting of previously fertilized dry *Ferric Luvisols* at 80 % water holding capacity (error bars represent standard deviations).

Although, composite dry soils from plots treated with SA 120 and U 120 showed higher N_2O-N fluxes on re-wetting, soil from the same treatments with less than 1 % moisture content exhibited negligible flux rate. In many cases it was found to show negative flux rate. Similar results were also observed from dry soil sampled from plots that received no mineral N fertilizer.

Generally, the non-existent N_2O-N fluxes from dried soils is probably because of the associated increases in air-filled porosity which enhanced oxygen inhibition of the denitrifying bacteria and enzymes, and the corresponding decreases in soil volumetric water content that also reduced bacteria motility, and substrate diffusion rates across bacteria cell walls (Sommers et al., 1981) as well as substrate diffusion between and within soil aggregates. This, however, affected denitrification bacterial respiration and the overall bacteria activity and therefore uses the minimum energy to keep body metabolism instead of denitrification. But

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again, as remarked earlier, nitrification could have significantly contributed to N_2O fluxes, if it might not have been the dominant process. Again, the most likely process of N_2O emission was nitrification, and any microbial activity in the dry soil was very likely moisture-limited. The increased soil moisture therefore reduced soil air-filled porosity, increased anaerobic conditions and improved mass diffusion of substrates within bacteria cell wall as well as between and within soil aggregates.

In this study, soil WFPS before rewetting was below 1 %, the N_2O-N fluxes obtained after rewetting was on the average 80 % higher than the fluxes from dried soil irrespective of the treatments. Furthermore, soil from high N fertilized plots showed higher N_2O-N fluxes and was significantly different from plots without N fertilization and also the dry soil. Xiaobin, Craig, Xueming, Daniel and Ruqin (2013) reported higher N_2O emissions from soils with 10 % water filled porosity and below which is contradictory to the findings of this study. Furthermore, studies by Groffman and Tiedje (1991) and Davidson (1992) also showed that N_2O production by denitrification following rewetting of soil was associated with an increase in substrates availability. Probably the greater the degree of soil drying before rewetting the greater the concentrations of microbial, soluble, and respiratory pools of C in the soil as reported by Williams and Xia (2009) and this may probably be the case in this study. Again, the study by Xiaobin et al. (2013) on normalized denitrification enzyme activity (DEA) indicated that soil denitrifier activity decreased significantly during soil drying, but increased significantly after rewetting. Guo, Drury, Yang and Zhang (2010) also found that repeated drying and rewetting cycles could increase soil DEA. In that study, the normalized DEA values

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after rewetting the driest soils (10 and 20% WFPS) were similar, but the corresponding N_2O emissions differed substantially. Hence, they concluded that substrate availability could contribute significantly to enhancing N_2O emissions after rewetting dry soils. Although normalized DEA was not studied under this experiment, the rewetting is, however, peculiar to this study, and therefore the difference in N_2O-N emission observed in the present study after rewetting that was found to be higher in soils with higher N input could be attributed to the substrate availability.

Nitric Oxides (NO) and Nitrogen Dioxide (NO₂) Emissions after Rewetting of Previously Dry Fertilized Ferric Luvisols Soil

Nitric oxide (NO) measured following dry conditions and subsequent rewetting showed significant ($p < 0.001$) values between N source fertilizer and amount. Nitrous oxide flux following rewetting of dry soil at 60 % water holding capacity was significantly high among treatments. Nitric oxide mixing ratios at 60 % WHC monitored for 14 h was between 1 ± 0.01 and 80 ± 5 ppb from soils that have been previously planted with maize and received N fertilization. (Figure 79).

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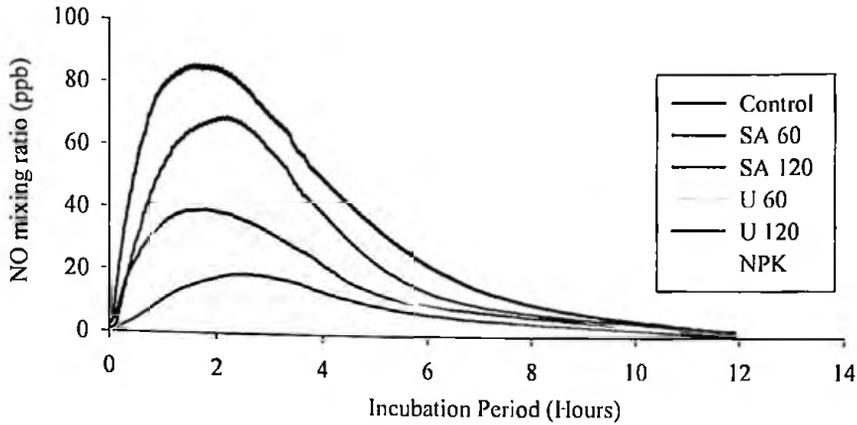
Figure 79: NO production after re-wetting of previously fertilized dry *Ferric Luvisols* at 60 % water holding capacity

The highest NO mixing ratio at 60 % water holding capacity occurred with soil from plots treated with SA 120 and U 120 while the least observed fluxes were from plots without N fertilization throughout the 14 h incubation period (Figure 79) respectively. Nitric oxide flux showed significant differences ($p < 0.001$; LSD = 0.073) among treatment means upon rewetting to 60 % water holding capacity. Mean NO flux h^{-1} was in the order of soils with N fertilization < SA 60 < U 60 < NPK 60-40-40 < U 120 < SA120.

During the incubation period, highest emissions were recorded between 2 and 4 hours after incubation after which emission rate declined. There was a sharp increase in emission immediately after rewetting for the first hour of incubation which stabilized for approximately 30 minutes and then declined sharply. The rate of NO emission was significantly reduced after 6 h of incubation. Cumulatively, rewetting of soils to 80 % water holding capacity showed a contrary pattern. Incubation period lasted for approximately 6 hours. Soils treated with SA 60 showed the highest peak emissions approximately 2 h after incubation although NO

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emissions at this period was lower than when soils were rewetted to 60 % water holding capacity (Figure 80).
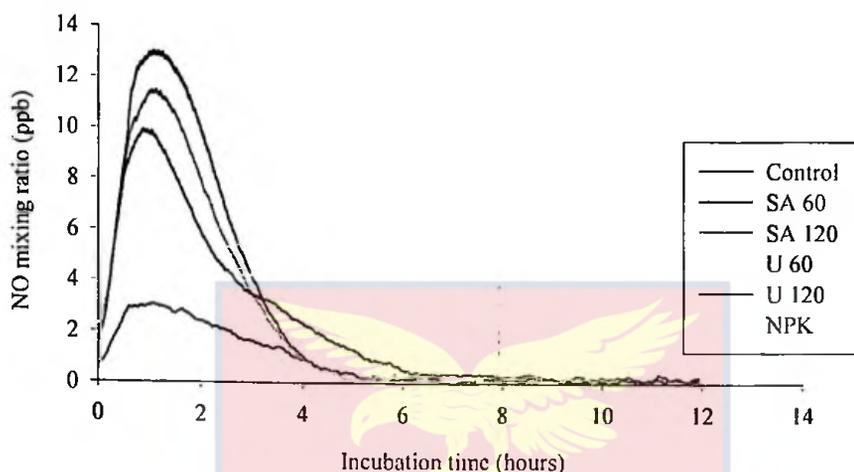
Figure 80: NO production after re-wetting of previously fertilized dry *Ferric Luvisols* at 80 % water holding capacity

Although soils which were fertilized with SA 60 showed the highest peak flux, substantial significant NO flux ended approximately 4.5 hours after incubation. Soil that was treated with U 120 continued to show NO flux until 6 h of incubation. However, rewetting at both 60 and 80 % water holding capacities and without N fertilizer had the lowest emission rate throughout the incubation period.

Mean NO flux soil was between 0.045 ± 0.01 and 2.10 ± 0.40 µg NO-N flux kg^{-1} dry soil h^{-1} (Figure 81) for the control and SA 120 treatments, respectively. Again, NO fluxes from the application of SA 60 and U 60 were found not to be significantly different from control, whereas soils treated with SA 120 and U 120 were found to be significantly higher from the control treatment. Mean NO fluxes

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$m^{-2} h^{-1}$ obtained was between 12 ± 2.6 and 554 ± 106 µg NO-N $m^{-2} h^{-1}$ (Figure 82) for the control and SA 120, respectively.
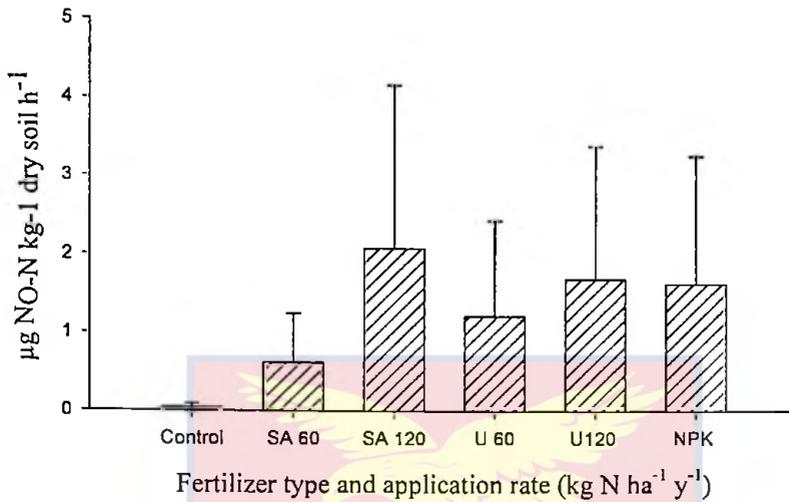
Figure 81: Mean NO flux (µg NO-N $m^{-2} h^{-1}$) following re-wetting of previously fertilized dry *Ferric Luvisols* to 60 % water holding capacity (error bars represent standard deviations)
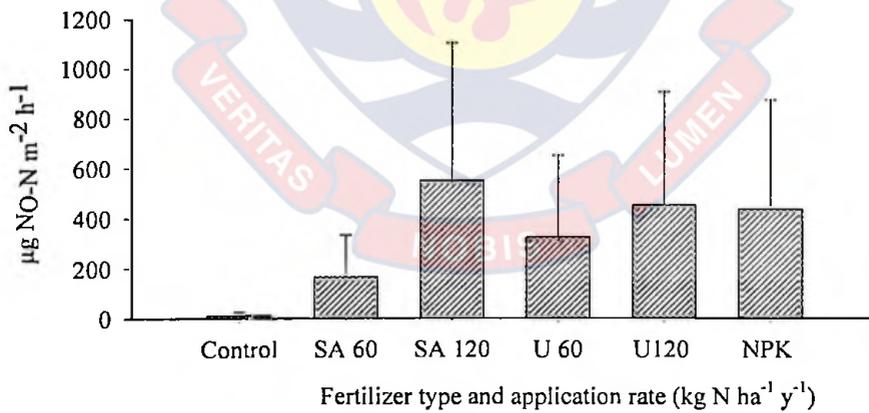
Figure 82: Mean NO flux (µg NO-N $kg^{-1} h^{-1}$ dry soil) following re-wetting of previously fertilized dry *Ferric Luvisols* to 60 % water holding capacity (error bars represent standard deviations)

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However, there was no significant effect ($P > 0.05$) of rewetting soil to 80 % water holding capacity on NO-N flux rate (Appendix 7). Highest NO flux was detected from soils treated with U 60 kg N ha^{-1} y^{-1}. Nitric oxide was between 0.031 ± 0.01 and 0.15 ± 0.001 µg NO-N flux kg^{-1} dry soil h^{-1} (Figure 83). Mean NO flux recorded from plots treated with U 120, SA 60 and U 60 were significantly higher ($p < 0.05$) than from plots that received no mineral N fertilizer (LSD = 0.058; Appendix 8).
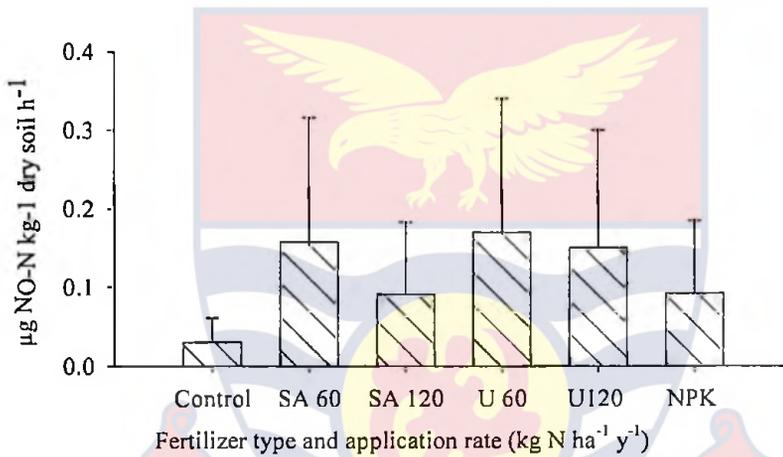
Figure 83: Mean NO-N flux (µg NO-N kg^{-1} dry soil) following re-wetting of previously fertilized dry *Ferric Luvisols* to 80 % water holding capacity (error bars represent standard deviations)

Rewetting to 80 % water holding capacity affected NO flux significantly ($p < 0.05$; Appendix 9). Mean NO fluxes observed from plots treated with U 120, SA 60 and U 60 were significantly higher ($p < 0.05$) than the mean NO-N flux from the control treatment. Mean NO-N flux ranged between 8.2 ± 4.54 and 45 ± 0.35 µg NO-N flux m^{-2} (Figure 84).

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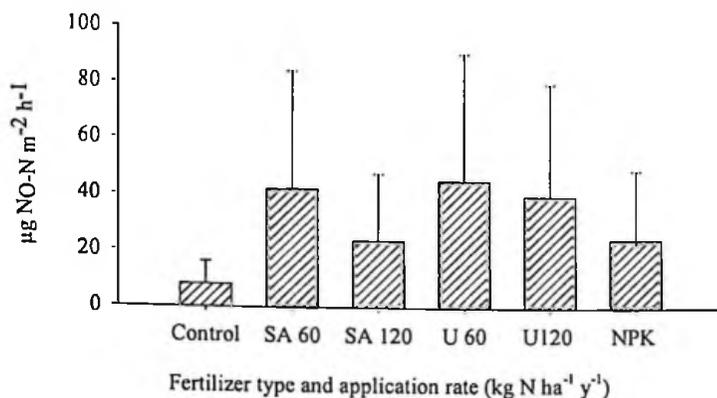
Figure 84: Mean NO-N flux (μg NO-N m^{-2} h^{-1}) following re-wetting of previously fertilized dry *Ferric Luvisols* to 80 % water holding (error bars represent standard deviations)

Mean fluxes obtained were in the order of no fertilization < SA 120 < NPK 60-40-40 < U 120 < SA 60 < U 60. Meanwhile, mean NO fluxes m^{-2} h^{-1} from fertilized plots were all found not to be significantly different (LSD= 16.04) from each other.

Nitrogen dioxide emission in most cases ended after 10 h of incubation even though it was measured simultaneously with NO. Similar to NO emissions, at 60 % water holding capacity, higher emission peaks were observed 2 h after incubation followed by a sharp decline 3 h after. Also, higher NO$_2$ emission peaks were obtained from plots treated with U 120 and SA 120. During the incubation period, application of U120 showed the highest mixing ratio peak of 18 ± 5.82 ppb (Figure 85). Again application of SA 120 showed the highest mixing ratio peak when soil was rewetted to 80 % WHC (Figure 86).

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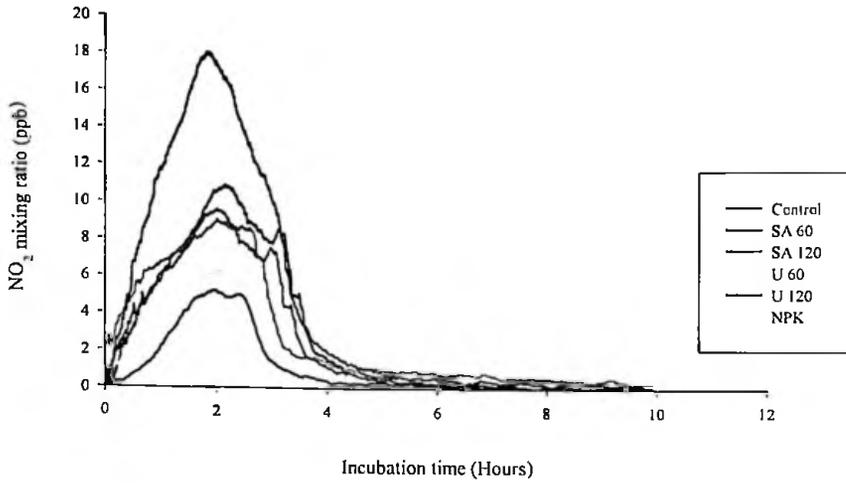
Figure 85: NO_2 production after re-wetting of previously fertilized dry *Ferric Luvisols* to 60 % water holding capacity

Figure 86: NO_2 production after re-wetting of previously fertilized dry *Ferric Luvisols* to 80 % water holding capacity

Both NO_2 flux on soil dry weight or on a soil area basis followed similar response. Highest NO_2-N flux kg^{-1} dry soil h^{-1} was obtained from U 120 kg N ha^{-1} y^{-1} with plots that received no N fertilizer. NO_2 flux obtained was between 0.6 ± 0.03 and 0.77 ± 0.50 µg NO_2 flux kg^{-1} dry soil h^{-1} for plots that received no N fertilizer, and U 120 (Figure 87). Similarly, NO_2 flux on an area basis was between 0.1 ± 0.1 and 20.6 ± 8.1 µg NO_2-N flux m^{-2} h^{-1} for plots that received no N fertilizer and U 120,

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respectively (Figure 88). Again, only SA 120 and U 120 exhibited NO_2 flux on area basis that was significantly higher than from the control (See Appendix 10).
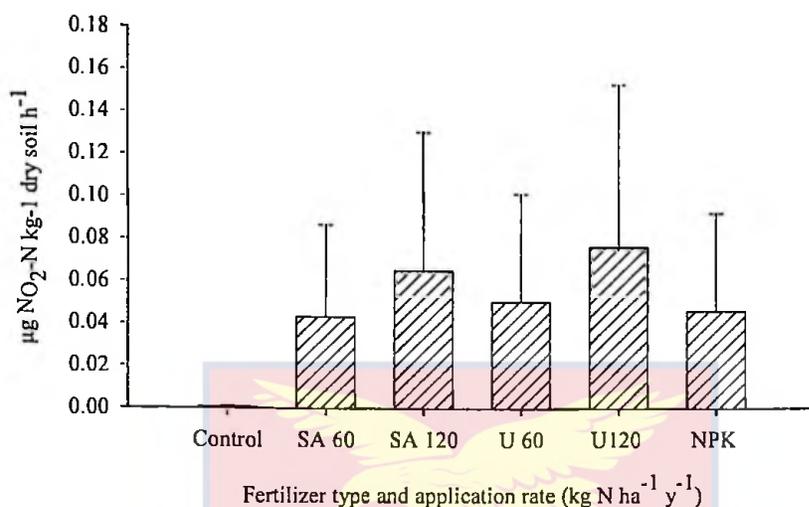
Figure 87: Mean NO_2 flux (μg NO_2-N kg^{-1} dry soil h^{-1}) following re-wetting of previously fertilized dry *Ferric Luvisols* at 60 % water holding capacity (error bars represent standard deviations)
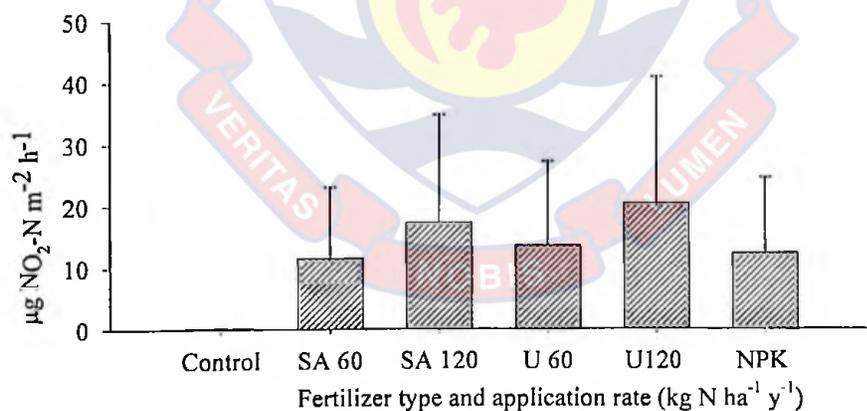
Figure 88: Mean NO_2 flux (μg NO_2-N m^{-2} h^{-1}) following re-wetting of previously fertilized dry *Ferric Luvisols* at 60 % water holding capacity (error bars represent standard deviations)

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Finally, rewetting to 80 % water holding capacity did not influence NO_2-N flux significantly (p > 0.05). Although all treatments exhibited higher NO_2 fluxes that were higher than the control, ANOVA showed no significant difference among them (p > 0.05). Only plots of SA 120 and U 120 exhibited NO_2 fluxes that were significantly higher than the fluxes recorded from soils without N fertilization (Appendix 11). Neither the fertilizer rate nor the type applied had a significant influence on the flux rates (Figures 89 and 90).

