Greenhouse gas emissions in croplands and downslope riparian buffer strips with varying vegetation

BY

Jerry Celumusa Dlamini

Submitted in fulfilment of the requirements for the degree
Doctor of Philosophy (Ph.D.): Agronomy

In the
Department of Plant and Soil Sciences
Faculty of Natural and Agricultural Sciences
University of Pretoria

Supervisors:

Prof. Eyob Habte Tesfamariam
Dr. Laura Maritza Cárdenas

July 2022

DECLARATION

I, **Jerry Celumusa Dlamini**, declare that the thesis, which I hereby submit for the degree of **Ph.D. Agronomy** at the University of Pretoria is my work and has not been submitted by me for a degree at this or any other tertiary institution.

SIGNATURE:

DATE: July 2022

ACKNOWLEDGEMENTS

The South African Department of Higher Education and Training (New Generation Gap of Academics Program) and National Research Foundation-Thuthuka (Grant Number: *117964*) are acknowledged for financially supporting this study. The main experiment was funded by the UKRI (UK Research and Innovation) Biotechnology and Biological Sciences Research Council (BBSRC) SARIC (Sustainable Agriculture and Research Innovation Club) project "*Impacts of different vegetation in riparian buffer strips on hydrology and water quality*" (BB/N004248/1; awarded to Prof. Adrian Collins). The British Council is also thanked for a Researcher Links Travel Grant (2017-RLTG9-1069) that initiated this collaboration between myself and Rothamsted Research. UKRI-BBSRC supports Rothamsted Research through its Institute Strategic Programme grants including projects BBS/E/C/000I0320 and BBS/E/C/000I0330.

I would like to express my utmost gratitude to my supervisors: Prof. Eyob Tesfamariam and Dr. Laura Cárdenas. Not only did they give me the opportunity to work on greenhouse gas emissions, a dream I held on to for too long, but they also invested all their resources in terms of expertise, time, patience, and motivation. During my experiments in NorthWyke, I worked very closely and extensively, particularly with Laura. I have always envied her enthusiasm, deep understanding of greenhouse gas production and subsequent emissions from soils due to various agronomic management practices, and further exploring mitigation practices. The ease with which she disintegrated a complex problem into small units easy to deal with was remarkable for me. I am grateful for the opportunities Laura has availed to me regarding access to world-class scientific community and cutting-edge experimental facilities at Rothamsted Research. Through working with Laura, I have gained valuable knowledge and interpersonal skills which I think no single school program can offer and I will forever be indebted to her.

I am forever indebted to my late grandmother Mrs. Elizah Dlamini who strongly believed in me and afforded me the torch of education throughout the years despite persistent financial difficulties. All my friends and family members are acknowledged for the support they offered me at different levels over the duration of the study. I appreciate Phephile Ngwenya, who became my wife during my studies, for all her undying emotional support and love at all times.

DEDICATION

This thesis is dedicated to my daughter Lakhile Kimberley Dlamini. I missed many experiences from her first few years of life while doing experiments and writing up the study's findings. Let education be always your light and foundation.

ABSTRACT

Greenhouse gas emissions in croplands and downslope riparian buffer strips with varying vegetation.

BY

Jerry Celumusa Dlamini

Supervisors:
Prof. Eyob Habte Tesfamariam
Dr. Laura Maritza Cárdenas

Degree: Ph.D. Agronomy

Vegetated riparian buffer areas are implemented as an intervention to intercept, retain and process diffuse non-point source pollutants (NPS), including nitrate (NO_3^-), phosphorus (P), herbicides, and pesticides emitted from immediately adjacent agricultural lands. Due to their location in landscapes, riparian buffers maintain high organic matter (OM), increasing soil carbon (C) contents, retain high soil moisture from the periodically high water table, and contain higher nitrogen (N) content intercepted from upslope agricultural land. In turn, these conditions promote the production of gases including nitric oxide (NO), nitrous oxide (N_2O), nitrogen gas (N_2), methane (CH_4), and carbon dioxide (CO_2) through various soil processes, including denitrification, methanogenesis, and respiration. Earlier recommendations to the Intergovernmental Panel for Climate Change (IPCC) suggested that greenhouse gas (GHG) i.e., N_2O, inventories for agricultural lands could be improved by including gas

measurements from riparian buffer areas. However, little information is available regarding the dynamics of unintended emissions of soil gases in these commonplace features of agroecosystems primarily installed for water quality functions and how the dynamics compare to those for adjacent croplands.

In order to understand the dynamics and drivers of N_2O in riparian buffers and their immediately adjacent croplands, a meta-analysis of studies comparing N_2O emissions and their drivers from riparian buffers and adjacent croplands was conducted. It was identified that while there is growing literature quantifying N_2O emissions from different types of riparian buffer vegetation, comparative assessments of N_2O emissions from riparian buffers and croplands remain limited. This was evident in the literature database summarizing data from 13 studies, with 44 data points from croplands: $n = 22$, and riparian buffers: $n = 22$, published between 1980 and 2021. The meta-analysis showed that the croplands generated significantly greater N_2O emissions than the riparian buffers. In both the croplands and riparian buffers, emissions of N_2O were mainly driven by elevation ($p = 0.029$), land use ($p < 0.0001$), soil texture ($p = 0.018$), soil bulk density (BD) ($p < 0.0001$), total carbon (C) ($p < 0.0001$), C: N ratio ($p < 0.0001$), and NH_4^+-N ($p < 0.0001$).

To further understand the dynamics of soil N_2O, CH_4, and CO_2 fluxes from permanent pasture and maize (*Zea mays* L.) and contiguous riparian buffer strips with different (grass, willow, and woodland) vegetation as well control with no buffer vegetation, measurements on an existing experiment were carried out using the static chamber technique on a replicated plot-scale facility. For the experiment, including a permanent pasture, gas fluxes were measured periodically with soil and environmental variables between June 2018 and February 2019 at North Wyke, United Kingdom. During most of the sampling days, the no-buffer control treatment showed significantly (*p <0.05*) greater N_2O fluxes and cumulative N_2O emissions than the other treatments. The results also showed that the grass riparian buffer strip was a sink of N_2O equivalent to -2310.2 g N ha^{-1} (95% confidence intervals: -535.5-492). Event-based water quality results obtained during storms showed that the willow riparian buffer treatment had the highest flow-weighted mean N concentrations (FWMC-N) of 0.041 ± 0.022 and 0.031 ± 0.015 mg N L^{-1} during the 12 November 2018 and 11 February 2019 storms, respectively, when compared to the other treatments.

Soils under all treatments were sinks of soil CH_4, with the willow riparian buffer strip (-2555 ± 318.7 g ha^{-1}) being the largest soil CH_4 sink followed by the grass riparian buffer (-2532 ± 318.7 g ha^{-1}), woodland riparian buffer (-2318.0 ± 246.4 g ha^{-1}), no-buffer strip control (-1938.0 ± 