The results obtained from this study indicate that NO flux was influenced by availability of soil moisture as dry soils did not show significant emission rate, either on a soil dry weight or also on an area basis. Generally, initial rewetting to 60 % water holding capacity affected NO fluxes positively. Also the presence of substrate N played a major role in the NO emissions. Nitrogen containing fertilizers sulphate of ammonia, urea and NPK compound fertilizer influenced significantly
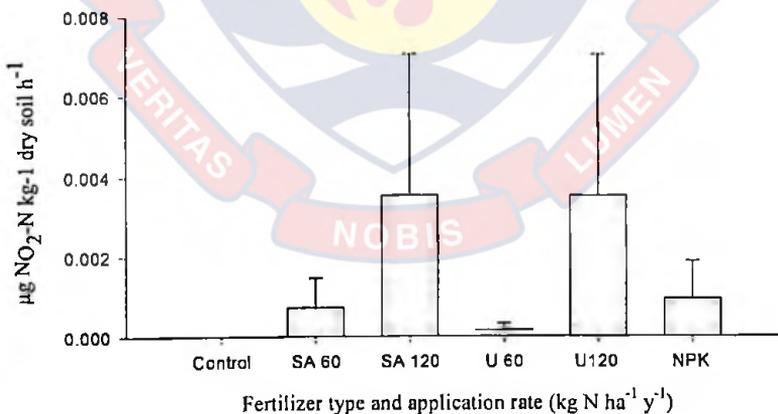
Figure 89: Mean NO_2-N flux ($\mu g\ NO_2$-N kg^{-1} dry soil h^{-1}) following re-wetting of previously fertilized dry *Ferric Luvisols* at 80 % water holding capacity (error bars represent standard deviations)

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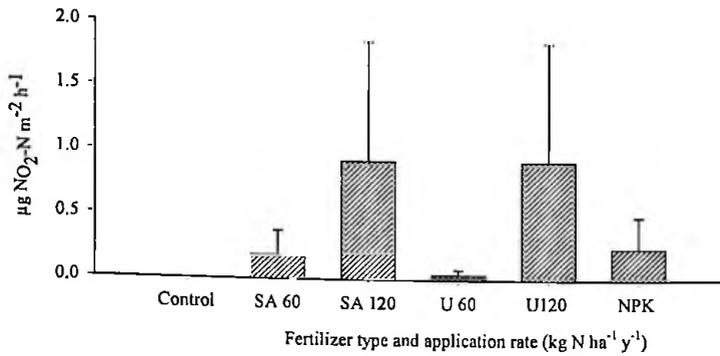
Figure 90: Mean NO_2-N flux (μg NO_2-N m^{-2} h^{-1}) following re-wetting of previously fertilized dry *Ferric Luvisols* at 80 % water holding capacity (error bars represent standard deviations)

NO flux. At 60 % water holding capacity, NO flux rate was greatly influenced by the type and rate of N fertilizer applied. In most cases, soil from plots that received sulphate of ammonia had higher NO-N fluxes than those from urea-fertilized plots even though differences were not significant. The results further showed that higher N of 120 kg N ha^{-1} y^{-1}, also affected NO flux when soil moisture was initially at 60 % water holding capacity and when it was subsequently increased to 80 %. However, at 80 % water holding capacity, NO flux was not affected by type of N source. In general, significant flux at 60 % water holding capacity occurred between one and 4 h within the 14 h period, whereas at 80 % water holding capacity, emissions occurred in the first three hours of incubation. However, in almost 70 % of the incubation period, emission was below detectable levels and this therefore accounted for the higher standard deviation of means.

The sharp increase in NO and NO_2 emissions for the initial 2 h of incubation is probably due to higher cell number proliferation of bacteria responsible for nitrification at the initial stages when water holding capacity was increased from <

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1 to 60 %, however, the decline of only NO and NO_2 after 3 h of incubation may be due to higher NO consumption and may not possibly be a result of low NO production. The presence of ammonia oxidizing bacteria, which includes a few different kinds of bacteria that all make a living by generating reducing power from the oxidation of ammonia and using that energy to fix carbon dioxide might have caused the increment (Bock & Wagner, 2006). It can therefore be stated in this study that NO was by nitrification in the initial stages of incubation, however, at higher water content, the process shifted to denitrification which resulted in a continuous production of N_2O after 3 hours of incubation.

Results of linear correlation of NO with N_2O (Figure 91) in this study further confirms the above assertions. Positive correlation of NO with N_2O was observed with an r^2 of 0.70.
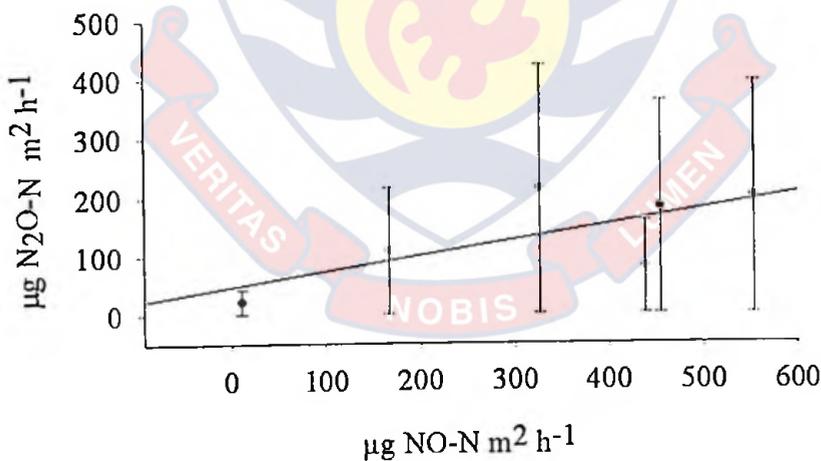
Figure 91: Correlation between NO and N_2O flux rate at 80 % water holding capacity (error bars represent standard deviation)

Soil N Mineralization and Immobilization

Soil from plots that received no N fertilizer, SA 60, U 120 and U 60 had higher NH_4^+ concentration before incubation compared with concentrations obtained after incubation. On the other hand, soils SA 120 and NPK showed the opposite except. Statistically, the results showed no significant differences ($p > 0.05$) among treatment means of NH_4^+ concentrations obtained before and after incubation. Mean NH_4^+-N values before incubation was between 0.67 ± 0.04 and 0.84 ± 0.22 mg kg^{-1} dry soil (Figure 92) while the NH_4^+-N concentration recorded after incubation ranged between 7.98 ± 3.87 and 10.47 ± 2.43 mg kg^{-1} dry soil from plots that received no N fertilizer and SA 120, respectively.

The results in Figure 90 showed that only soil that was previously fertilized with U 60 and SA 120 had higher NO_3^- concentration before incubation. Whiles the rest of the treatments produced lower levels of NO_3^--N before incubation. Mean concentrations of 0.44 ± 0.08 and 0.56 ± 0.17 mg NO_3^- kg^{-1} dry soil for soils of
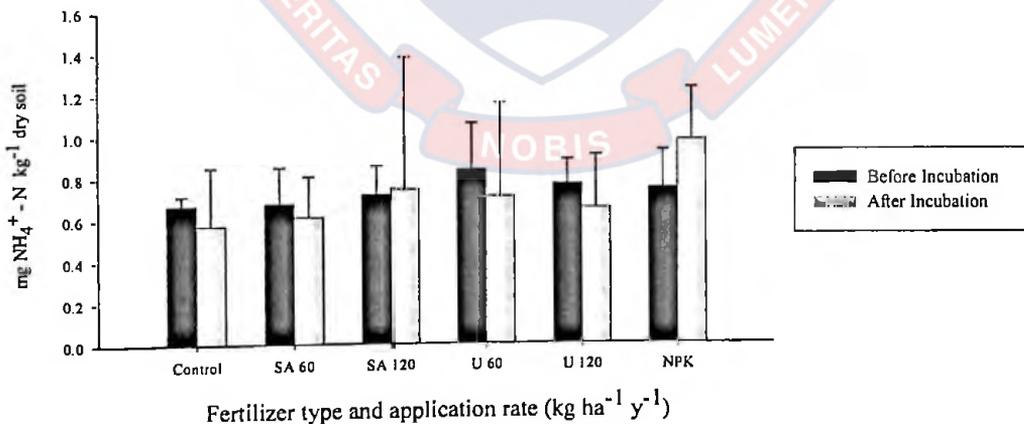
Figure 92: Mean soil NH_4^+ content before and after incubation (error bars represent standard deviation)

NPK 60-40-40 and SA 120, respectively were obtained (Figure 93). The results further showed that, after 14 h of incubation, application of SA 60, U 120 and NPK 60-40-40 increased the NO_3^- concentrations although not significantly over the control ($p > 0.05$) of the increments. A decline in NO_3^- concentration due to the application of U 60 and SA 120 was observed but the differences were not significant ($P > 0.05$). Mean values recorded ranged between 6.81± 0.89 and 11.3 ± 2.35 mg NO_3 kg^{-1} dry soil and 0.44 ± 0.08 and 0.58 ± 0.24 mg NO_3-N kg^{-1} dry soil for soils without N fertilization and NPK 60-40-40, respectively (Figure 93).
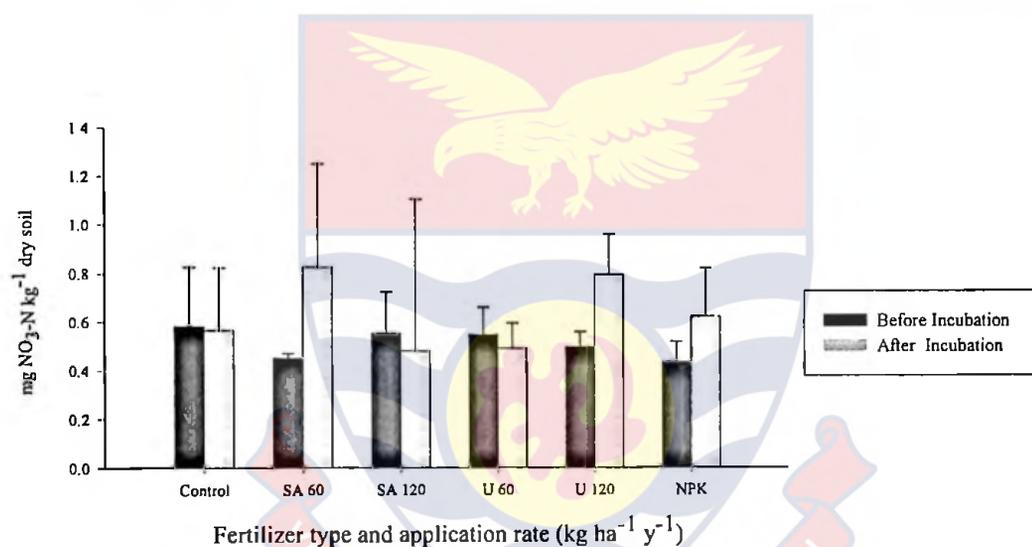
Figure 93: Mean soil NO_3^- content before and after incubation (error bars represent standard deviation)

The results clearly suggest both nitrification and denitrification processes occurred during the incubation period. NH_4^+-N concentrations increased at 30 and 4.1 % for soils that received NPK 60-40-40 and SA 120, respectively, whereas soils without N fertilization, as well as SA 60, U 60 and U 120 had NH_4^+ reduced by between 9 and 15 %, respectively (See Figure 92, page 147). However, there were

increases in NO_3^- concentration in soils following the application of NPK 60-40-40, and U 120 at 43, and 60 % WHC respectively. There was a significant decline in NH_4^+ and NO_3 concentrations in soils without N fertilization. Both NH_4^+ and NO_3 concentration reduced by 14 and 2.4 %, respectively. This is evident from the N_2O and other N trace gas data obtained in this study, where consistently soils from NPK 60-40-40 showed lowest N emissions whereas soils of U 120 also showed considerable amount of NO and NO_2 emissions.

Analysis of soil total nitrogen showed no significant differences among treatment means. Higher initial total N was recorded from soils treated with U 60 (Figure 94) although as stated earlier, the difference was not significantly different from the control treatment ($p > 0.05$; Appendix 12). The NPK treatment showed the highest N after 24 h of incubation while U 60 treatment had the lowest total N content (Figure 94). Again, after 24 h of incubation, treatments SA 120 and U60 showed a decline in total N content of 12 and 15 % respectively.
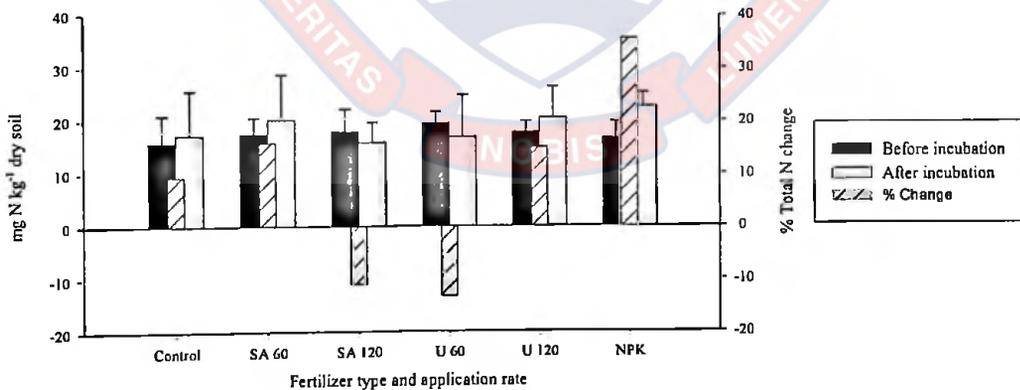
Figure 94: Mean total soil N before and after incubation (error bars represent standard deviation)

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Fate of Excess Fertilizer N in Soils

Results of the ^{15}N isotopic tracing experiment in the laboratory to determine the fate of excess N fertilizer applied to soils in the laboratory study is presented and discussed in this section with emphasis on isotopic signature of N_2O emissions from soils without N fertilizer and with ^{15}N-labeled urea fertilizer. All the soils that received N fertilizer had ^{15}N atom % values higher than plots that received no N fertilizer, However, only the NPK 60-40-40 treatment was significantly different ($p < 0.05$) from all the other treatments, i.e. no mineral N fertilizer, SA 60, SA 120, U 60 and U 120 kg N ha^{-1} y^{-1} (Figure 95).
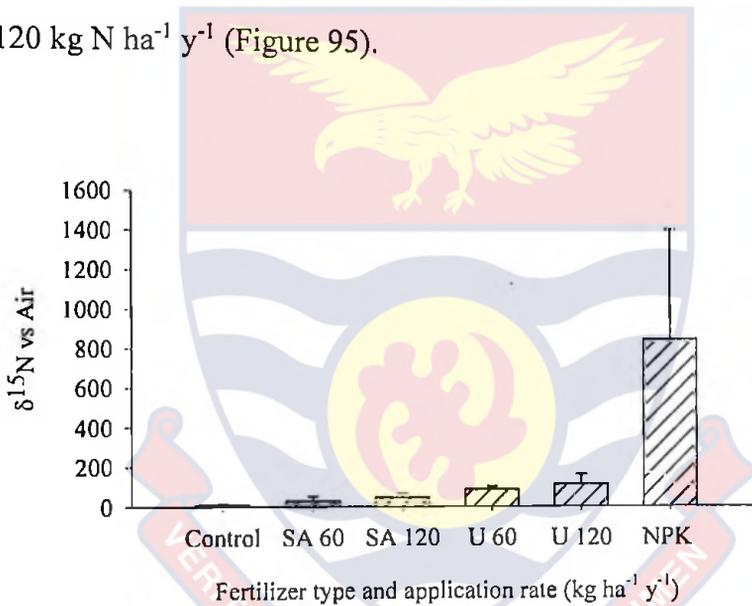
Figure 95: δ ^{15}N value of the measured N_2O from soils after fertilization (error bars represent in standard deviation)

Furthermore, ^{15}N atom % obtained for SA 60 and 120 were found to be lower than those obtained when U 60 and U 120 were applied. The ^{15}N atom % values were 0.391 ± 0.007, 0.397 ± 0.005, 0.411 ± 0.005, 0.420 ± 0.01 for of SA 60, SA 120, U 60 and U 120, respectively. However, they were not significantly

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different (p > 0.05) from each other (LSD = 0.008). The ^{15}N-depleted N losses during microbial decomposition of organic matter alongside the downward movement of residual substrate and continues application of inorganic fertilizer over time are the possible causes of higher $\delta^{15}N$ values in soils treated with N fertilizer than in the non-N fertilized soils. This results is consistent with findings by Yuqing et al. (2010) who reported higher $\delta^{15}N$ values of top-soils that exhibited significant dependence on the cumulative rates of NH_3 volatilization, net nitrification and denitrification. The implications are that, higher $\delta^{15}N$ from soils will have a strong influence on chemical composition of crops. This mechanism could be used to determine whether farm products were cultivated using chemical or organic fertilizers.

Meanwhile, $\delta^{15}N$ values for the central and terminal N atom followed the same pattern as observed in the δ^{15} N (Figure 96). The $\delta^{18}O$ values spread out over a higher variability among replicates than $\delta^{15}N$ values (Figure 97). $\delta^{18}O$ values obtained in this study ranged between +26.69 ‰ and +63. 78‰ for soils without N fertilization and the N fertilized soils. This result is contradictory to the findings of Voerkelius (1990); Durka, Schulze, Gebauer, and Voerkelius (1994) who reported a relatively tight cluster of $\delta^{18}O$ values in the range of +55 to +75 ‰. However, considering the limited data on the $\delta^{18}O$ of nitrate in atmospheric deposition, with almost nothing known about possible spatial or temporal variability, or their causes which influences the nitrate content of soil, the large range in $\delta^{18}O$ values observed in this study could be due to fractionations associated with nitrate formation in thunderstorms and photochemical reactions in the

Other studies have also established the range of $\delta^{18}O$ into two modes. The lower mode of $\delta^{18}O$ is between +22 and +28 ‰, and the higher mode has values ranging from +56 to +64 ‰. Meanwhile it is speculated that natural atmospheric nitrate of $\delta^{18}O$ values might be around +23 ‰, the $\delta^{18}O$ value of atmospheric O_2. However, given the large $\delta^{15}N$ range of nitrate and ammonium produced by different reactions and degrees of equilibration in the atmosphere (Heaton, 1987; Freyer, 1991) and continues N fertilization in the Guinea Savanna agro-ecological zone could have pushed the $\delta^{18}O$ values in this study to the higher mode.

The higher $\delta^{18}O$ values in this study would influence temperature of precipitation and groundwater or mineral interactions. Epstein, Buchsbaum, Lowenstam and Urey (1953) estimated that a $\delta^{18}O$ increase of 0.22 ‰ is equivalent to a cooling of 1 °C. Finally, the $\delta^{18}O$ in this study also reflects local evaporation.

Results of soil samples analyzed for ammonium, nitrate and nitrite before and after incubation showed no significant differences among treatments. The N content was determined using an elemental analyzer (vario EL Cube, Elementar Analysensysteme, Hanau, Germany). Average nitrate and nitrite content before incubation were found to be < 0.3 and < 0.1 µg/L for both fertilized and unfertilized plots, respectively and remained unchanged even after 24 h of incubation. On the contrary, ammonium concentration before incubation ranged between 0.8 ± 0.28 in the control and 1.7 ± 0.22 mg kg^{-1} soil for the U 120 treatment (Figure 98). There was consumption of ammonium during the incubation period. Ammonium concentration of plots without N fertilization decreased by 20 %, whereas that of the plots that received N fertilizer reduced by 38 %. Statistical analysis indicated

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that apart from U 120 treatment that yielded significantly higher NH_4^+-N than the non-fertilized plots, and NPK treatment, the rest of the treatments did not significantly influence the NH_4^+-N concentration in the soil ($p > 0.05$).
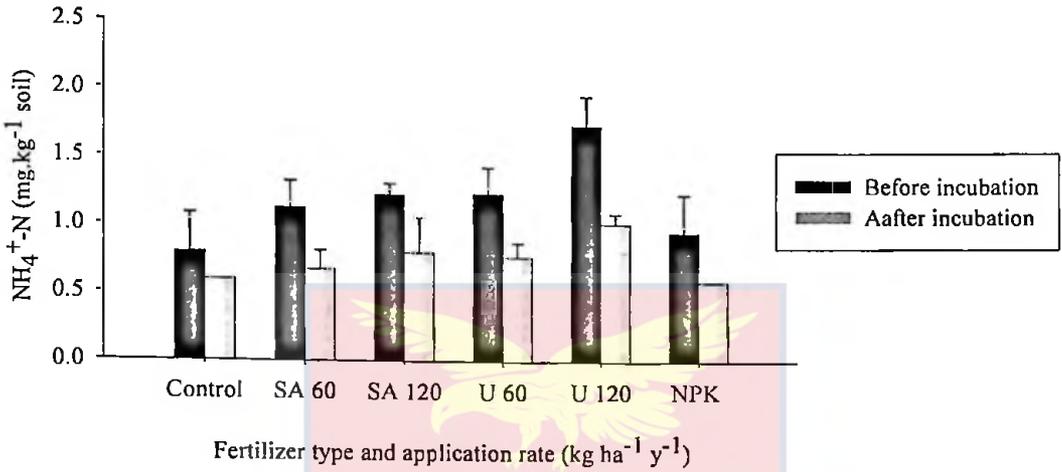
Figure 98: Mean soil NH_4^+ content before and after incubation with addition of ^{15}N-labeled fertilizer (error bars are standard deviation)

Calibration and Validation of DNDC Model to Predict N_2O Flux

The annual N_2O emission for the different treatments estimated using observed data were in the range of 0.5 to 4.5 kg N_2O -N ha^{-1} y^{-1} from soils that received no fertilizer application and urea was applied at 120 kg ha^{-1} y^{-1} (See Figure 73, page 128). The DNDC simulation resulted in an annual flux range of between 2.27 to 5.25 kg N_2O -N ha^{-1} y^{-1}, for plots that were not treated with fertilizer and plots treated with 120 kg N ha^{-1} y^{-1}. The was positive relationship between measured and modeled annual N_2O fluxes from *Ferric Luvisols* for 2013 field experiments with an r^2 of 0.7773 y = 0.1383x + 4.6483 (Figure 99).

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For the validation period (2013) the predicted N_2O emissions simulation agreed practically well with the observed data (See Figure 73, page 128). For all treatments the measured annual N_2O fluxes ranged from 0.3 to 4.2 kg N_2O-N ha^{-1} y^{-1}. Mean annual N_2O fluxes varied considerably between N amount applied and source with maximum emission from soils treated with 120 kg N ha^{-1} in both measured and simulated data. Across all treatments, mean N_2O flux ranged from 2.27 to 2.56 kg N_2O -N ha^{-1} y^{-1} for simulated data.
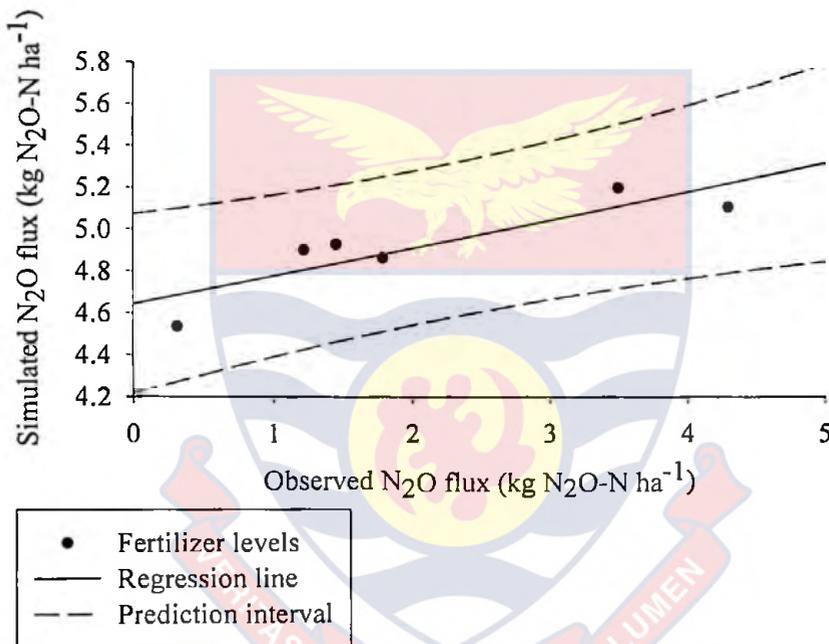
Figure 99: Validation of DNDC model to predict N_2O flux from N fertilized maize plots in the Guinea Savanna agro-ecological zone of Ghana

These results showed that the DNDC model can be used to predict greenhouse gases especially N_2O flux from the Guinea Savanna agro-ecological conditions of Ghana. Simulated results further indicate that application of 120 kg N ha^{-1} in the form of sulphate of ammonia or urea increases the heat trapping

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capacities of the atmosphere compared to application of same N source at 60 kg N ha^{-1} (Figure 100).

Application of 60 kg N ha^{-1} as urea or sulphate of ammonia resulted in improved crop N uptake compared with when 120 kg N ha^{-1} was applied as urea and sulphate of ammonia (Figure 101). This is in agreement with results obtained from the field measurement where agronomic N use efficiency was higher for application of 60 kg N ha^{-1} urea or ammonia, (See Table 4, page 126). The low crop N uptake and increased N leached from plots without N fertilization could be as a result of poor crop canopy that leaves the soil surface bare exposing it to intense rains which leached N beyond crop root zones.
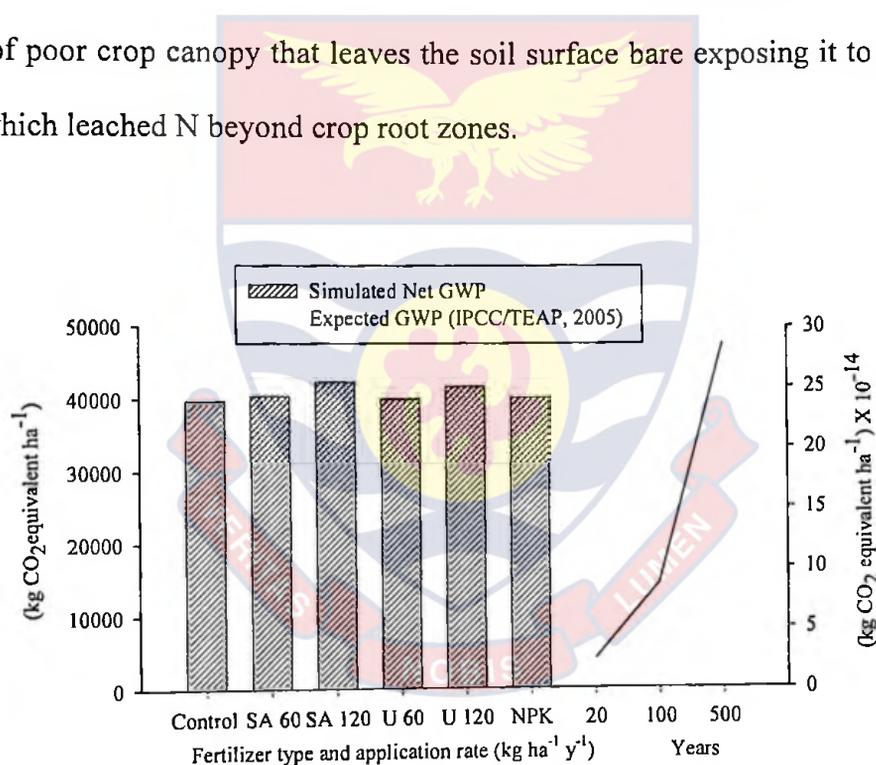
Figure 100: Simulated Global warming potential of N fertilized maize plots at Akukayilli in the Guinea Savanna agro-ecological zone of Ghana

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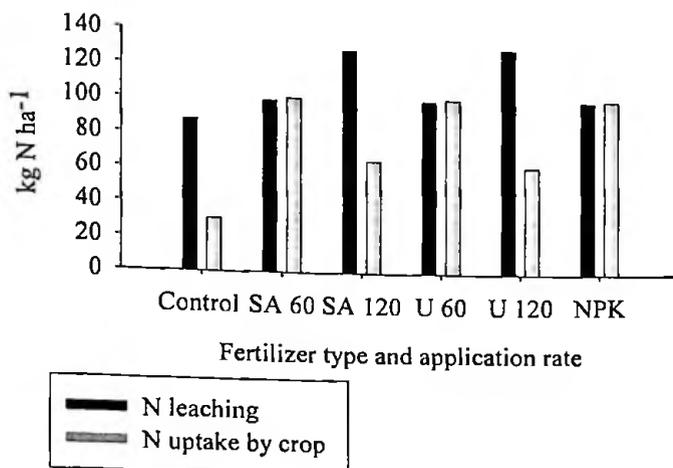
Figure 101: Simulated N uptake and leaching with calibrated field conditions of Akukayilli in the Guinea Savanna agro-ecological zone of Ghana

Microbial decomposition was found to be below 20 kg C ha^{-1} at the beginning of the year when precipitation was very low and environmental temperatures were high (See Figure 1, page 69). It then peaked at 90th day of the year when there was enough moisture (Figure 102). However, the highest simulated microbial decomposition was observed between 225th and 300th day of the year when fertilizer application occurred. The simulated results further showed intermittent microbial decomposition activity with onset of rainfall and declined after October when moisture was limited with application of 60 kg N ha^{-1} as sulphate of ammonia showing the highest response to microbial decomposition. This was however, similar to observed data (See Figures 19 and 20; pages 88 and 89).

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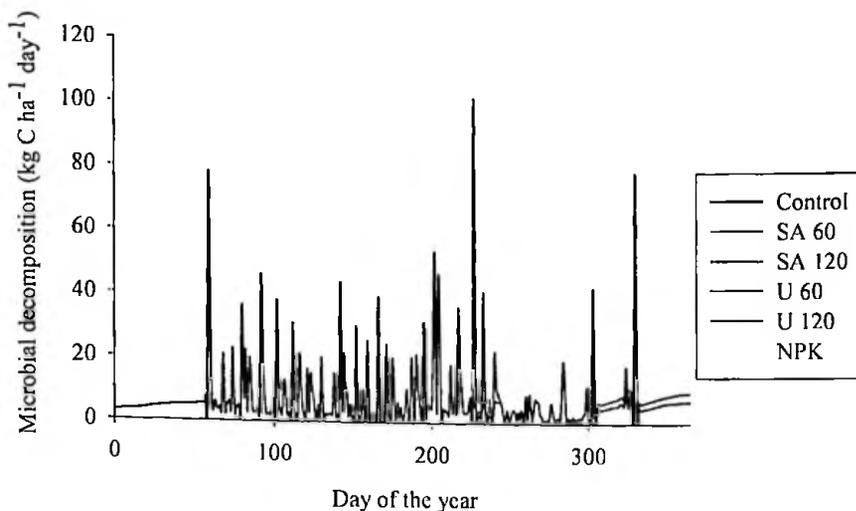
Figure 102: Simulated microbial decomposition from fertilized maize plots with calibrated field conditions of Akukayilli

The pattern of daily nitrification rate was similar to microbial decomposition with application of 60 and 120 kg N ha^{-1} or urea or sulphate of ammonia being the highest (Figure 103). However, N transformation through nitrification was low for application of NPK. On the contrary, N transformation by denitrification was highest for application of NPK (Figure 104). In both nitrification and denitrification, simulated highest peaks were observed after fertilizer application.

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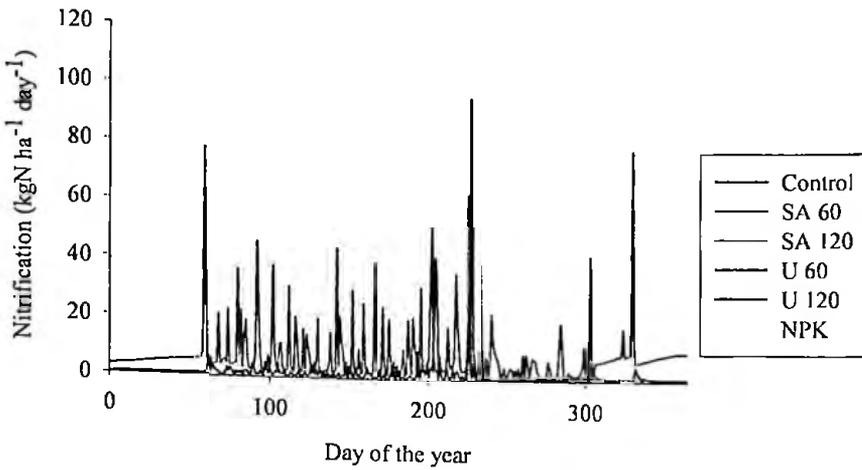
Figure 103: Simulated nitrification from fertilized maize plots with calibrated field conditions of Akukayilli in the Guinea Savanna agro-ecological zone of Ghana
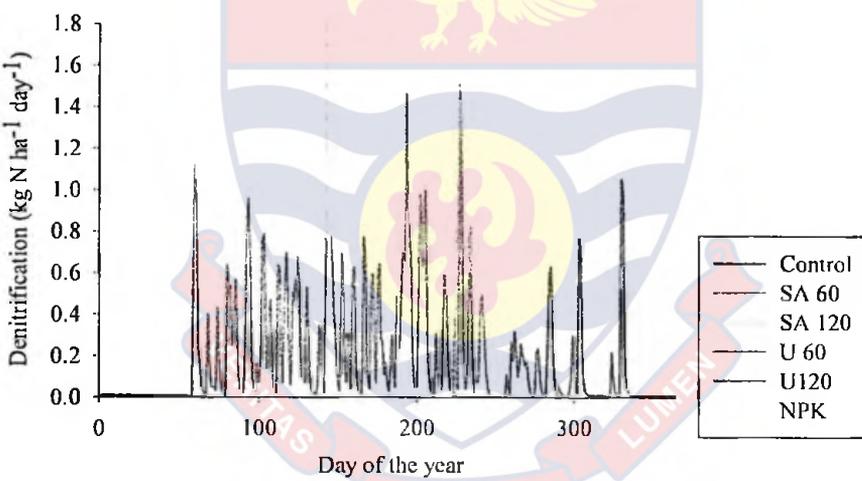
Figure 104: Simulated denitrification from fertilized maize plots with calibrated field conditions of Akukayilli in the Guinea Savanna agro-ecological zone of Ghana

Simulation of soil depth effect on nitrification and denitrification was done to 50 cm. Highest total annual nitrification occurred between 0-10 cm in the soil. Nitrification rate was highest at 0-10 cm depth on application of 120 kg ha^{-1} as urea or sulphate of ammonium, respectively (Figure 105). The nitrification rate was affected by soil depth. On the contrary, application of N fertilizer did not influence

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nitrification at 30-40 and 40-50 cm depth respectively. On the contrary, denitrification was found to be higher at 10-20 and 20-30 cm depth (Figure 106). Nitrogen transformation by denitrification was higher at 30-40 and 40-50 cm depth respectively.
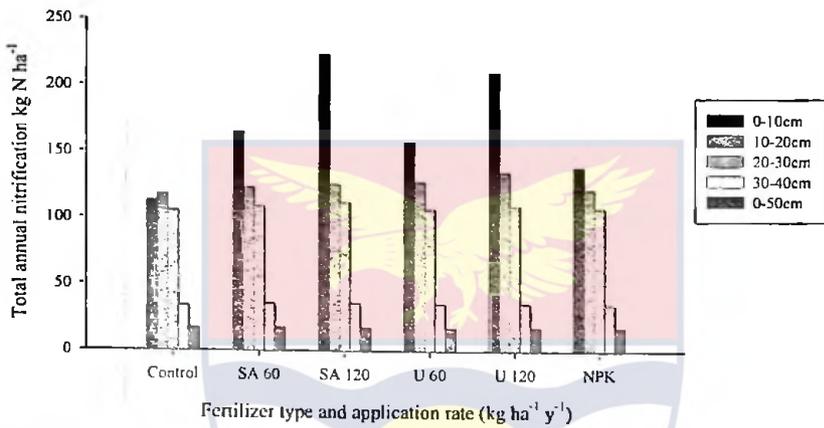
Figure 105: Effect of soil depth and N fertilizer application on nitrification
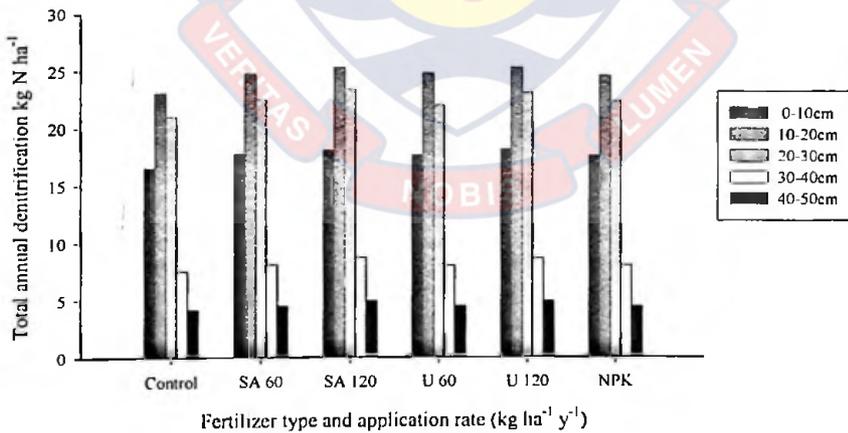
Figure 106: Effect of soil depth and N fertilizer application on denitrification

The results however, showed that greenhouse gas flux could only occur when environmental conditions such as adequate moisture and substrate are present

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which will promote enhanced microbial activity. The increased nitrification at the top soil could be probably due to the presence of decomposed organic matter with increased nitrifying bacterial activities. Also among the various factors, soil matrix, water status, aeration, temperature, and pH have strong influence on nitrification. These results are in agreement with findings from field experiments conducted in 2013 and 2014 season in this study where plots treated with 120 kg N ha^{-1} produced higher greenhouse gas fluxes.

Furthermore, the differences in both nitrification and denitrification at various soil depth in this study could be due to differences in microbial ecology, soil temperature and soil aeration. General trends indicate that nitrification activity is higher with no-till and reduced till cultivation compared with conventional tillage practices. This may be caused by changes in soil physical properties such as soil bulk density and improved water relations that are associated with reduced tillage practices.
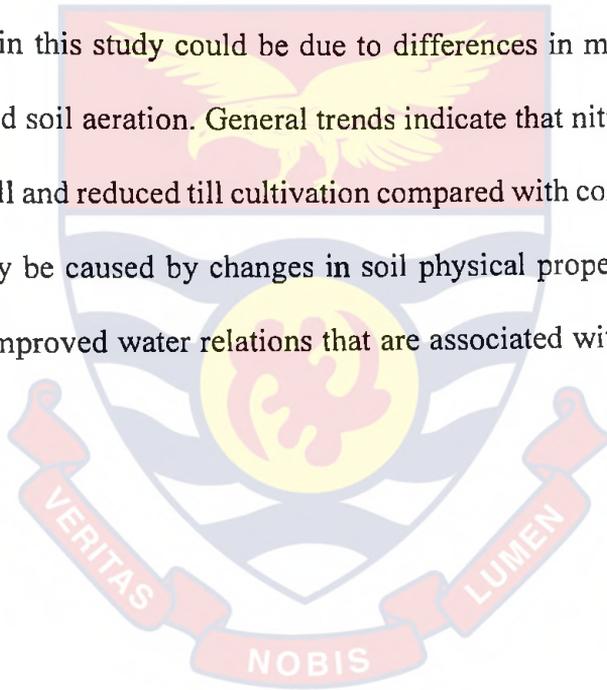
CHAPTER FIVE

SUMMARY, CONCLUSIONS AND RECOMMENDATION

This chapter presents the summary, conclusions and recommendations from this study.

Summary

Carbon dioxide and nitrous oxide are two important greenhouse gases that contribute to global warming. Nitrous oxide has a 298 times higher warming potential than CO_2 and stays in the atmosphere for more than 100 years which can also cause damage to the ozone layer. Agriculture being a contributor and a major source of employment in Ghana, knowledge of its contribution to global warming would facilitate the planning of early mitigation strategies. This study therefore considered the continuous use of N fertilizers to replenish soil fertility in the Guinea savanna agro-ecological zone of Ghana and its influence on these greenhouse gases emission and concluded as follows:

The soils at the experimental sites were found to be low in nitrogen, available phosphorus and organic matter that resulted in low grain yield obtained from plots without N fertilization. Therefore, there was the need to improve fertility status through the application of N fertilizers to increase productivity.

On field greenhouse gas flux measurements, application of 120 kg N ha^{-1} y^{-1} sulphate of ammonia (SA) showed the highest CO_2 emission (140 mg m^{-2} h^{-1}) at peak flux period (one to two weeks after application) and was significantly higher ($p < 0.05$) than fluxes from the other treatments. The application of NPK, U 120,

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SA 60 and U 60 emitted 2 to 5 times less CO_2 flux as compared to the use of 120 kg N ha^{-1} sulphate of ammonia and were not significantly higher ($P > 0.05$) than from plots that received no mineral N fertilizer. Application of 60 and 60-40-40 kg ha^{-1} y^{-1} of sulphate of ammonia and NPK released the least CO_2-C kg^{-1} grain produced compared to all other treatments. Furthermore, it can therefore be concluded that N source and amount significantly influenced CO_2 flux and CO_2-C kg^{-1} grain produced. Also, higher CO_2-C kg^{-1} grain was released without N fertilization. Application of sulphate of ammonia enhanced CO_2 flux significantly but did not increase CO_2-C kg^{-1} grain produced due to higher grain yield obtained compared to non-fertilized plots. Two kilograms CO_2-C kg^{-1} grain were released on application of 120 kg ha^{-1} y^{-1} of sulphate of ammonia which was significantly different from non-fertilized plots and the other treatments.

The results of the study indicated that application of 120 kg N ha^{-1} y^{-1} of sulphate of ammonia and urea, influenced N_2O flux emissions that were significantly higher than when 60 kg N ha^{-1} y^{-1} of the same N source were applied. Also application of 60-40-40 NPK and 60 kg N ha^{-1} y^{-1} of urea and sulphate of ammonia released 1-5 times less N_2O flux compared to application of 120 kg ha^{-1} y^{-1} urea and sulphate of ammonia, respectfully. Higher N_2O flux kg^{-1} grain was released on application of 120 kg ha^{-1} y^{-1} of urea and sulphate of ammonia, respectfully. However, application of urea resulted in higher N_2O flux as well as N_2O flux kg^{-1} grain produced. N_2O flux and N_2O-N kg^{-1} grain was therefore, highly influenced by N input rate and source.

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Carbon dioxide emission correlated poorly with soil surface temperature as well as soil temperature at 10 cm depth. However, a positive correlation, even though not significant, was found between N_2O emission and soil temperature both at the surface and at 10 cm depth. Although CO_2 and N_2O emissions increased significantly with increased WFPS, the correlation between N_2O and WFPS was stronger than CO_2 emission. In all, CO_2 emission and nitrification increased linearly with increasing soil water content. Furthermore with high N_2O emission associated with N source, quantities applied and the correlation between N_2O emission, and soil temperature, an anticipated increase in ambient temperature by 1-2 °C in the next 50 years would impact N_2O emission significantly. However, N_2O emission in the Guinea Savanna agro-ecological zone of Ghana is further likely to increase due to increase demand for food and the need to improve soil fertility to accommodate high nutrient demand, especially N by hybrid maize being introduced to farmers in the region. Higher rainfall and uneven distribution would also impact on, denitrification and probably be a major source of N_2O production and gaseous N losses from soil.

Average N-induced N_2O emission factors as a result of application of N fertilizers ranged between 0.10 % and 0.22 %, with an overall emission factor value of 0.15 %. Although, the overall emission factor was independent of the N source, emission factors were highly influenced by amount of N applied. This study therefore concludes that application of N fertilizer at 60 and 120 kg ha^{-1} as urea or sulphate of ammonia is unlikely to increase global warming. However, the demand for increased productivity to satisfy the growing Ghanaian population with the

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consequential decrease in soil nutrients, especially N, will result in an increased demand for N fertilization. This will however lead to an elevated emission factor that would affect global warming. Bearing in mind that the measured emissions of N_2O are in agreement with those obtained from similar soils and cropped with maize in other studies, the N_2O emission factors (EF) obtained from this work could be used, as a first good approximation, to prepare the National Inventory of Greenhouse Gases, rather than the use of "default emission factors" from the Intergovernmental Panel on Climate Change (IPCC) Guidelines.

Soils treated with 60 or 120 kg ha^{-1} y^{-1} urea, respectively showed higher initial N_2O emission compared to soils treated with 60 or 120 kg ha^{-1} y^{-1} of sulphate of ammonia when rewetted to 60 % water holding capacity. Application of 60 and 60-40-40 kg ha^{-1} y^{-1} of sulphate of ammonia and NPK released N_2O slowly and emissions were significantly higher at 7 h of incubation, with soils that were treated with 120 kg ha^{-1} y^{-1} of sulphate of ammonia and urea releasing the highest N_2O flux within the same period.

From the study, emissions from soils treated with 120 kg ha^{-1} y^{-1} urea showed detectable NO flux until 6 h when rewetted to 80 % water holding capacity. Emission from soils treated with 120 kg ha^{-1} y^{-1} of sulphate of ammonia and urea released the highest NO-N flux m^{-2}. Highest NO_2-N flux kg^{-1} dry soil h^{-1} was obtained from plots that received U 120 kg N ha^{-1} y^{-1} with plots that received no N fertilizer exhibiting the lowest. Generally, initial rewetting to 60 % water holding capacity affected NO-N flux positively and it was influenced by the presence of N fertilizer. Again rewetting dry soil cumulatively from 60 to 80 % water holding

capacity did not influence either NO or NO_2 fluxes significantly. Nitric oxide and NO_2 emissions were more rapid and lasted for a few hours when dry soils were rewetted and these were found to be highly dependent on the presence of N substrate level.

Results of the ^{15}N incubation study showed that the $\delta^{15}N$ values of N_2O were in the range of 8 and 852 ‰. Soil from plots that received no N fertilizer had the lowest $\delta^{15}N$ value whereas values from plot of NPK 60-40-40 kg ha^{-1} y^{-1} showed the highest. The study therefore, concludes that plots treated with NPK had the lowest soil N fixation rate. Mineral nitrogen is therefore lost through N_2O emissions.

Denitrification decomposition model predicted N_2O emissions in the Guinea Savanna agro-ecological zone of Ghana with an r^2 of 0.77. The model was also able to predict N_2O emissions under different fertilizer application rates and sources. Furthermore, the modelled results were in close agreement with peak N_2O emission periods after fertilizer application. The results showed that nitrification occurs within the soil at 0-10 cm depth whereas denitrification occurs at 10-20 cm within the soil.

Conclusions

1. Application of sulphate of ammonia at 120 kg N ha^{-1} enhanced CO_2 flux significantly but did not increase CO_2-C kg^{-1} grain produced due to higher grain yield obtained compared to non-fertilized plots.

2. The 60 kg N ha^{-1} y^{-1} is better 120 kg N ha^{-1} y^{-1} regardless of the N type in producing maize grain with higher N use efficiency on the *Ferric Luvisols*. The significant decrease in N_2O fluxes, 2-2.5 times lower emitted N_2O-CO_2 equivalents and less than 50 % N_2O kg^{-1} grain emitted following application of 60 kg N ha^{-1} y^{-1} suggest that the use of the current fertilizer formulation 60-(40-40) in the Guinea Savanna agro-ecological zone of Ghana is unlikely to increase global warming. Using a conversion factor of 298 proposed by the Intergovernmental Panel on Climate Change (IPCC), the study has established an approximate N_2O emission factor of 0.15 % for the Northern Savanna zone of Ghana.

3. The high emissions of greenhouse N gases observed on the re-wetted *Ferric Luvisols* treated with N fertilizers are indicative of rapid mechanisms that enhance the great losses of applied N under excessive soil moisture conditions that enhance the process of denitrification. Large substrate availability (120 kg N ha^{-1} y^{-1}) was found to greatly contribute to the phenomenon that occurred and importance of split and proper timing of N fertilizer application to synchronize with the period of high demand of N by crops.

4. The high $\delta^{15}N$ values of N_2O obtained from the *Ferric Luvisols* treated with N fertilizers over the non-fertilized plots are indicative of enhanced fixation of applied N under minimum soil moisture conditions. Application of compound fertilizer N-P_2O_5-K_2O fixed higher nitrogen in the soil than

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application of urea and sulphate of ammonia. With its associated low N_2O emission, these results support the current maize fertilization regime of using NPK as basal and sulphate of ammonia for topped-dress in the Guinea Savanna agro-ecological zone of Ghana.

This study therefore, accepted the hypotheses that (Ho_1) different types of N fertilizer increased N_2O, NO and NO_2 emissions from the *Ferric Luvisols*; (Ho_2) application of N fertilizer at different levels significantly increased N_2O, NO and NO_2 emissions from *Ferric Luvisols*; and (Ho_3) soil-moisture characteristics significantly increased N_2O, NO and NO_2 emissions but did not influence CO_2 emissions.

Recommendations

Considering the fact that farmers cannot influence climatic conditions under which they work, this study recommends that efforts should be made towards maintaining a good soil structure that enables good drainage and avoids waterlogging and thus reduces N losses through denitrification.

The choice of the right N fertilizer product and rate under the given conditions can help minimize N_2O emissions from the soil. As a result, application of NPK 40-40-40 kg N ha^{-1} y^{-1}, and top-dress with sulphate of ammonia at 20 kg ha^{-1} y^{-1} is recommended by this study. Furthermore, N application should be adjusted to the crop N demand by considering soil nutrient content, especially N, for instance, through split application to reduce N_2O emission.

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Suggestions for Further Research

Field work should be carried out to obtain emission factor under rice growing ecologies and other farming systems to improve the inventory of greenhouse gas emission in Ghana.

REFERENCES

Ackah, M., Agyemang, O., Anim, A. K., Osei, J., Bentil, N. O., Kpattah, L., ... & Hanson, J. E. K. (2011). Assessment of groundwater quality for drinking and irrigation: the case study of Teiman-Oyarifa Community, Ga East Municipality, Ghana. *Proceedings of the International Academy of Ecology and Environmental Sciences, 1*(3-4), 186-194.

Agboola, A. A., & Ayodele, O. J. (1985, April). Prospects and problems of using soil testing for adoption of fertilizer use in Ekiti-Akoko agricultural development project area. In *Proceedings of Workshop on Appropriate Technologies for Farmers in Semi-Arid West Africa* (pp. 123-136).

Al-Kaisi, M. M., & Yin, X. (2005). Tillage and crop residue effects on soil carbon and carbon dioxide emission in corn–soybean rotations. *Journal of Environmental Quality, 34*(2), 437-445.

Allison, S. D., Wallenstein, M. D., & Bradford, M. A. (2010). Soil-carbon response to warming dependent on microbial physiology. *Nature Geoscience, 3*(5), 336-340.

Amos, B., Arkebauer, T. J., & Doran, J. W. (2005). Soil surface fluxes of greenhouse gases in an irrigated maize-based agroecosystem. *Soil Science Society of America Journal, 69*(2), 387-395.

Anderson, J. M., & Ingram, J. S. I. (1993). Colorimetric determination of ammonium. *Tropical Soil Biology and Fertility, A Handbook of Methods, second ed. CAB International, Wallingford, UK*, 73-74.

Annamalai, K., & Puri, I. K. (2006). *Combustion science and engineering*. CRC press.

Bailey, V. L., Fansler, S. J., Smith, J. L., & Bolton, H. (2011). Reconciling apparent variability in effects of biochar amendment on soil enzyme activities by assay optimization. *Soil Biology and Biochemistry, 43*(2), 296-301.

Bajracharya, R. M., Lal, R., & Kimble, J. M. (2000). Diurnal and Seasonal CO–C Flux from Soil as Related to Erosion Phases in Central Ohio. *Soil Science Society of America Journal, 64*(1), 286-293.

Beare, M. H., Hendrix, P. F., Cabrera, M. L., & Coleman, D. C. (1994). Aggregate-protected and unprotected organic matter pools in conventional-and no-tillage soils. *Soil Science Society of America Journal, 58*(3), 787-795.

Benneh, G., Agyepong, G. T., & Allotey, J. A. (1990). *Land degradation in Ghana*. Food Production and Rural Development Division, Commonwealth Secretariat.

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Bergstrom, D. W., duction and flux from soil under sod following application of different nitrogen fertilizers. *Communications in soil science and plant analysis*, *32*(3-4), 553-570.

Binswanger, H., & Pingali, P. (1988). Technological priorities for farming in sub-Saharan Africa. *The World Bank Research Observer*, *3*(1), 81-98.

Bock, E., & Wagner, M. (2006). Oxidation of inorganic nitrogen compounds as an energy source. In *The prokaryotes* (pp. 457-495). Springer New York.

Bonsu, M., Ofosu, K. Y., & Kwakye, P. K. (1996). Soil management action plan for Ghana. *A consultancy report prepared for the World Bank, Washington, USA.*

Bouwman, A. F., Fung, I., Matthews, E., & John, J. (1993). Global analysis of the potential for N$_2$O production in natural soils. *Global Biogeochemical Cycles*, *7*(3), 557-597.

Bouwman, A. F., Boumans, L. J. M., & Batjes, N. H. (2002). Modeling global annual N2O and NO emissions from fertilized fields. *Global Biogeochemical Cycles*, *16*(4).

Bouwman, A. F. (1990). Background. *Soils and the greenhouse effect.* 25-192.

Bowman, R. A., & Focht, D. D. (1974). The influence of glucose and nitrate concentrations upon denitrification rates in sandy soils. *Soil Biology and Biochemistry*, 6(5), 297-301.

Bray, R. H., & Kurtz, L. T. (1945). Determination of total, organic, and available forms of phosphorus in soils. *Soil science*, 59(1), 39-46.

Bundy, L. G., Andraski, T. W., & Powell, J. M. (2001). Management practice effects on phosphorus losses in runoff in corn production systems. *Journal of Environmental Quality*, 30(5), 1822-1828.

Buresh, R. J., & De Datta, S. K. (1991). Nitrogen dynamics and management in rice-legume cropping systems. *Advances in Agronomy*, 45, 1-59.

Buresh, R. J., & Datta, S. K. (1990). Denitrification losses from puddled rice soils in the tropics. *Biology and Fertility of Soils*, 9(1), 1-13.

Byrnes, B. H., Holt, L. S., & Austin, E. R. (1993). The emission of nitrous oxide upon wetting a rice soil following a dry season fallow. *Journal of Geophysical Research: Atmospheres*, 98(D12), 22925-22929.

Calderon, F. J., & Jackson, L. E. (2002). Rototillage, disking, and subsequent irrigation. *Journal of Environmental Quality*, 31(3), 752-758.

174

Camara, O., & Heinemann, E. D. (2006). Overview of the fertilizer situation in Africa. *Background Paper for the Abuja Fertilizer Summit.*

Cataldo, D. A., Maroon, M., Schrader, L. E., & Youngs, V. L. (1975). Rapid colorimetric determination of nitrate in plant tissue by nitration of salicylic acid 1. *Communications in Soil Science & Plant Analysis, 6*(1), 71-80.

Chapin III, F. S., Matson, P. A., & Vitousek, P. (2011). *Principles of terrestrial ecosystem ecology.* Springer Science & Business Media.

Chase, C., Duffy, M., Webb, J., & Voss, R. (1991). An economic assessment of maintaining high phosphorus and potassium soil test levels. *American Journal of Alternative Agriculture, 6*(02), 83-86.

Clayton, H., Arah, J. R. M., & Smith, K. A. (1994). Measurement of nitrous oxide emissions from fertilized grassland using closed chambers. *Journal of Geophysical Research: Atmospheres, 99*(D8), 16599-16607.

Conant, R. T., Easter, M., Paustian, K., Swan, A., & Williams, S. (2007). Impacts of periodic tillage on soil C stocks: A synthesis. *Soil and Tillage Research, 95*(1), 1-10.

Halvorson, A. D., Del Grosso, S. J., & Reule, C. A. (2008). Nitrogen, tillage, and crop rotation effects on nitrous oxide emissions from irrigated cropping systems. *Journal of Environmental Quality, 37*(4), 1337-1344.

Cox, F. R., & Lins, I. D. G. (1984). A phosphorus soil test interpretation for corn grown on acid soils varying in crystalline clay content 1. *Communications in Soil Science & Plant Analysis, 15*(12), 1481-1491.

Coxson, D. S., & Parkinson, D. (1987). Winter respiratory activity in aspen woodland forest floor litter and soils. *Soil Biology and Biochemistry, 19*(1), 49-59.

Curtin, D., Wang, H., Selles, F., McConkey, B. G., & Campbell, C. A. (2000). Tillage effects on carbon fluxes in continuous wheat and fallow–wheat rotations. *Soil Science Society of America Journal, 64*(6), 2080-2086.

Davidson, E. A. (2009). The contribution of manure and fertilizer nitrogen to atmospheric nitrous oxide since 1860. *Nature Geoscience, 2*(9), 659-662.

Davidson, E. A., & Schimel, J. P. (1995). Microbial processes of production and consumption of nitric oxide, nitrous oxide and methane. *Biogenic Trace Gases: Measuring Emissions from Soil and Water*, 327-357.

Davidson, E. A. (1992). Sources of nitric oxide and nitrous oxide following wetting of dry soil. *Soil Science Society of America Journal*, *56*(1), 95-102.

Rogers, J. E., & Whitman, W. B. (1991). *Microbial production and consumption of greenhouse gases: methane, nitrogen oxides, and halomethanes.*

Deng, J., Zhu, B., Zhou, Z., Zheng, X., Li, C., Wang, T., & Tang, J. (2011). Modeling nitrogen loadings from agricultural soils in southwest China with modified DNDC. *Journal of Geophysical Research: Biogeosciences*, *116*(G2).

Denmead, O. (1979). Chamber systems for measuring nitrous oxide emission from soils in the field. *Soil Science Society of America Journal*, *43*(1), 89-95.

Denmead, O. T., Freney, J. R., & Simpson, J. R. (1979). Studies of nitrous oxide emission from a grass sward. *Soil Science Society of America Journal*, *43*(4), 726-728.

Desai, G. M., & Gandhi, V. P. (1990). Policy Issues in Growth of Fertilizer Use in Sub-Saharan Africa. *IFPRI, Washington, DC, USA.*

De Santo, A. V., Alfani, A., & Sapio, S. (1976). Soil metabolism in beech forests of Monte Taburno (Campania Apennines). *Oikos*, 144-152.

Dick, W. A., Cheng, L., & Wang, P. (2000). Soil acid and alkaline phosphatase activity as pH adjustment indicators. *Soil Biology and Biochemistry*, *32*(13), 1915-1919.

Dong, Y., Zhang, S., Qi, Y., Chen, Z., & Geng, Y. (2000). Fluxes of CO_2, N_2O and CH_4 from a typical temperate grassland in Inner Mongolia and its daily variation. *Chinese Science Bulletin*, *45*(17), 1590-1594.

Douglas, L. A., & Tedrow, J. C. F. (1959). ORGANIC MATTER DECOMPOSITION RATES IN ARCTIC SOILS. *Soil Science*, *88*(6), 305-hyhen.

Reuler, H. V., & Prins, W. H. (1993). The role of plant nutrients for sustainable food crop production in Sub-Saharan Africa.

Durka, W., Schulze, E. D., Gebauer, G., & Voerkelius, S. (1994). Effects of forest decline on uptake and leaching of deposited nitrate determined from (15) N and (18) O measurements. *Nature*, *372*(6508), 765.

Eichner, M. J. (1990). Nitrous oxide emissions from fertilized soils: summary of available data. *Journal of environmental quality*, *19*(2), 272-280.

Epstein, S., Buchsbaum, R., Lowenstam, H. A., & Urey, H. C. (1953). Revised carbonate-water isotopic temperature scale. *Geological Society of America Bulletin*, *64*(11), 1315-1326.

Howden, S. M., Soussana, J. F., Tubiello, F. N., Chhetri, N., Dunlop, M., & Meinke, H. (2007). Adapting agriculture to climate change. *Proceedings of the national academy of sciences, 104*(50), 19691-19696.

Juss, I. (2006). FAO, 2006. *World base reference for soil resources. Report on World Soil Resources. FAO. Rome, Italy.*

Enti-Brown, S., Yeboah, P. O., Akoto-Bamford, S., Anim, A. K., Abole, H., Kpattah, L. & Gyamfi, E. T. (2012). Quality control analysis of imported fertilizers used in Ghana: the macronutrients perspective. *Proceedings of the International Academy of Ecology and Environmental Sciences, 2*(1), 27.

Firestone, M. K., & Davidson, E. A. (1989). Microbiological basis of NO and N_2O production and consumption in soil. *Exchange of trace gases between terrestrial ecosystems and the atmosphere, 47,* 7-21.

Flessa, H., Dörsch, P., & Beese, F. (1995). Seasonal variation of N_2O and CH_4 fluxes in differently managed arable soils in southern Germany. *Journal of Geophysical Research: Atmospheres, 100*(D11), 23115-23124.

Follett, R. F., & Hatfield, J. L. (2001). Nitrogen in the environment: sources, problems, and management. *The Scientific World Journal, 1,* 920-926.

Follett, R. F., Shafer, S. R., Jawson, M. D., & Franzluebbers, A. J. (2005). Research and implementation needs to mitigate greenhouse gas emissions from agriculture in the USA. *Soil and Tillage Research, 83*(1), 159-166.

Frame, C. H., & Casciotti, K. L. (2010). Biogeochemical controls and isotopic signatures of nitrous oxide production by a marine ammonia-oxidizing bacterium. *Biogeosciences, 7*(9), 2695.

Bradford, J., & Fraser, E. D. (2008). Local authorities, climate change and small and medium enterprises: identifying effective policy instruments to reduce energy use and carbon emissions. *Corporate Social Responsibility and Environmental Management, 15*(3), 156-172.

Froment, A. (1972). Soil respiration in a mixed oak forest. *Oikos*, 273-277.

Balu, L., Johnson, M., & Fuentes, P. A. B. (2012). Improving regional fertilizer markets in West Africa.

Galloway, J. N., & Cowling, E. B. (2002). Reactive nitrogen and the world: 200 years of change. *AMBIO: A Journal of the Human Environment, 31*(2), 64-71.

Greef, J. M., Hansen, F., Pasda, G., & Diepenbrock, W. (1993). Die Strahlungs-, Energie- und Kohlendioxidbindung landwirtschaftlicher Kulturpflanzen—Ergebnisse und Modellrechnungen. *Ber. Landw, 71*, 554-566.

Guo, X., Drury, C. F., Yang, X., & Zhang, R. (2010). Influence of constant and fluctuating water contents on nitrous oxide emissions from soils under varying crop rotations. *Soil Science Society of America Journal, 74*(6), 2077-2085.

Hall, S. J., Matson, P. A., & Roth, P. M. (1996). NOx emissions from soil: implications for air quality modeling in agricultural regions. *Annual Review of Energy and the Environment, 21*(1), 311-346.

Hashemidezfooli, A., Koochaki, A., & Banayanavval, M. (1998). Crop plant improvement (translation). *Jehad Daneshgahi Mashhad press. Mashhad. Iran, 3,* 248.

Heaton, T. H. E. (1990). 15N/14N ratios of NOx from vehicle engines and coal-fired power stations. *Tellus B, 42*(3), 304-307.

Hodge, A., Robinson, D., & Fitter, A. (2000). Are microorganisms more effective than plants at competing for nitrogen?. *Trends in plant science, 5*(7), 304-308.

Howarth, R. W. (2004). Human acceleration of the nitrogen cycle: drivers, consequences, and steps toward solutions. *Water Science and Technology, 49*(5-6), 7-13.

Hyde, B. P., Hawkins, M. J., Fanning, A. F., Noonan, D., Ryan, M., O'toole, P., & Carton, O. T. (2006). Nitrous oxide emissions from a fertilized and grazed grassland in the South East of Ireland. *Nutrient Cycling in Agroecosystems*, *75*(1), 187-200.

Intergovernmental Panel on Climate Change. (2014). *Climate Change 2014–Impacts, Adaptation and Vulnerability: Regional Aspects*. Cambridge University Press.

Bernstein, L., Bosch, P., Canziani, O., Chen, Z., Christ, R., & Riahi, K. (2008). *IPCC, 2007: climate change 2007: synthesis report*. IPCC.

Syakila, A., & Kroeze, C. (2011). The global nitrous oxide budget revisited. *Greenhouse Gas Measurement and Management*, *1*(1), 17-26.

Smithson, P. A. (2002). IPCC, 2001: climate change 2001: the scientific basis. Contribution of Working Group 1 to the Third Assessment Report of the Intergovernmental Panel on Climate Change, edited by JT Houghton, Y. Ding, DJ Griggs, M. Noguer, PJ van der Linden, X. Dai, K. Maskell and CA Johnson (eds). Cambridge University Press, Cambridge, UK, and New York, USA, 2001. No. of pages: 881. Price£ 34.95, US $49.95, ISBN 0-521-01495-6 (paperback).£ 90.00, US $130.00, ISBN 0-521-80767-0 (hardback). *International Journal of Climatology*, *22*(9), 1144-1144.

Jastrow, J. D., Miller, R. M., & Boutton, T. W. (1996). Carbon dynamics of aggregate-associated organic matter estimated by carbon-13 natural abundance. *Soil Science Society of America Journal*, *60*(3), 801-807.

Kachanoski, R. G., O'Halloran, I., & Rochette, P. (2003). Site-specific application of fertilizer N for reducing greenhouse gas emissions. *Climate change funding initiative in Agriculture. Canadian Agri-Food Research Council, Ottawa.*

Kaiser, J., Röckmann, T., & Brenninkmeijer, C. A. (2003). Complete and accurate mass spectrometric isotope analysis of tropospheric nitrous oxide. *Journal of Geophysical Research: Atmospheres*, *108*(D15).

Kempers, A. J., & Zweers, A. (1986). Ammonium determination in soil extracts by the salicylate method. *Communications in Soil Science & Plant Analysis*, *17*(7), 715-723.

Kessel, M., Grieser, J., Wobrock, W., Jaeschke, W., Fuzzi, S., Facchini, M. C., & Orsi, G. (1992). Nitrogen oxides concentrations and soil emission fluxes in the Po Valley. *Tellus B*, *44*(5), 522-532.

Kowalenko, C. G., & Ivarson, K. C. (1978). Effect of moisture content, temperature and nitrogen fertilization on carbon dioxide evolution from field soils. *Soil Biology and Biochemistry*, *10*(5), 417-423.

183

Kucera, C., & Kirkham, D. R. (1971). Soil respiration studies in tallgrass prairie in Missouri. *Ecology*, *52*(5), 912-915.

Larson, B. A., & Frisvold, G. B. (1996). Fertilizers to support agricultural development in sub-Saharan Africa: What is needed and why. *Food policy*, *21*(6), 509-525.

Li, C., Zhuang, Y., Cao, M., Crill, P., Dai, Z., Frolking, S. & Wang, X. (2001). Comparing a process-based agro-ecosystem model to the IPCC methodology for developing a national inventory of N2O emissions from arable lands in China. *Nutrient Cycling in Agro-ecosystems*, *60*(1), 159-175.

Li, C. S. (2000). Modeling trace gas emissions from agricultural ecosystems. *Nutrient Cycling in Agro-ecosystems*, *58*(1-3), 259-276.

Li, C., Narayanan, V., & Harriss, R. C. (1996). Model estimates of nitrous oxide emissions from agricultural lands in the United States. *Global Biogeochemical Cycles*, *10*(2), 297-306.

Li, C., Frolking, S., & Harriss, R. (1994). Modeling carbon biogeochemistry in agricultural soils. *Global biogeochemical cycles*, *8*(3), 237-254.

Li, C., Frolking, S., & Frolking, T. A. (1992). A model of nitrous oxide evolution from soil driven by rainfall events: 1. Model structure and sensitivity. *Journal of Geophysical Research: Atmospheres*, *97*(D9), 9759-9776.

Linn, D. M., & Doran, J. W. (1984). Effect of water-filled pore space on carbon dioxide and nitrous oxide production in tilled and non-tilled soils. *Soil Science Society of America Journal*, *48*(6), 1267-1272.

Liu, X. J., Mosier, A. R., Halvorson, A. D., & Zhang, F. S. (2005). Tillage and nitrogen application effects on nitrous and nitric oxide emissions from irrigated corn fields. *Plant and Soil*, *276*(1), 235-249.

Liu, X. J., Mosier, A. R., Halvorson, A. D., & Zhang, F. S. (2006). The impact of nitrogen placement and tillage on NO, N_2O, CH_4 and CO_2 fluxes from a clay loam soil. *Plant and soil*, *280*(1), 177-188.

Logan, J. A. (1983). Nitrogen oxides in the troposphere: Global and regional budgets. *Journal of Geophysical Research: Oceans*, *88*(C15), 10785-10807.

Longoria-Ramírez, R., Mar-Morales, B. E., & Ruiz-Suárez, L. G. (2007). Influence of soil characteristics and nitrogen amendments on nitrous oxide emissions in a corn production system. *Terra Latinoamericana*, *25*(4), 345-355.

MacKenzie, A. F., Fan, M. X., & Cadrin, F. (1998). Nitrous oxide emission in three years as affected by tillage, corn-soybean-alfalfa rotations, and nitrogen fertilization. *Journal of environmental quality, 27*(3), 698-703.

Al-Kaisi, M. M., Kruse, M. L., & Sawyer, J. E. (2008). Effect of nitrogen fertilizer application on growing season soil carbon dioxide emission in a corn–soybean rotation. *Journal of environmental quality, 37*(2), 325-332.

Malhi, S. S., Lemke, R., Wang, Z. H., & Chhabra, B. S. (2006). Tillage, nitrogen and crop residue effects on crop yield, nutrient uptake, soil quality, and greenhouse gas emissions. *Soil and Tillage Research, 90*(1), 171-183.

Maidl, F. X., & Fischbeck, G. (1988). Effects of different tillage practices on yield formation and nitrogen uptake of sugarbeet on farms with and without livestock. *Journal of Agronomy and Crop Science, 160*, 29-37.

Matlon, P. J., & Spencer, D. S. (1984). Increasing food production in Sub-Saharan Africa: Environmental problems and inadequate technological solutions. *American Journal of Agricultural Economics, 66*(5), 671-676.

McSwiney, C. P., & Robertson, G. P. (2005). Nonlinear response of N_2O flux to incremental fertilizer addition in a continuous maize (Zea mays L.) cropping system. *Global Change Biology, 11*(10), 1712-1719.

McTaggart, I. P., & Tsuruta, H. (2003). The influence of controlled release fertilisers and the form of applied fertiliser nitrogen on nitrous oxide emissions from an andosol. *Nutrient Cycling in Agroecosystems*, *67*(1), 47-54.

Mellor, J. W., Delgado, C. L., & Blackie, M. J. (1987). Accelerating food production in Sub-Saharan Africa.

Merchán Paniagua, S. (2006). *Use of slow-release N fertilizer to control nitrogen losses due to spatial and climatic differences in soil moisture conditions and drainage in claypan soils* (Doctoral dissertation, University of Missouri--Columbia).

Miller, R. D., & Johnson, D. D. (1964). The effect of soil moisture tension on carbon dioxide evolution, nitrification, and nitrogen mineralization. *Soil Science Society of America Journal*, *28*(5), 644-647.

Yawson, D. O., Armah, F. A., Afrifa, E. K., & Dadzie, S. K. (2010). Ghana's fertilizer subsidy policy: Early field lessons from farmers in the central region. *Journal of sustainable development in Africa*, *12*(3), 191-203.

Mogge, B., Kaiser, E. A., & Munch, J. C. (1999). Nitrous oxide emissions and denitrification N-losses from agricultural soils in the Bornhöved Lake region: influence of organic fertilizers and land-use. *Soil Biology and Biochemistry*, *31*(9), 1245-1252.

Mohn, J., Wolf, B., Toyoda, S., Lin, C. T., Liang, M. C., Brüggemann, N. & Ostrom, N. E. (2014). Inter-laboratory assessment of nitrous oxide isotopomer analysis by isotope ratio mass spectrometry and laser spectroscopy: current status and perspectives. *Rapid communications in mass spectrometry*, 28(18), 1995-2007.

Mollenhauer, K., & Tschöke, H. (Eds.). (2010). *Handbook of diesel engines*. Springer Science & Business Media.

Mosier, A. R. (2002). Environmental challenges associated with needed increases in global nitrogen fixation. *Nutrient Cycling in Agro-ecosystems*, 63(2-3), 101-116.

Mosier, A., Kroeze, C., Nevison, C., Oenema, O., Seitzinger, S., & Van Cleemput, O. (1998). Closing the global N_2O budget: nitrous oxide emissions through the agricultural nitrogen cycle. *Nutrient cycling in Agro-ecosystems*, 52(2-3), 225-248.

Mosier, A. R., Guenzi, W. D., & Schweizer, E. E. (1986). Soil losses of dinitrogen and nitrous oxide from irrigated crops in northeastern Colorado. *Soil Science Society of America Journal*, 50(2), 344-348.

Motavalli, P. P., Goyne, K. W., & Udawatta, R. P. (2008). Environmental impacts of enhanced-efficiency nitrogen fertilizers. *Crop Management*, 7(1), 0-0.

Motavalli, P., Nelson, K., Kitchen, N., Anderson, S., & Scharf, P. (2006). Variable source N fertilizer applications to optimize crop N use efficiency. *Missouri Soil Fertility and Fertilizers Research Updates*, 07-01.

Mwangi, W. M. (1996). Low use of fertilizers and low productivity in sub-Saharan Africa. *Nutrient cycling in Agroecosystems*, 47(2), 135-147.

Ha, N., Feike, T., Back, H., Xiao, H., & Bahrs, E. (2015). The effect of simple nitrogen fertilizer recommendation strategies on product carbon footprint and gross margin of wheat and maize production in the North China Plain. *Journal of environmental management*, *163*, 146-154.

Berbert, J. H., Brownd, J., Felsentreger, T., Harris, D., Johnson, T. S., Khan, M. A. & Reece, J. (1977). National Aeronautics and Space Administration/Goddard Space Flight Center. *NASA Special Publication*, *365*, 293.

Nash, P. R., Motavalli, P. P., & Nelson, K. A. (2012). Nitrous oxide emissions from claypan soils due to nitrogen fertilizer source and tillage/fertilizer placement practices. *Soil Science Society of America Journal*, 76(3), 983-993.

Nelson, D. W. & Sommers L. W. (1982). Total organic carbon and organic matter. In Page A.C. (ed.). *Methods of Soil Analysis, part 2. Chemical and microbiological properties*. Agronomy Monograph, No. 7 Madison W, USA.

Ogle, S. M., Breidt, F. J., & Paustian, K. (2005). Agricultural management impacts on soil organic carbon storage under moist and dry climatic conditions of temperate and tropical regions. *Biogeochemistry, 72*(1), 87-121.

Orchard, V. A., & Cook, F. J. (1983). Relationship between soil respiration and soil moisture. *Soil Biology and Biochemistry, 15*(4), 447-453.

Page, A. L., Miller, R. H. & Keeney, D. R. (eds.) (1982*). Methods of soil analysis. Part 2. Chemical and microbiological properties*. 2nd edition. Agronomy Series 9, ASA, SSSA, Madison, Wis.

Pal, D., & Broadbent, F. E. (1975). Influence of moisture on rice straw decomposition in soils. *Soil Science Society of America Journal, 39*(1), 59-63.

Papen, H., & Butterbach-Bahl, K. (1999). A 3-year continuous record of nitrogen trace gas fluxes from untreated and limed soil of a N-saturated spruce and beech forest ecosystem in Germany: 1. N_2O emissions. *Journal of Geophysical Research: Atmospheres, 104*(D15), 18487-18503.

Parkin, T. B., & Kaspar, T. C. (2006). Nitrous oxide emissions from corn–soybean systems in the Midwest. *Journal of environmental quality, 35*(4), 1496-1506.

Parkin, T. B., & Kaspar, T. C. (2003). Temperature controls on diurnal carbon dioxide flux. *Soil Science Society of America Journal*, 67(6), 1763-1772.

Stewart, C. E., Paustian, K., Conant, R. T., Plante, A. F., & Six, J. (2009). Soil carbon saturation: Implications for measurable carbon pool dynamics in long-term incubations. *Soil Biology and Biochemistry*, 41(2), 357-366.

Paustian, K., Collins, H. P., & Paul, E. A. (1997). *Management controls on soil carbon* (pp. 15-49). 1997a, CRC Press: Boca Raton, FL, USA. p.

Groffman, P. M., & Tiedje, J. M. (1991). Relationships between denitrification, CO_2 production and air-filled porosity in soils of different texture and drainage. *Soil Biology and Biochemistry*, 23(3), 299-302.

Pilegaard, K., Skiba, U., Ambus, P., Beier, C., Brüggemann, N., Butterbach-Bahl, K. & Gasche, R. (2006). Factors controlling regional differences in forest soil emission of nitrogen oxides (NO and N_2O). *Biogeosciences*, 3(4), 651-661.

Power, J. F., Wiese, R. & Flowerday, D. (2001). Managing farming systems for nitrate control: A research review from Management Systems Evaluation Areas. *Journal of Environmental Quality*. (30) 1866-1880.

Reicosky, D. C., & Lindstrom, M. J. (1993). Fall tillage method: effect on short-term carbon dioxide flux from soil. *Agronomy Journal, 85*(6), 1237-1243.

Reiners, W. A. (1968). Carbon dioxide evolution from the floor of three Minnesota forests. *Ecology, 49*(3), 471-483.

Robertson, G. P., & Vitousek, P. M. (2009). Nitrogen in agriculture: balancing the cost of an essential resource. *Annual Review of Environment and Resources, 34*, 97-125.

Rochette, P., & Flanagan, L. B. (1997). Quantifying rhizosphere respiration in a corn crop under field conditions. *Soil Science Society of America Journal, 61*(2), 466-474.

Schils, R., Kuikman, P., Liski, J., Van Oijen, M., Smith, P., Webb, J. & Emmett, B. (2008). Review of existing information on the interrelations between soil and climate change.(ClimSoil). Final report.

Schlentner, R. E., & Cleve, K. V. (1985). Relationships between CO_2 evolution from soil, substrate temperature, and substrate moisture in four mature forest types in interior Alaska. *Canadian Journal of Forest Research, 15*(1), 97-106.

Sexstone, A. J., Parkin, T. B., & Tiedje, J. M. (1985). Temporal response of soil denitrification rates to rainfall and irrigation. *Soil Science Society of America Journal, 49*(1), 99-103.

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Jamaati-e-Somarin, S., Zabihi-e-Mahmoodabad, R., Yari, A., Khayatnezhad, M., & Gholamin, R. (2010). Study of Agronomical Nitrogen Use Efficiency of Durum Wheat, Affected by Nitrogen Fertilizer and Plant Density. *World Applied Sciences Journal*, *11*(6), 674-681.

Shoji, S., Delgado, J., Mosier, A., & Miura, Y. (2001). Use of controlled release fertilizers and nitrification inhibitors to increase nitrogen use efficiency and to conserve air andwater quality. *Communications in Soil Science and Plant Analysis*, *32*(7-8), 1051-1070.

Signor, D., & Cerri, C. E. P. (2013). Nitrous oxide emissions in agricultural soils: a review. *Pesquisa Agropecuária Tropical*, *43*(3), 322-338.

Six, J., Bossuyt, H., Degryze, S., & Denef, K. (2004). A history of research on the link between (micro) aggregates, soil biota, and soil organic matter dynamics. *Soil and Tillage Research*, *79*(1), 7-31.

Skiba, U., Sheppard, L., Pitcairn, C. E. R., Leith, I., Crossley, A., Van Dijk, S., ... & Fowler, D. (1998). Soil nitrous oxide and nitric oxide emissions as indicators of elevated atmospheric N deposition rates in seminatural ecosystems. *Environmental Pollution*, *102*(1), 457-461.

Slemr, F., & Seiler, W. (1984). Field measurements of NO and NO2 emissions from fertilized and unfertilized soils. *Journal of Atmospheric Chemistry, 2*(1), 1-24.

Slemr, F., & Seiler, W. (1991). Field study of environmental variables controlling the NO emissions from soil and the NO compensation point. *Journal of Geophysical Research: Atmospheres, 96*(D7), 13017-13031.

Smaling, E. M. A. (1993). *An agro-ecological framework for integrated nutrient management, with special reference to Kenya* (Doctoral dissertation, [sn]).

Smaling, E. M., & Braun, A. R. (1996). Soil fertility research in sub-Saharan Africa: New dimensions, new challenges. *Communications in Soil Science & Plant Analysis, 27*(3-4), 365-386.

Smith, W. N., Grant, B. B., Desjardins, R. L., Worth, D., Li, C., Boles, S. H., & Huffman, E. C. (2010). A tool to link agricultural activity data with the DNDC model to estimate GHG emission factors in Canada. *Agriculture, ecosystems & environment, 136*(3), 301-309.

Skinner, C., Gattinger, A., Muller, A., Mäder, P., Fließbach, A., Stolze, M. & Niggli, U. (2014). Greenhouse gas fluxes from agricultural soils under organic and non-organic management—a global meta-analysis. *Science of the Total Environment, 468*, 553-563.

194

Smith, K. A., Thomson, P. E., Clayton, H., McTaggart, I. P., & Conen, F. (1998). Effects of temperature, water content and nitrogen fertilisation on emissions of nitrous oxide by soils. *Atmospheric Environment, 32*(19), 3301-3309.

Smith, K. (1997). The potential for feedback effects induced by global warming on emissions of nitrous oxide by soils. *Global Change Biology, 3*(4), 327-338.

Smith, P., Powlson, D. S., Glendining, M. J., & Smith, J. U. (1998). Preliminary estimates of the potential for carbon mitigation in European soils through no-till farming. *Global Change Biology, 4*(6), 679-685.

Snyder, C. S., Bruulsema, T. W., Jensen, T. L., & Fixen, P. E. (2009). Review of greenhouse gas emissions from crop production systems and fertilizer management effects. *Agriculture, Ecosystems & Environment, 133*(3), 247-266.

Snyder, C. S., Bruulsema, T. W., & Jensen, T. L. (2007). Best management practices to minimize greenhouse gas emissions associated with fertilizer use. *Better crops, 91*, 16-18.

Sommers, L. E., Gilmour, C. M., Wildung, R. E., & Beck, S. M. (1981). The effect of water potential on decomposition processes in soils. *Water potential relations in soil microbiology*, (water potential), 97-117.

Speir, T. W., Townsend, J. A., More, R. D., & Hill, L. F. (1999). Short-lived isotopic method to measure nitrous oxide emissions from a soil under four low-fertility management systems. *Soil Biology and Biochemistry, 31*(10), 1413-1421.

Bergström, S., Carlsson, B., Gardelin, M., Lindström, G., Pettersson, A., & Rummukainen, M. (2001). Climate change impacts on runoff in Sweden assessments by global climate models, dynamical downscaling and hydrological modelling. *Climate research, 16*(2), 101-112.

Stewart, W. M., Dibb, D. W., Johnston, A. E., & Smyth, T. J. (2005). The contribution of commercial fertilizer nutrients to food production. *Agronomy Journal, 97*(1), 1-6.

Stoorvogel, J. J., Smaling, E. A., & Janssen, B. H. (1993). Calculating soil nutrient balances in Africa at different scales. *Nutrient Cycling in Agroecosystems, 35*(3), 227-235.

Tel, D. A., & Hagarty, M. (Eds.). (1984). *Soil and Plant Analyses: Study Guide for Agricultural Laboratory Directors and Technologists Working in Tropical Regions*. International Institute of Tropical Agriculture.

Tiedje, J. M., Sexstone, A. J., Parkin, T. B., Revsbech, N. P., & Shelton, D. R. (1984). Anaerobic processes in soil. In *Biological processes and soil fertility* (pp. 197-212). Springer Netherlands.

Tisdale, S. L., Nelson, W. L., Beatour, T. D. & Havlin, J. L. (1993). *Soil fertility and fertilizer*. 5th edition. Macmillan Publishers, N.Y. p.144.

Tiwari, R. N. (2011). Assessment of groundwater quality and pollution potential of Jawa block Rewa district, Madhya Pradesh, India. *Proceedings of the international academy of ecology and environmental sciences, 1*(3-4), 202.

Toyoda, S., Mutobe, H., Yamagishi, H., Yoshida, N., & Tanji, Y. (2005). Fractionation of N_2O isotopomers during production by denitrifier. *Soil Biology and Biochemistry, 37*(8), 1535-1545.

Toyoda, S., & Yoshida, N. (1999). Determination of nitrogen isotopomers of nitrous oxide on a modified isotope ratio mass spectrometer. *Analytical Chemistry, 71*(20), 4711-4718.

Udawatta, R. P., Motavalli, P. P., Garrett, H. E., & Krstansky, J. J. (2006). Nitrogen losses in runoff from three adjacent agricultural watersheds with claypan soils. *Agriculture, Ecosystems & Environment, 117*(1), 39-48.

Udawatta, R. P., Krstansky, J. J., Henderson, G. S., & Garrett, H. E. (2002). Agroforestry practices, runoff, and nutrient loss. *Journal of Environmental Quality, 31*(4), 1214-1225.

Vallejo, A., Diez, J. A., López-Valdivia, L. M., Gascó, A., & Jiménez, C. (2001). Nitrous oxide emission and denitrification nitrogen losses from soils treated with isobutylenediurea and urea plus dicyandiamide. *Biology and Fertility of Soils, 34*(4), 248-257.

Veldkamp, E., & Keller, M. (1997). Nitrogen oxide emissions from a banana plantation in the humid tropics. *Journal of Geophysical Research: Atmospheres, 102*(D13), 15889-15898.

Veldkamp, E., Keller, M., & Nuñez, M. (1998). Effects of pasture management on N2O and NO emissions from soils in the humid tropics of Costa Rica. *Global Biogeochemical Cycles, 12*(1), 71-79.

Velthof, G. L., Oudendag, D. A., & Oenema, O. (2007). *Development and application of the integrated nitrogen model MITERRA-EUROPE. Task 1 Service contract" Integrated measures in agriculture to reduce ammonia emissions"* (No. 1663.1). Alterra.

Velthof, G. L., Brader, A. B., & Oenema, O. (1996). Seasonal variations in nitrous oxide losses from managed grasslands in The Netherlands. *Plant and Soil, 181*(2), 263-274.

Vitousek, P. M., Aber, J. D., Howarth, R. W., Likens, G. E., Matson, P. A., Schindler, D. W., ... & Tilman, D. G. (1997). Human alteration of the global nitrogen cycle: sources and consequences. *Ecological applications, 7*(3), 737-750.

Vlek, P. L. (1990). The role of fertilizers in sustaining agriculture in sub-Saharan Africa. *Fertilizer research, 26*(1-3), 327-339.

Voerkelius, S. (1990). *Isotopendiskriminierungen bei der Nitrifikation und Denitrifikation: Grundlagen und Anwendungen der Herkunfts-Zuordnung von Nitrat und Distickstoffmonoxid.* na.

Weitz, A. M., Linder, E., Frolking, S., Crill, P. M., & Keller, M. (2001). N_2O emissions from humid tropical agricultural soils: effects of soil moisture, texture and nitrogen availability. *Soil Biology and Biochemistry, 33*(7), 1077-1093.

West, T. O., & Post, W. M. (2002). Soil organic carbon sequestration rates by tillage and crop rotation. *Soil Science Society of America Journal, 66*(6), 1930-1946.

Williams, M. A., & Xia, K. (2009). Characterization of the water soluble soil organic pool following the rewetting of dry soil in a drought-prone tallgrass prairie. *Soil Biology and Biochemistry, 41*(1), 21-28.

Williams, E. J., Hutchinson, G. L., & Fehsenfeld, F. C. (1992). NOx and N₂O emissions from soil. *Global Biogeochemical Cycles, 6*(4), 351-388.

Wolf, I., & Russow, R. (2000). Different pathways of formation of N₂O, N₂ and NO in black earth soil. *Soil Biology and Biochemistry, 32*(2), 229-239.

Wuebbles, D. J. (2009). Nitrous oxide: no laughing matter. *Science, 326*(5949), 56-57.

Guo, X., Drury, C. F., Yang, X., Daniel Reynolds, W., & Fan, R. (2014). The extent of soil drying and rewetting affects nitrous oxide emissions, denitrification, and nitrogen mineralization. *Soil Science Society of America Journal, 78*(1), 194-204.

Yates, T. T. (2006). *Spatial and temporal patterns of nitrous oxide and their relationship to soil water and soil properties* (Doctoral dissertation).

Xu, Y., He, J., Cheng, W., Xing, X., & Li, L. (2010). Natural 15N abundance in soils and plants in relation to N cycling in a rangeland in Inner Mongolia. *Journal of Plant Ecology, 3*(3), 201-207.

Zhang, W., & Zhang, X. (2007). A forecast analysis on fertilizers consumption worldwide. *Environmental monitoring and Assessment, 133*(1), 427-434.

Zhang, J., & Han, X. (2008). N$_2$O emission from the semi-arid ecosystem under mineral fertilizer (urea and superphosphate) and increased precipitation in northern China. *Atmospheric Environment, 42*(2), 291-302.

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APPENDICES

Appendix 1

Simplified N cycle

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APPENDIX 2

0.17 m

0.25 m

0.5 m

0.03 m

0.25 m

0.5 m

Syringe with 3-way tap

Chamber

Collar
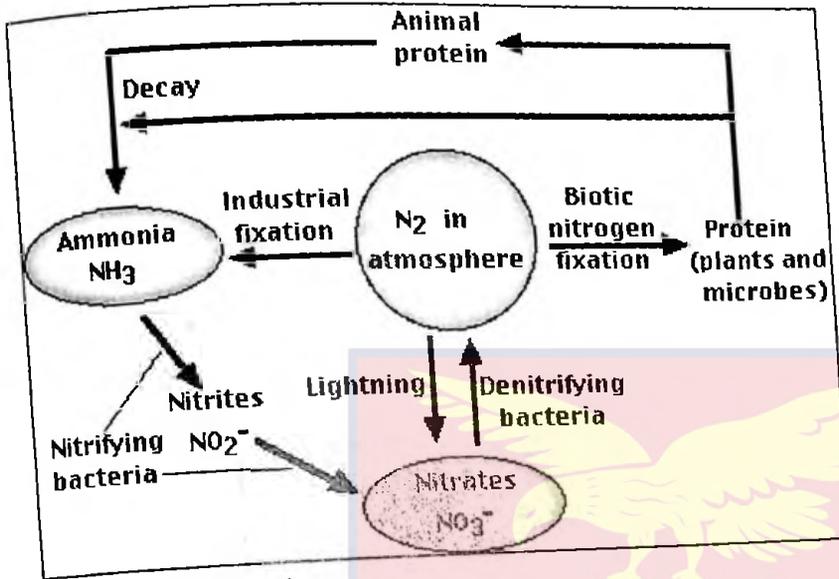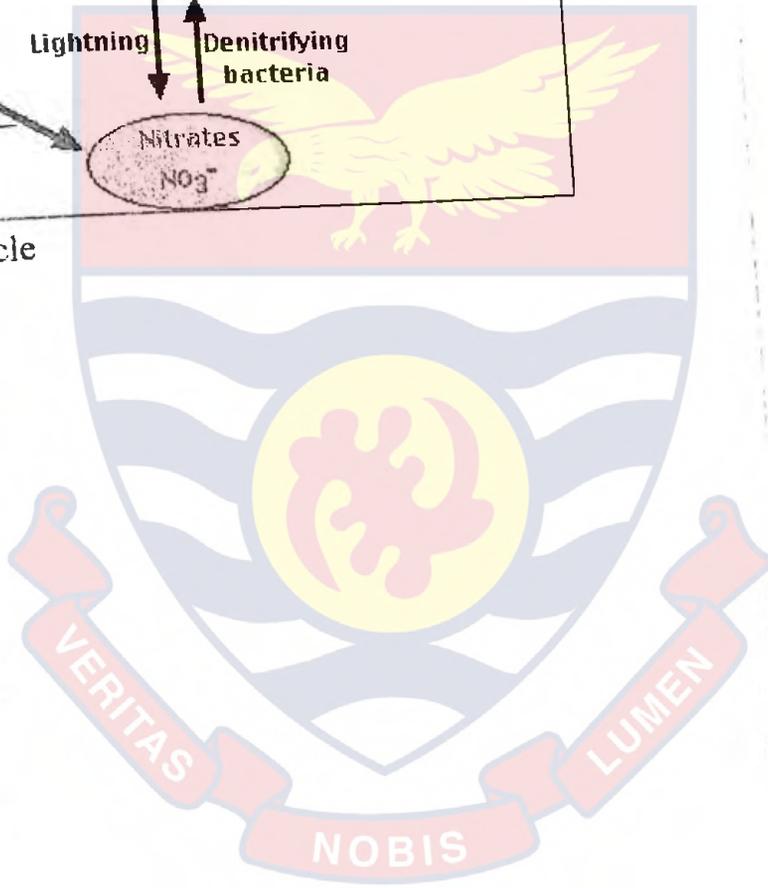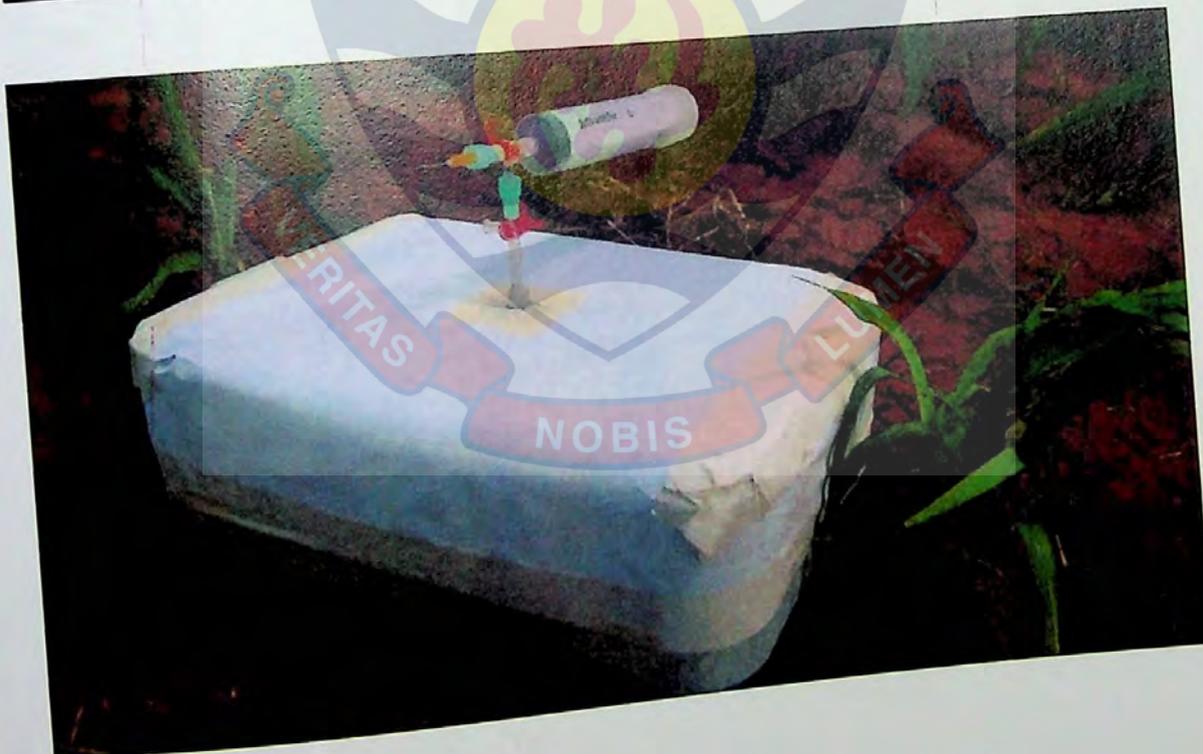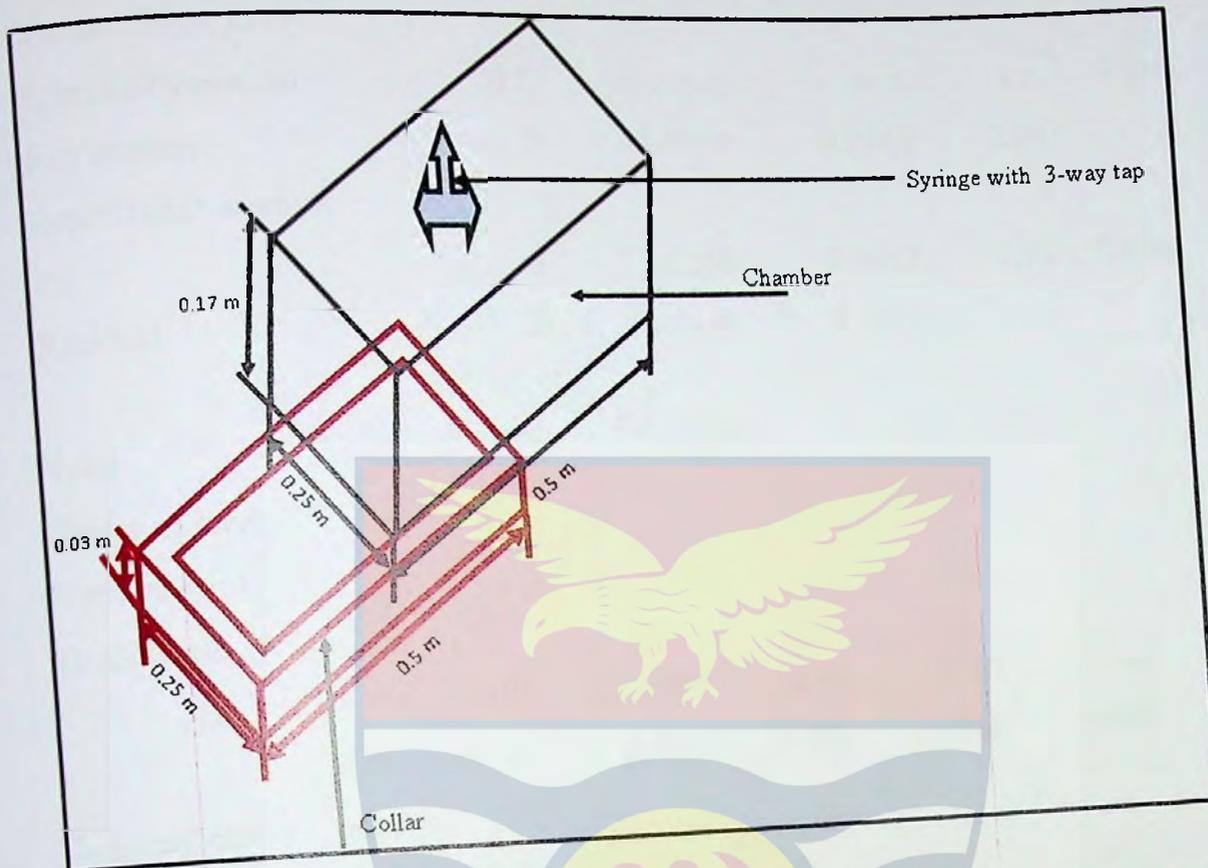
Setup for collection of N2O gas

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APPENDIX 3

ANOVA for field measurement of NH_4^+ and NO_3^-

Variate: NH4_D19

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Rep stratum	2	0.4969	0.2484	2.04	
Rep.*Units* stratum					
Trt	5	0.2266	0.0453	0.37	0.856
Residual	10	1.2149	0.1215		
Total	17	1.9383			

Tables of means

Variate: NH4_D19

Grand mean 0.784

Trt	Cont	NPK	SA 120	sa 60	U 60	U120
	0.880	0.583	0.736	0.753	0.930	0.820

Standard errors of means

Table	Trt
rep.	3
d.f.	10
e.s.e.	0.2012

Standard errors of differences of means

Table	Trt
rep.	3
d.f.	10
s.e.d.	0.2846

Least significant differences of means (5% level)

Table	Trt
rep.	3

d.f.	10
l.s.d.	0.6341

Stratum standard errors and coefficients of variation

Variate: NH4_D19

Stratum	d.f.	s.e.	cv%
Rep	2	0.2035	26.0
Rep.*Units*	10	0.3486	44.5

Analysis of variance

Variate: NH4_D20

Source of variation	d.f.	(m.v.)	s.s.	m.s.	v.r.	F pr.
Rep stratum	2		1.0875	0.5437	4.01	
Rep.*Units* stratum						
Trt	5		3.0350	0.6070	4.48	0.025
Residual	9	(1)	1.2206	0.1356		
Total	16	(1)	4.9016			

Tables of means

Variate: NH4_D20

Grand mean 1.239

Trt	Cont	NPK	SA 120	sa 60	U 60	U120
	0.525	0.860	1.570	1.304	1.597	1.579

Standard errors of means

Table	Trt
rep.	3
d.f.	9

e.s.e.   0.2126

(Not adjusted for missing values)

Standard errors of differences of means

Table	Trt
rep.	3
d.f.	9
s.e.d.	0.3007

(Not adjusted for missing values)

Least significant differences of means (5% level)

Table	Trt
rep.	3
d.f.	9
l.s.d.	0.6802

(Not adjusted for missing values)

Stratum standard errors and coefficients of variation

ariate: NH4_D20

Stratum	d.f.	s.e.	cv%
Rep	2	0.3010	24.3
Rep.*Units*	9	0.3683	29.7

Missing values

Variate: NH4_D20

Unit	estimate
13	1.885

Analysis of variance

Variate: NH4_D21

Source of variation	d.f. (m.v.)	s.s.	m.s.	v.r.	F pr.
Rep stratum	2	27.158	13.579	8.37	

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Rep.*Units* stratum

Trt		5		26.438	5.288	3.26
0.059					
Residual		9	(1)	14.603	1.623
Total		16	(1)	64.755	

Tables of means

Variate: NH$_4$_D21

Grand mean 2.57

Trt	Cont	NPK	SA 120	sa 60	U 60	U120
	0.49	1.89	2.65	3.04	4.49	2.87

Standard errors of means

Table	Trt
rep.	3
d.f.	9
e.s.e.	0.735

(Not adjusted for missing values)

Standard errors of differences of means

Table	Trt
rep.	3
d.f.	9
s.e.d.	1.040

(Not adjusted for missing values)

Least significant differences of means (5% level)

Table	Trt
rep.	3
d.f.	9
l.s.d.	2.353

(Not adjusted for missing values)

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Stratum standard errors and coefficients of variation

Variate: NH$_4$_D21

Stratum	d.f.	s.e.	cv%
Rep	2	1.504	58.5
Rep.*Units*	9	1.274	49.6

Missing values

Variate: NH$_4$_D21

Unit	estimate

Analysis of variance

Variate: NH$_4$_D22

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Rep stratum	2	1.2135	0.6067	1.63	
Rep.*Units* stratum					
Trt	5	11.9280	2.3856	6.40	0.006
Residual	10	3.7298	0.3730		
Total	17	16.8713			

Message: the following units have large residuals.

Rep 3 *units* 3	1.31	s.e.	0.46

Tables of means

Variate: NH4_D22

Grand mean 1.80

Trt	Cont	NPK	SA 120	sa 60	U 60	U120
	0.44	2.41	1.81	3.04	1.34	1.75

Standard errors of means

Table	Trt
rep.	3
d.f.	10

208

e.s.e.   0.353

Standard errors of differences of means

Table	Trt
rep.	3
d.f.	10
s.e.d.	0.499

Least significant differences of means (5% level)

Table	Trt
rep.	3
d.f.	10
l.s.d.	1.111

Stratum standard errors and coefficients of variation

Variate: NH$_4$_D22

Stratum	d.f.	s.e.	cv%
Rep	2	0.318	17.7
Rep.*Units*	10	0.611	33.9

Analysis of variance

Variate: NH$_4$_D23

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Rep stratum	2	65.843	32.922	11.43	
Rep.*Units* stratum					
Trt	5	38.489	7.698	2.67	0.087
Residual	10	28.797	2.880		
Total	17	133.130			

Message: the following units have large residuals

Rep 1 *units* 3   -2.76   s.e.   1.26

Tables of means

209

Variate: NH4_D23

Grand mean 2.75

Trt	Cont	NPK	SA 120	sa 60	U 60	U120
	0.18	3.73	3.32	3.78	1.36	4.14

Standard errors of means

Table	Trt
rep.	3
d.f.	10
e.s.e.	0.980

Standard errors of differences of means

Table	Trt
rep.	3
d.f.	10
s.e.d.	1.386

Least significant differences of means (5% level)

Table	Trt
rep.	3
d.f.	10
l.s.d.	3.087

Stratum standard errors and coefficients of variation

Variate: NH4_D23

Stratum	d.f.	s.e.	cv%
Rep	2	2.342	85.1
Rep.*Units*	10	1.697	61.7

Analysis of variance

210

Variate: NH4_D30

Source of variation	d.f.	(m.v.)	s.s.	m.s.	v.r.	F pr.
Rep stratum	2		11.685	5.843	2.15	
Rep.*Units* stratum						
Trt	5		20.525	4.105	1.51	0.278
Residual	9	(1)	24.477	2.720		
Total	16	(1)	52.407			

Message: the following units have large residuals.

Rep 1 *units* 2   3.10   s.e.   1.17
Rep 3 *units* 6   -3.10   s.e.   1.17

Tables of means

Variate: NH4_D30

Grand mean 1.66

Trt	Cont	NPK	SA 120	sa 60	U 60	U120
	0.57	1.43	1.28	1.12	3.93	1.64

Standard errors of means

Table	Trt
rep.	3
d.f.	9
e.s.e.	0.952

(Not adjusted for missing values)

Standard errors of differences of means

Table	Trt
rep.	3
d.f.	9

211

s.e.d.   1.347

(Not adjusted for missing values)

Least significant differences of means (5% level)

Table	Trt
rep.	3
d.f.	9
l.s.d.	3.046

(Not adjusted for missing values)

Stratum standard errors and coefficients of variation

Variate: NH4_D30

Stratum	d.f.	s.e.	cv%
Rep	2	0.987	59.3
Rep.*Units*	9	1.649	99.1

Missing values

Variate: NH4_D30

Unit	estimate
10	3.67

Analysis of variance ammonium_2014

Variate: NH4_D19

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Rep stratum	2	0.4969	0.2484	2.04	
Rep.*Units* stratum					
Trt	5	0.2266	0.0453	0.37	0.856
Residual	10	1.2149	0.1215		
Total	17	1.9383			

Tables of means

212

Variate: NH$_4$_D19

Grand mean 0.784

Trt	Cont	NPK	SA 120	sa 60	U 60	U120
	0.880	0.583	0.736	0.753	0.930	0.820

Standard errors of means

Table	Trt
rep.	3
d.f.	10
e.s.e.	0.2012

Standard errors of differences of means

Table	Trt
rep.	3
d.f.	10
s.e.d.	0.2846

Least significant differences of means (5% level)

Table	Trt
rep.	3
d.f.	10
l.s.d.	0.6341

Stratum standard errors and coefficients of variation

Variate: NH$_4$_D19

Stratum	d.f.	s.e.	cv%
Rep	2	0.2035	26.0
Rep.*Units*	10	0.3486	44.5

Analysis of variance

Variate: NH$_4$_D20

213

Source of variation pr.	d.f.	(m.v.)	s.s.	m.s.	v.r. F
Rep stratum	2		1.0875	0.5437	4.01
Rep.*Units* stratum					
Trt 0.025	5		3.0350	0.6070	4.48
Residual	9	(1)	1.2206	0.1356	
Total	16	(1)	4.9016		

Tables of means

Variate: NH4_D20

Grand mean 1.239

Trt	Cont	NPK	SA 120	sa 60	U 60	U120
	0.525	0.860	1.570	1.304	1.597	1.579

Standard errors of means

Table	Trt
rep.	3
d.f.	9
e.s.e.	0.2126

(Not adjusted for missing values)

Standard errors of differences of means

Table	Trt
rep.	3
d.f.	9
s.e.d.	0.3007

(Not adjusted for missing values)

Least significant differences of means (5% level)

214

Table

	Trt
rep.	3
d.f.	9
l.s.d.	0.6802

(Not adjusted for missing values)

Stratum standard errors and coefficients of variation

Variate: NH_4_D20

Stratum	d.f.	s.e.	cv%
Rep	2	0.3010	24.3
Rep.*Units*	9	0.3683	29.7

Missing values

Variate: $NH4\_D20$

Unit	estimate
13	1.885

Analysis of variance

Variate: NH_4_D21

Source of variation	d.f.	(m.v.)	s.s.	m.s.	v.r.	F pr.
Rep stratum	2		27.158	13.579	8.37	
Rep.*Units* stratum						
Trt	5		26.438	5.288	3.26	0.059
Residual	9	(1)	14.603	1.623		
Total	16	(1)	64.755			

Tables of means

Variate: NH_4_D21

Grand mean 2.57

215

Trt	Cont	NPK	SA 120	sa 60	U 60	U120
	0.49	1.89	2.65	3.04	4.49	2.87

Standard errors of means

Table	Trt
rep.	3
d.f.	9
e.s.e.	0.735

(Not adjusted for missing values)

Standard errors of differences of means

Table	Trt
rep.	3
d.f.	9
s.e.d.	1.040

(Not adjusted for missing values)

Least significant differences of means (5% level)

Table	Trt
rep.	3
d.f.	9
l.s.d.	2.353

(Not adjusted for missing values)

Stratum standard errors and coefficients of variation

Variate: NH_4_D21

Stratum	d.f.	s.e.	cv%
Rep	2	1.504	58.5
Rep.*Units*	9	1.274	49.6

Missing values

Variate: NH_4_D21

Unit	estimate
13	4.37

Analysis of variance

216

Variate: NH$_4$_D22

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Rep stratum	2	1.2135	0.6067	1.63	
Rep.*Units* stratum					
Trt	5	11.9280	2.3856	6.40	0.006
Residual	10	3.7298	0.3730		
Total	17	16.8713			

Message: the following units have large residuals.

Rep 3 *units* 3

1.31   s.e. 0.46

Tables of means

Variate: NH$_4$_D22

Grand mean 1.80

Trt	Cont	NPK	SA 120	sa 60	U 60	U120
	0.44	2.41	1.81	3.04	1.34	1.75

Standard errors of means

Table	Trt
rep.	3
d.f.	10
e.s.e.	0.353

Standard errors of differences of means

Table	Trt
rep.	3
d.f.	10
s.e.d.	0.499

Least significant differences of means (5% level)

Table	Trt
rep.	3

217

d.f.   10

l.s.d.   1.111

Stratum standard errors and coefficients of variation

Variate: NH4_D22

Stratum	d.f.	s.e.	cv%
Rep	2	0.318	17.7
Rep.*Units*	10	0.611	33.9

Analysis of variance

Variate: NH4_D23

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Rep stratum	2	65.843	32.922	11.43	
Rep.*Units* stratum					
Trt	5	38.489	7.698	2.67	0.087
Residual	10	28.797	2.880		
Total	17	133.130			

Message: the following units have large residuals.

Rep 1 *units* 3   -2.76   s.e. 1.26

Tables of means

Variate: NH4_D23

Grand mean 2.75

Trt	Cont	NPK	SA 120	sa 60	U 60	U120
	0.18	3.73	3.32	3.78	1.36	4.14

Standard errors of means

Table	Trt
rep.	3
d.f.	10
e.s.e.	0.980

218

Standard errors of differences of means

Table	Trt
rep.	3
d.f.	10
s.e.d.	1.386

Least significant differences of means (5% level)

Table	Trt
rep.	3
d.f.	10
l.s.d.	3.087

Stratum standard errors and coefficients of variation

Variate: NH_4_D23

Stratum	d.f.	s.e.	cv%
Rep	2	2.342	85.1
Rep.*Units*	10	1.697	61.7

Analysis of variance

Variate: NH_4_D30

Source of variation	d.f. (m.v.)	s.s.	m.s.	v.r.	F pr.
Rep stratum	2	11.685	5.843	2.15	
Rep.*Units* stratum					
Trt	5	20.525	4.105	1.51	0.278
Residual	9 (1)	24.477	2.720		
Total	16 (1)	52.407			

Message: the following units have large residuals.

Rep 1 *units* 2   3.10   s.e. 1.17

219

Rep 3 *units* 6

Tables of means   -3.10   s.e. 1.17

Variate: NH$_4$_D30

Grand mean 1.66

Trt	Cont	NPK	SA 120	sa 60	U 60	U120
	0.57	1.43	1.28	1.12	3.93	1.64

Standard errors of means

Table	Trt
rep.	3
d.f.	9
e.s.e.	0.952

(Not adjusted for missing values)

Standard errors of differences of means

Table	Trt
rep.	3
d.f.	9
s.e.d.	1.347

(Not adjusted for missing values)

Least significant differences of means (5% level)

Table	Trt
rep.	3
d.f.	9
l.s.d.	3.046

(Not adjusted for missing values)

Stratum standard errors and coefficients of variation

220

Variate: NH$_4$_D30

Stratum	d.f.	s.e.	cv%
Rep	2	0.987	59.3
Rep.*Units*	9	1.649	99.1

Missing values

Variate: NH$_4$_D30

Unit	estimate
10	3.6

Analysis of variance

Variate: NO$_3$_D19

Source of variation pr.	d.f. (m.v.)	s.s.	m.s.	v.r. F
Rep stratum	2	0.015591	0.007796	0.99
Rep.*Units* stratum				
Trt 0.575	5	0.031473	0.006295	0.80
Residual	9 (1)	0.070535	0.007837	
Total	16 (1)	0.116372		

Message: the following units have large residuals.

Rep 3 *units* 3   -0.157   s.e. 0.063

Tables of means

Variate: NO$_3$_D19

Grand mean 6.141

Trt	Cont	NPK	SA 120	sa 60	U 60	U120
	6.173	6.136	6.131	6.085	6.212	6.106

Standard errors of means

Table	Trt
rep.	3
d.f.	9

221

e.s.e.   0.0511

(Not adjusted for missing values)

Standard errors of differences of means

Table	Trt
rep.	3
d.f.	9
s.e.d.	0.0723

(Not adjusted for missing values)

Least significant differences of means (5% level)

Table	Trt
rep.	3
d.f.	9
l.s.d.	0.1635

(Not adjusted for missing values)

Stratum standard errors and coefficients of variation

Variate: NO$_3$_D19

Stratum	d.f.	s.e.	cv%
Rep	2	0.0360	0.6
Rep.*Units*	9	0.0885	1.4

Missing values

Variate: NO$_3$_D19

Unit	estimate
18	6.175

Analysis of variance

Variate: NO$_3$_D20

Source of variation	d.f. (m.v.)	s.s.	m.s.	v.r.	F pr.

Rep stratum	2		0.024801	0.012400	1.97
Rep.*Units* stratum					
Trt	5		0.033524	0.006705	1.07
0.445					
Residual	8	(2)	0.050339	0.006292	
Total	15	(2)	0.088874		

Message: the following units have large residuals.

Rep 3 *units* 1   -0.122   s.e. 0.053

Tables of means

Variate: NO_3_D20

Grand mean 6.155

Trt	Cont	NPK	SA 120	sa 60	U 60	U120
	6.138	6.108	6.182	6.157	6.233	6.111

Standard errors of means

Table	Trt
rep.	3
d.f.	8
e.s.e.	0.0458

(Not adjusted for missing values)

Standard errors of differences of means

Table	Trt
rep.	3
d.f.	8
s.e.d.	0.0648

(Not adjusted for missing values)

Least significant differences of means (5% level)

Table	Trt

223

rep.	3
d.f.	8
l.s.d.	0.1494

(Not adjusted for missing values)

Stratum standard errors and coefficients of variation

Variate: NO_3_D20

Stratum	d.f.	s.e.	cv%
Rep	2	0.0455	0.7
Rep.*Units*	8	0.0793	1.3

Missing values

Variate: NO_3_D20

Unit	estimate
12	6.103
18	6.284

Analysis of variance

Variate: NO_3_D21

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Rep stratum	2	0.028409	0.014205	1.81	
Rep.*Units* stratum					
Trt	5	0.034163	0.006833	0.87	0.533
Residual	10	0.078429	0.007843		
Total	17	0.141001			

Message: the following units have large residuals.

Rep 1 *units* 1   -0.133   s.e. 0.066

Tables of means

Variate: NO_3_D21

224

Grand mean 6.146

Trt	Cont	NPK	SA 120	sa 60	U 60	U120
	6.079	6.166	6.120	6.168	6.127	6.216

Standard errors of means

Table	Trt
rep.	3
d.f.	10
e.s.e.	0.0511

Standard errors of differences of means

Table	Trt
rep.	3
d.f.	10
s.e.d.	0.0723

Least significant differences of means (5% level)

Table	Trt
rep.	3
d.f.	10
l.s.d.	0.1611

Stratum standard errors and coefficients of variation

Variate: NO_3_D21

Stratum	d.f.	s.e.	cv%
Rep	2	0.0487	0.8
Rep.*Units*	10	0.0886	1.4

Analysis of variance

Variate: NH_4_D22

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Rep stratum	2	1.2135	0.6067	1.63	
Rep.*Units* stratum					

225

Trt	5	11.9280	2.3856	6.40	0.006
Residual	10	3.7298	0.3730		
Total	17	16.8713			

Message: the following units have large residuals.

Rep 3 *units* 3

1.31   s.e. 0.46

Tables of means

Variate: NH$_4$_D22

Grand mean 1.80

Trt	Cont	NPK	SA 120	sa 60	U 60	U120
	0.44	2.41	1.81	3.04	1.34	1.75

Standard errors of means

Table	Trt
rep.	3
d.f.	10
e.s.e.	0.353

Standard errors of differences of means

Table	Trt
rep.	3
d.f.	10
s.e.d.	0.499

Least significant differences of means (5% level)

Table	Trt
rep.	3
d.f.	10
l.s.d.	1.111

Stratum standard errors and coefficients of variation

226

Variate: NH$_4$_D22

Stratum	d.f.	s.e.	cv%
Rep	2	0.318	17.7
Rep.*Units*	10	0.611	33.9

Analysis of variance

Variate: NO$_3$_D22

Source of variation	d.f. (m.v.)	s.s.	m.s.	v.r.	F pr.
Rep stratum	2	0.002391	0.001196	0.24	
Rep.*Units* stratum					
Trt	5	0.080780	0.016156	3.29	0.058
Residual	9 (1)	0.044157	0.004906		
Total	16 (1)	0.115454			

Message: the following units have large residuals.

Rep 1 *units* 3   -0.101   s.e. 0.050

Tables of means

Variate: NO$_3$_D22

Grand mean 6.157

Trt	Cont	NPK	SA 120	sa 60	U 60	U120
	6.159	6.059	6.267	6.095	6.177	6.189

Standard errors of means

Table	Trt
rep.	3
d.f.	9
e.s.e.	0.0404

227

(Not adjusted for missing values)

Standard errors of differences of means

Table	Trt
rep.	3
d.f.	9
s.e.d.	0.0572

(Not adjusted for missing values)

Least significant differences of means (5% level)

Table	Trt
rep.	3
d.f.	9
l.s.d.	0.1294

(Not adjusted for missing values)

Stratum standard errors and coefficients of variation

Variate: NO_3_D22

Stratum	d.f.	s.e.	cv%
Rep	2	0.0141	0.2
Rep.*Units*	9	0.0700	1.1

Missing values

Variate: NO_3_D22

Unit	estimate
8	6.052

Analysis of variance

Variate: NO_3_D23

Source of variation	d.f. (m.v.)	s.s.	m.s.	v.r.	F pr.

228

Rep stratum	2			
Rep.*Units* stratum		0.004922	0.002461	0.44
Trt	5			
0.426		0.030388	0.006078	1.09
Residual	9 (1)	0.049955	0.005551	
Total	16 (1)	0.083310		

Message: the following units have large residuals.

Rep 2 *units* 3

0.116   s.e. 0.053

Tables of means

Variate: NO$_3$_D23

Grand mean 6.154

Trt	Cont	NPK	SA 120	sa 60	U 60	U120
	6.143	6.170	6.106	6.223	6.106	6.174

Standard errors of means

Table	Trt
rep.	3
d.f.	9
e.s.e.	0.0430

(Not adjusted for missing values)

Standard errors of differences of means

Table	Trt
rep.	3
d.f.	9
s.e.d.	0.0608

(Not adjusted for missing values)

229

Least significant differences of means (5% level)

Table	Trt
rep.	3
d.f.	9
l.s.d.	0.1376

(Not adjusted for missing values)

Stratum standard errors and coefficients of variation

Variate: NO_3_D23

Stratum	d.f.	s.e.	cv%
Rep	2	0.0203	0.3
Rep.*Units*	9	0.0745	1.2

Missing values

Variate: NO_3_D23

Unit	estimate
5	6.197

Analysis of variance

Variate: NO_3_D30

Source of variation	d.f.	(m.v.)	s.s.	m.s.	v.r.	F pr.
Rep stratum	2		0.001506	0.000753	0.16	
Rep.*Units* stratum						
Trt	5		0.037925	0.007585	1.62	0.249
Residual	9	(1)	0.042124	0.004680		
Total	16	(1)	0.075198			

Tables of means

230

Variate: NO₃_D30

Grand mean 6.132

Trt	Cont	NPK	SA 120	sa 60	U 60	U120
	6.095	6.072	6.136	6.157	6.215	6.120

Standard errors of means

Table	Trt
rep.	3
d.f.	9
e.s.e.	0.0395

(Not adjusted for missing values)

Standard errors of differences of means

Table	Trt
rep.	3
d.f.	9
s.e.d.	0.0559

(Not adjusted for missing values)

Least significant differences of means (5% level)

Table	Trt
rep.	3
d.f.	9
l.s.d.	0.1264

(Not adjusted for missing values)

Stratum standard errors and coefficients of variation

Variate: NO₃_D30

Stratum	d.f.	s.e.	cv%
Rep	2	0.0112	0.2

231

Rep.*Units*	9	0.0684	1.1	

Missing values

Variate: NO_3_D30

Unit	estimate
18	6.210

Max. no. iterations 2

Analysis of variance nitrate-2014

Variate: NO_3_D19

Source of variation	d.f.	(m.v.)	s.s.	m.s.	v.r.	F pr.
Rep stratum	2		0.015591	0.007796	0.99	
Rep.*Units* stratum						
Trt	5		0.031473	0.006295	0.80	0.575
Residual	9	(1)	0.070535	0.007837		
Total	16	(1)	0.116372			

Message: the following units have large residuals.

Rep 3 *units* 3   -0.157   s.e. 0.063

Tables of means

Variate: NO_3_D19

Grand mean 6.141

Trt	Cont	NPK	SA 120	sa 60	U 60	U120
	6.173	6.136	6.131	6.085	6.212	6.106

Standard errors of means

Table	Trt
rep.	3

232

d.f.	9
e.s.e.	0.0511

(Not adjusted for missing values)

Standard errors of differences of means

Table	Trt
rep.	3
d.f.	9
s.e.d.	0.0723

(Not adjusted for missing values)

Least significant differences of means (5% level)

Table	Trt
rep.	3
d.f.	9
l.s.d.	0.1635

(Not adjusted for missing values)

Stratum standard errors and coefficients of variation

Variate: NO_3_D19

Stratum	d.f.	s.e.	cv%
Rep	2	0.0360	0.6
Rep.*Units*	9	0.0885	1.4

Missing values

Variate: NO_3_D19

Unit	estimate
18	6.175

233

Analysis of variance

Variate: NO$_3$_D20

Source of variation pr.	d.f.	(m.v.)	s.s.	m.s.	v.r. F
Rep stratum	2		0.024801	0.012400	1.97
Rep.*Units* stratum					
Trt 0.445	5		0.033524	0.006705	1.07
Residual	8	(2)	0.050339	0.006292	
Total	15	(2)	0.088874		

Message: the following units have large residuals.

Rep 3 *units* 1   -0.122   s.e. 0.053

Tables of means

Variate: NO$_3$_D20

Grand mean 6.155

Trt	Cont	NPK	SA 120	sa 60	U 60	U120
	6.138	6.108	6.182	6.157	6.233	6.111

Standard errors of means

Table	Trt
rep.	3
d.f.	8
e.s.e.	0.0458

(Not adjusted for missing values)

Standard errors of differences of means

Table	Trt
rep.	3
d.f.	8

s.e.d.   0.0648

(Not adjusted for missing values)

Least significant differences of means (5% level)

Table	Trt
rep.	3
d.f.	8
l.s.d.	0.1494

(Not adjusted for missing values)

Stratum standard errors and coefficients of variation

Variate: NO$_3$_D20

Stratum	d.f.	s.e.	cv%
Rep	2	0.0455	0.7
Rep.*Units*	8	0.0793	1.3

Missing values

Variate: NO$_3$_D20

Unit	estimate
12	6.103
18	6.284

Analysis of variance

Variate: NO$_3$_D21

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Rep stratum	2	0.028409	0.014205	1.81	
Rep.*Units* stratum					
Trt	5	0.034163	0.006833	0.87	0.533

235

Residual	10	0.078429	0.007843
Total	17	0.141001	

Message: the following units have large residuals.

Rep 1 *units* 1

-0.133   s.e. 0.066

Tables of means

Variate: NO_3_D21

Grand mean 6.146

Trt	Cont	NPK	SA 120	sa 60	U 60	U120
	6.079	6.166	6.120	6.168	6.127	6.216

Standard errors of means

Table	Trt
rep.	3
d.f.	10
e.s.e.	0.0511

Standard errors of differences of means

Table	Trt
rep.	3
d.f.	10
s.e.d.	0.0723

Least significant differences of means (5% level)

Table	Trt
rep.	3
d.f.	10
l.s.d.	0.1611

236

Stratum standard errors and coefficients of variation

Variate: NO_3_D21

Stratum	d.f.	s.e.	cv%
Rep	2	0.0487	0.8
Rep.*Units*	10	0.0886	1.4

Analysis of variance

Variate: NH_4_D22

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Rep stratum	2	1.2135	0.6067	1.63	
Rep.*Units* stratum					
Trt	5	11.9280	2.3856	6.40	0.006
Residual	10	3.7298	0.3730		
Total	17	16.8713			

Message: the following units have large residuals.

Rep 3 *units* 3		1.31	s.e.	0.46

Tables of means

Variate: NH_4_D22

Grand mean 1.80

Trt	Cont	NPK	SA 120	sa 60	U 60	U120
	0.44	2.41	1.81	3.04	1.34	1.75

Standard errors of means

Table	Trt
rep.	3
d.f.	10
e.s.e.	0.353

Standard errors of differences of means

237

Table	Trt
rep.	3
d.f.	10
s.e.d.	0.499

Least significant differences of means (5% level)

Table	Trt
rep.	3
d.f.	10
l.s.d.	1.111

Stratum standard errors and coefficients of variation

Variate: NH$_4$_D22

Stratum	d.f.	s.e.	cv%
Rep	2	0.318	17.7
Rep.*Units*	10	0.611	33.9

Analysis of variance

Variate: NO$_3$_D22

Source of variation	d.f. (m.v.)	s.s.	m.s.	v.r.	F pr.
Rep stratum	2	0.002391	0.001196	0.24	
Rep.*Units* stratum					
Trt	5	0.080780	0.016156	3.29	0.058
Residual	9 (1)	0.044157	0.004906		
Total	16 (1)	0.115454			

238

Message: the following units have large residuals.

Rep 1 *units* 3

Tables of means

$$-0.101 \qquad \text{s.e.} \quad 0.050$$

Variate: NO_3_D22

Grand mean 6.157

Trt	Cont	NPK	SA 120	sa 60	U 60	U120
	6.159	6.059	6.267	6.095	6.177	6.189

Standard errors of means

Table	Trt
rep.	3
d.f.	9
e.s.e.	0.0404

(Not adjusted for missing values)

Standard errors of differences of means

Table	Trt
rep.	3
d.f.	9
s.e.d.	0.0572

(Not adjusted for missing values)

Least significant differences of means (5% level)

Table	Trt
rep.	3
d.f.	9
l.s.d.	0.1294

(Not adjusted for missing values)

Stratum standard errors and coefficients of variation

Variate: NO3_D22

Stratum	d.f.	s.e.	cv%
Rep	2	0.0141	0.2
Rep.*Units*	9	0.0700	1.1

Missing values

Variate: NO3_D22

Unit	estimate
8	6.052

Analysis of variance

Variate: NO3_D23

Source of variation	d.f.	(m.v.)	s.s.	m.s.	v.r.	F pr.
Rep stratum	2		0.004922	0.002461	0.44	
Rep.*Units* stratum						
Trt	5		0.030388	0.006078	1.09	0.426
Residual	9	(1)	0.049955	0.005551		
Total	16	(1)	0.083310			

Message: the following units have large residuals.

Rep 2 *units* 3   0.116   s.e. 0.053

Tables of means

Variate: NO3_D23

Grand mean 6.154

Trt	Cont	NPK	SA 120	sa 60	U 60	U120
	6.143	6.170	6.106	6.223	6.106	6.174

240

Standard errors of means

Table	Trt
rep.	3
d.f.	9
e.s.e.	0.0430

(Not adjusted for missing values)

Standard errors of differences of means

Table	Trt
rep.	3
d.f.	9
s.e.d.	0.0608

(Not adjusted for missing values)

Least significant differences of means (5% level)

Table	Trt
rep.	3
d.f.	9
l.s.d.	0.1376

(Not adjusted for missing values)

Stratum standard errors and coefficients of variation

Variate: NO3_D23

Stratum	d.f.	s.e.	cv%
Rep	2	0.0203	0.3
Rep.*Units*	9	0.0745	1.2

Missing values

Variate: NO_3_D23

Unit   estimate

241

5   6.197

Analysis of variance

Variate: NO$_3$_D30

Source of variation pr.	d.f.	(m.v.)	s.s.	m.s.	v.r.	F
Rep stratum	2		0.001506	0.000753	0.16	
Rep.*Units* stratum						
Trt 0.249	5		0.037925	0.007585	1.62	
Residual	9	(1)	0.042124	0.004680		
Total	16	(1)	0.075198			

Tables of mean

Variate: NO$_3$_D30

Grand mean 6.132

Trt	Cont	NPK	SA 120	sa 60	U 60	U120
	6.095	6.072	6.136	6.157	6.215	6.120

Standard errors of means

Table	Trt
rep.	3
d.f.	9
e.s.e.	0.0395

(Not adjusted for missing values)

Standard errors of differences of means

Table	Trt
rep.	3
d.f.	9

s.e.d.   0.0559

(Not adjusted for missing values)

Least significant differences of means (5% level)

Table	Trt
rep.	3
d.f.	9
l.s.d.	0.1264

(Not adjusted for missing values)

Stratum standard errors and coefficients of variation

Variate: NO_3_D30

Stratum	d.f.	s.e.	cv%
Rep	2	0.0112	0.2
Rep.*Units*	9	0.0684	1.1

Missing values

Variate: NO_3_D30

Unit	estimate
18	6.210

Max. no. iterations 2

243
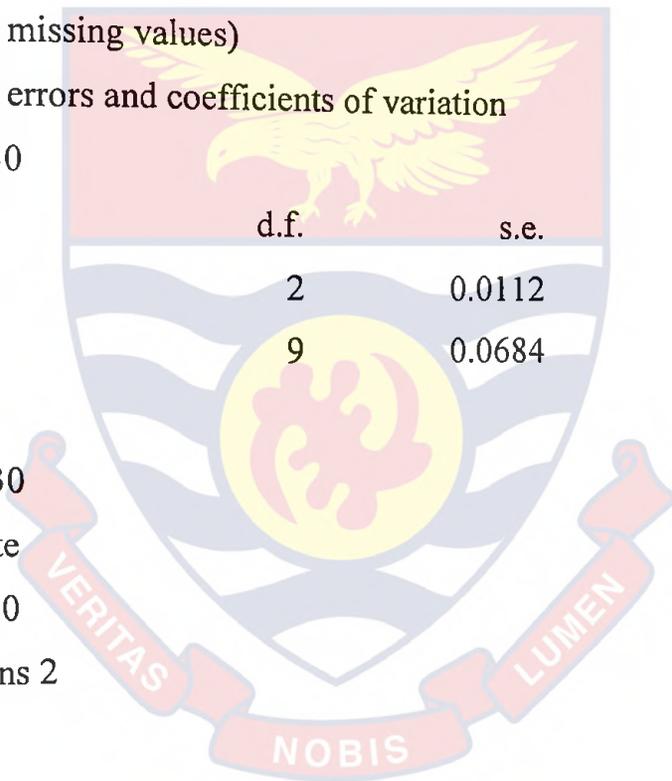
APPENDIX 4

ANOVA for N$_2$O-N on dry soil basis

Variate: %_g_N$_2$O_N_kg_1dry_soil_h_1

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Rep stratum	2	0.39205	0.19602	9.11	
Rep.*Units* stratum					
Treatment	5	1.24921	0.24984	11.61	<.001
Residual	10	0.21520	0.02152		
Total	17	1.85646			

Analysis of variance

Variate: %_g_N$_2$O_m^{-2}_h^{-1}

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Rep stratum	2	273912.	136956.	9.11	
Rep.*Units* stratum					
Treatment	5	872787.	174557.	11.61	<.001
Residual	10	150353.	15035.		
Total	17	1297052.			

244
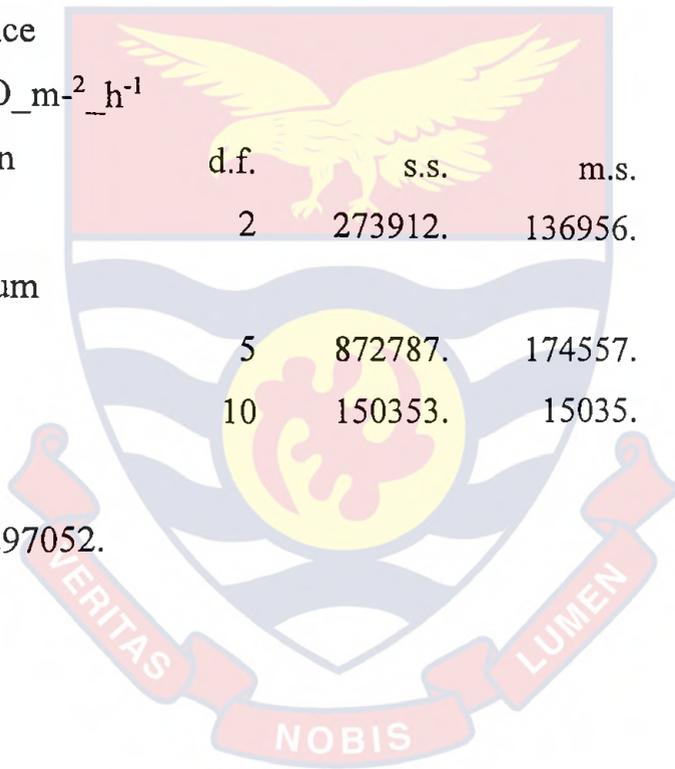
APPENDIX 5

ANOVA of NO-N flux rate at 60 % water holding capacity

Variate: %_g_NO_N_h_1

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Rep stratum	2	0.010213	0.005107	3.14	
Rep.*Units* stratum					
Treat	5	0.087072	0.017414	10.72	<.001
Residual	10	0.016239	0.001624		
Total	17	0.113524			

245

APPENDIX 6

ANOVA of NO-N at 60 % water holding capacity on dry soil basis

Variate: %_g_NO_N_kg_Dry_soil_h_1

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Rep stratum	2	1.0187	0.5094	3.13	
Rep.*Units* stratum					
Treat	5	8.8080	1.7616	10.82	<.001
Residual	10	1.6283	0.1628		
Total	17	11.4550			

Message: the following units have large residuals.

Rep 1 *units* 6	0.621	s.e.	0.301
Rep 3 *units* 6	-0.700	s.e.	0.301

Tables of means

Variate: %_g_NO_N_kg_Dry_soil_h_1

Grand mean 1.227

Treat	Control	NPK	SA 120	SA 60	U 120	U 60
	0.045	1.650	2.101	0.627	1.712	1.230

Standard errors of means

Table	Treat
rep.	3
d.f.	10
e.s.e.	0.2330

Standard errors of differences of means

Table	Treat
rep.	3
d.f.	10

s.e.d.   0.3295

Least significant differences of means (5% level)

Table	Treat
rep.	3
d.f.	10
l.s.d.	0.7341

Stratum standard errors and coefficients of variation

Variate: %_g_NO_N_kg_Dry_soil_h_1

Stratum	d.f.	s.e.	cv%
Rep	2	0.2914	23.7
Rep.*Units*	10	0.4035	32.9

Studentized Maximum Modulus 95.0% confidence intervals

Equal number of observations per mean. (Input as scalar.)

MEAN, LOWER, UPPER are tables.

Treat	Mean	Lower	Upper
Control	0.045	-0.7006	0.790
NPK	1.650	0.9045	2.395
SA 120	2.101	1.3560	2.847
SA 60	0.627	-0.1183	1.373
U 120	1.712	0.9664	2.457
U 60	1.230	0.4841	1.975

80   ALLPAIRWISE [METHOD=bonferroni; DIRECTION=ascending;
PROB=0.05] MEANS=_mean; REPLICATION=_rep;\
81   VARIANCE=_var; DF=_rdf

All pairwise comparisons are tested.

Variance = 0.1628 with 10 degrees of freedom

Experimentwise error rate = 0.0500

SA 120   2.101 |

Analysis of variance

Variate: %_g_NO_N_sq_1_m_h_1

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Rep stratum	2	72241.	36121.	3.14	
Rep.*Units* stratum					
Treat	5	615887.	123177.	10.72	<.001
Residual	10	114863.	11486.		
Total	17	802991.			

Message: the following units have large residuals.

Rep 1 *units* 6	164.	s.e.	80.
Rep 3 *units* 6	-184.	s.e.	80.

Tables of means

Variate: %_g_NO_N_sq_1_m_h_1

Grand mean 326.

Treat	Control	NPK	SA 120	SA 60	U 120	U 60
	12.	439.	554.	167.	455.	327.

Standard errors of means

Table	Treat
	248

rep.	3
d.f.	10
e.s.e.	61.9

Standard errors of differences of means

Table	Treat
rep.	3
d.f.	10
s.e.d.	87.5

Least significant differences of means (5% level)

Table	Treat
rep.	3
d.f.	10
l.s.d.	195.0

Stratum standard errors and coefficients of variation

Variate: %_g_NO_N_sq_1_m_h_1

Stratum	d.f.	s.e.	cv%
Rep	2	77.6	23.8
Rep.*Units*	10	107.2	32.9

Studentized Maximum Modulus 95.0% confidence intervals
Equal number of observations per mean. (Input as scalar.)
MEAN, LOWER, UPPER are tables.

249

Treat	Mean	Lower	Upper
Control	11.9	-186.1	209.9
NPK	438.8	240.8	636.8
SA 120	553.7	355.8	751.7
SA 60	166.8	-31.2	364.8
U 120	455.3	257.3	653.3
U 60	327.0	129.0	525.0

All pairwise comparisons are tested.

Variance = 11486.3142 with 10 degrees of freedom

Bonferroni test

Experimentwise error rate = 0.0500

250

APPENDIX 7

ANOVA of NO-N flux rate at 80 % water holding capacity

Variate: %_g_NO_N_h_1

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Rep stratum	2	0.2168	0.1084	0.98	
Rep.*Units* stratum					
Treat	5	0.5529	0.1106	1.00	0.463
Residual	10	1.1010	0.1101		
Total	17	1.8707			

Message: *the following units have large residuals.*

Rep 3 *units* 4	0.782	s.e.	0.247

Tables of means

Variate: %_g_NO_N_h_1

Grand mean 0.090

Treat	Control	NPK	SA 120	SA 60	U 120	U 60
	0.003	0.009	0.482	0.016	0.015	0.017

Standard errors of means

Table	Treat
rep.	3
d.f.	10
e.s.e.	0.1916

Standard errors of differences of means

Table	Treat
rep.	3
d.f.	10
s.e.d.	0.2709

251

Least significant differences of means (5% level)

Table	Treat
rep.	3
d.f.	10
l.s.d.	0.6037

Stratum standard errors and coefficients of variation

Variate: %_g_NO_N_h_1

Stratum	d.f.	s.e.	cv%
Rep	2	0.1344	148.5
Rep.*Units*	10	0.3318	366.7

Studentized Maximum Modulus 95.0% confidence intervals

Equal number of observations per mean. (Input as scalar.)

MEAN, LOWER, UPPER are tables.

Treat	Mean	Lower	Upper
Control	0.00306	-0.6099	0.6160
NPK	0.00933	-0.6036	0.6223
SA 120	0.48224	-0.1307	1.0952
SA 60	0.01593	-0.5970	0.6289
U 120	0.01517	-0.5978	0.6281
U 60	0.01720	-0.5958	0.6302

61   ALLPAIRWISE [METHOD=bonferroni; DIRECTION=ascending;
PROB=0.05] MEANS=_mean; REPLICATION=_rep;\

62   VARIANCE=_var; DF=_rdf

All pairwise comparisons are tested.

252

Variance = 0.1101 with 10 degrees of freedo

Bonferroni test

Experimentwise error rate = 0.0500

253

APPENDIX 8

ANOVA of NO-N flux at 80 % water holding capacity on dry soil basis

Variate: %_g_NO_N_kg_Dry_soil_h_1

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Rep stratum	2	0.005946	0.002973	2.87	
Rep.*Units* stratum					
Treat	5	0.043929	0.008786	8.49	0.002
Residual	10	0.010344	0.001034		
Total	17	0.060219			

Message: the following units have large residuals.

Rep 3 *units* 4	-0.0626	s.e. 0.0240

Tables of means

Variate: %_g_NO_N_kg_Dry_soil_h_1

Grand mean 0.1166

Treat	Control	NPK	SA 120	SA 60	U 120	U 60
	0.0306	0.0933	0.0924	0.1593	0.1517	0.1720

Standard errors of means

Table	Treat
rep.	3
d.f.	10
e.s.e.	0.01857

Standard errors of differences of means

Table	Treat
rep.	3
d.f.	10
s.e.d.	0.02626

Least significant differences of means (5% level)

254

Table	Treat
rep.	3
d.f.	10
l.s.d.	0.05851

Stratum standard errors and coefficients of variation

Variate: %_g_NO_N_kg_Dry_soil_h_1

Stratum	d.f.	s.e.	cv%
Rep	2	0.02226	19.1
Rep.*Units*	10	0.03216	27.6

Studentized Maximum Modulus 95.0% confidence intervals

Equal number of observations per mean. (Input as scalar.)

MEAN, LOWER, UPPER are tables.

Treat	Mean	Lower	Upper
Control	0.0306	-0.02877	0.0901
NPK	0.0933	0.03393	0.1528
SA 120	0.0924	0.03299	0.1518
SA 60	0.1593	0.09989	0.2187
U 120	0.1517	0.09231	0.2111
U 60	0.1720	0.11261	0.2314

All pairwise comparisons are tested

Variance = 0.0010 with 10 degrees of freedom

Bonferroni test

Experimentwise error rate = 0.0500

Comparisonwise error rate = 0.0033

255

APPENDIX 9

ANOVA of NO-N flux at 80 % water holding capacity on area basis

Variate: %_g_NO_N_sq_1_m_h_1

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Rep stratum	2	438.37	219.19	2.82	
Rep.*Units* stratum					
Treat	5	3125.04	625.01	8.04	0.003
Residual	10	777.50	77.75		
Total	17	4340.91			

Message: *the following units have large residuals.*

Rep 3 *units* 4		-17.4	s.e. 6.6

Tables of means

Variate: %_g_NO_N_sq_1_m_h_1

Grand mean 30.9

Treat	Control	NPK	SA 120	SA 60	U 120	U 60
	8.2	24.8	24.1	42.4	40.4	45.8

Standard errors of means

Table	Treat
rep.	3
d.f.	10
e.s.e.	5.09

Standard errors of differences of means

Table	Treat
rep.	3
d.f.	10
s.e.d.	7.20

Least significant differences of means (5% level)

Table	Treat
rep.	3
d.f.	10
l.s.d.	16.04

Stratum standard errors and coefficients of variation

Variate: %_g_NO_N_sq_1_m_h_1

Stratum	d.f.	s.e.	cv%
Rep	2	6.04	19.5
Rep.*Units*	10	8.82	28.5

Studentized Maximum Modulus 95.0% confidence intervals

Equal number of observations per mean. (Input as scalar.)

MEAN, LOWER, UPPER are tables.

Treat	Mean	Lower	Upper
Control	8.15	-8.14	24.44
NPK	24.83	8.54	41.11
SA 120	24.13	7.84	40.42
SA 60	42.37	26.08	58.66
U 120	40.35	24.06	56.64
U 60	45.75	29.46	62.04

All pairwise comparisons are tested.

Variance = 77.7497 with 10 degrees of freedom

Bonferroni test

Experimentwise error rate = 0.0500

Comparisonwise error rate = 0.0033

APPENDIX 10

ANOVA of NO_2-N flux at 60 % water holding capacity

Variate: %_g_NO₂_N_kg_Dry_soil_h_1

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Rep stratum	2	0.0040226	0.0020113	4.99	
Rep.*Units* stratum					
Treat	5	0.0104108	0.0020822	5.17	0.013
Residual	10	0.0040272	0.0004027		
Total	17	0.0184606			

Message: the following units have large residuals.

Rep 3 *units* 6	-0.0307	s.e.	0.0150

Tables of means

Variate: %_g_NO₂_N_kg_Dry_soil_h_1

Grand mean 0.0476

Treat	Control	NPK	SA 120	SA 60	U 120	U 60
	0.0006	0.0468	0.0659	0.0437	0.0775	0.0513

Standard errors of means

Table	Treat
rep.	3
d.f.	10
e.s.e.	0.01159

Standard errors of differences of means

Table	Treat
rep.	3
d.f.	10
s.e.d.	0.01639

Least significant differences of means (5% level)

Table	Treat
rep.	3
d.f.	10
l.s.d.	0.03651

Stratum standard errors and coefficients of variation

Variate: %_g_NO$_2$_N_kg_Dry_soil_h_1

Stratum	d.f.	s.e.	cv%
Rep	2	0.01831	38.4
Rep.*Units*	10	0.02007	42.1

Studentized Maximum Modulus 95.0% confidence intervals

Equal number of observations per mean. (Input as scalar.)

MEAN, LOWER, UPPER are tables.

Treat	Mean	Lower	Upper
Control	0.00056	-0.03651	0.03763
NPK	0.04676	0.00969	0.08383
SA 120	0.06593	0.02885	0.10300
SA 60	0.04371	0.00664	0.08078
U 120	0.07747	0.04039	0.11454
U 60	0.05134	0.01427	0.08841

All pairwise comparisons are tested.

Variance = 0.0004 with 10 degrees of freedom

Bonferroni test

Experimentwise error rate = 0.0500
Comparisonwise error rate = 0.0033

Analysis of variance

Variate: %_g_NO$_2$_N_sq_1_m_h_1

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Rep stratum	2	284.53	142.27	4.99	
Rep.*Units* stratum					
Treat	5	736.39	147.28	5.17	0.013
Residual	10	284.85	28.49		
Total	17	1305.77			

Message: the following units have large residuals.

Rep 3 *units* 6		-8.2	s.e.	4.0

Tables of means

Variate: %_g_NO$_2$_N_sq_1_m_h_1

Grand mean 12.7

Treat	Control	NPK	SA 120	SA 60	U 120	U 60
	0.1	12.4	17.5	11.6	20.6	13.7

Standard errors of means

Table	Treat
rep.	3
d.f.	10
e.s.e.	3.08

Standard errors of differences of means

Table	Treat
rep.	3
d.f.	10
s.e.d.	4.36

260

Least significant differences of means (5% level)

Table	Treat
rep.	3
d.f.	10
l.s.d.	9.71

Stratum standard errors and coefficients of variation

Variate: %_g_NO2_N_sq_1_m_h_1

Stratum	d.f.	s.e.	cv%
Rep	2	4.87	38.4
Rep.*Units*	10	5.34	42.1

Studentized Maximum Modulus 95.0% confidence intervals

Equal number of observations per mean. (Input as scalar.)

MEAN, LOWER, UPPER are tables.

Treat	Mean	Lower	Upper
Control	0.15	-9.710	10.01
NPK	12.44	2.576	22.30
SA 120	17.53	7.674	27.39
SA 60	11.63	1.766	21.48
U 120	20.60	10.743	30.46
U 60	13.65	3.794	23.51

Analysis of variance

Variate: %_g_NO2_N_kg_Dry_soil_h_1

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.

261

	d.f.	s.s.	m.s.	v.r.	F pr.
Rep stratum	2	3.279E-10	1.640E-10	0.00	
Rep.*Units* stratum					
Treat	5	4.009E-05	8.018E-06	2.92	0.070
Residual	10	2.747E-05	2.747E-06		
Total	17	6.757E-05			

Message: the following units have large residuals.

Rep 1 *units* 5	0.00312	s.e.	0.00124
Rep 2 *units* 5	-0.00316	s.e.	0.00124

Tables of means

Variate: %_g_NO$_2$_N_kg_Dry_soil_h_1

Grand mean 0.00148

Treat	Control	NPK	SA 120	SA 60	U 120	U 60
	-0.00004	0.00094	0.00354	0.00073	0.00353	0.00016

Standard errors of means

Table	Treat
rep.	3
d.f.	10
e.s.e.	0.000957

Standard errors of differences of means

Table	Treat
rep.	3
d.f.	10
s.e.d.	0.001353

Least significant differences of means (5% level)

Table	Treat
rep.	3
d.f.	10
l.s.d.	0.003016

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Stratum standard errors and coefficients of variation

Variate: %_g_NO2_N_kg_Dry_soil_h_1

Stratum	d.f.	s.e.	cv%
Rep	2	0.000005	0.4
Rep.*Units*	10	0.001658	112.3

Studentized Maximum Modulus 95.0% confidence intervals

Equal number of observations per mean. (Input as scalar.)

MEAN, LOWER, UPPER are tables.

Treat	Mean	Lower	Upper
Control	-0.000038	-0.003100	0.003024
NPK	0.000941	-0.002121	0.004003
SA 120	0.003540	0.000478	0.006602
SA 60	0.000726	-0.002336	0.003788
U 120	0.003532	0.000470	0.006594
U 60	0.000160	-0.002902	0.003222

All pairwise comparisons are tested.

Variance = 0.0000 with 10 degrees of freedom

Bonferroni test

Experimentwise error rate = 0.0500

Comparisonwise error rate = 0.0033

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APPENDIX 11

ANOVA of NO2-N flux at 80 % water holding capacity

Variate: %_g_NO$_2$_N_sq_1_m_h_1

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Rep stratum	2	0.0000	0.0000	0.00	
Rep.*Units* stratum					
Treat	5	2.8357	0.5671	2.92	0.070
Residual	10	1.9434	0.1943		
Total	17	4.7791			

Message: the following units have large residuals.

Rep 1 *units* 5	0.83	s.e. 0.33
Rep 2 *units* 5	-0.84	s.e. 0.33

Tables of means

Variate: %_g_NO$_2$_N_sq_1_m_h_1

Grand mean 0.39

Treat	Control	NPK	SA 120	SA 60	U 120	U 60
	-0.01	0.25	0.94	0.19	0.94	0.04

Standard errors of means

Table	Treat
rep.	3
d.f.	10
e.s.e.	0.255

Standard errors of differences of means

Table	Treat
rep.	3
d.f.	10

s.e.d.   0.360

Least significant differences of means (5% level)

Table	Treat
rep.	3
d.f.	10
l.s.d.	0.802

Stratum standard errors and coefficients of variation

Variate: %_g_NO$_2$_N_sq_1_m_h_1

Stratum	d.f.	s.e.	cv%
Rep	2	0.001	0.4
Rep.*Units*	10	0.441	112.3

Studentized Maximum Modulus 95.0% confidence intervals

Equal number of observations per mean. (Input as scalar.)

MEAN, LOWER, UPPER are tables.

Treat	Mean	Lower	Upper
Control	-0.0102	-0.8245	0.804
NPK	0.2502	-0.5642	1.065
SA 120	0.9415	0.1272	1.756
SA 60	0.1930	-0.6214	1.007
U 120	0.9394	0.1250	1.754
U 60	0.0424	-0.7719	0.857

All pairwise comparisons are tested.

Variance = 0.1943 with 10 degrees of freedom

Bonferroni test

Experimentwise error rate = 0.0500

Comparisonwise error rate = 0.0033

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APPENDIX 12

ANOVA of total N, before and after incubation

Variate: Total_N_mg_kg_1_soil

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Replication stratum	2	347.83	173.91	11.90	
Replication.*Units* stratum					
Treatment	11	142.47	12.95	0.89	0.566
Residual	22	321.47	14.61		
Total	35	811.77			

Tables of means

Variate: Total_N_g_kg_1_soil

Grand mean 18.25

Treatment	Control BF	Control F	NPK BF	NPK F	SA 120 BF
SA 120 F	15.81	17.29	16.71	22.67	

17.93 15.96

Treatment	SA 60 BF	SA 60 F	U 120 BF	U 120 F	U 60 BF	U
60 F	17.48	20.24	17.87	20.54	19.57	

16.96

Standard errors of means

Table	Treatment
rep.	3
d.f.	22
e.s.e.	2.207

Standard errors of differences of means

Table	Treatment

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rep.	3
d.f.	22
s.e.d.	3.121

Least significant differences of means (5% level)

Table	Treatment
rep.	3
d.f.	22
l.s.d.	6.473

Stratum standard errors and coefficients of variation

Variate: Total_N_g_kg_1_soil

Stratum	d.f.	s.e.	cv%
Replication	2	3.807	20.9
Replication.*Units*	22	3.823	20.9

Studentized Maximum Modulus 95.0% confidence intervals

Equal number of observations per mean. (Input as scalar.)

MEAN, LOWER, UPPER are tables.

Treatment	Mean	Lower	Upper
Control BF	15.81	8.84	22.78
Control F	17.29	10.32	24.26
NPK BF	16.71	9.74	23.68
NPK F	22.67	15.70	29.64
SA 120 BF	17.93	10.96	24.90
SA 120 F	15.96	8.99	22.93
SA 60 BF	17.48	10.51	24.46
SA 60 F	20.24	13.27	27.21
U 120 BF	17.87	10.90	24.84

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U 120 F	20.54	13.57	27.51
U 60 BF	19.57	12.60	26.54
U 60 F	16.96	9.99	23.93

All pairwise comparisons are tested.

Variance = 14.6124 with 22 degrees of freedom

Bonferroni test

Experimentwise error rate = 0.0500

Comparisonwise error rate = 0.0008

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VITA

Williams Kwame Atakora was born in Ghana in 1981. He grew up in Kumasi where he attended Osei Tutu Senior Secondary School and studied General Agriculture. He further studied at the University of Cape Coast for his BSc. Agriculture and also at Kwame Nkrumah University of Science and Technology for his MSc. Soil Science. Since 2006 he has been working at CSIR-Savanna Agricultural Research Institute. He is a Research Scientist with specialties in Soil Fertility, Crop Modeling, Climate Change and Agriculture. He is also an advocate of rhizobium inoculant and established the first cowpea and soybean rhizobium inoculant production laboratory in northern Ghana. Williams is a lead author of ten research articles published to improve smallholder farmer's knowledge in fertilizer recommendation for maize and rice, Integrated Soil Fertility Management technologies, climate variability and its influence on crop yields.

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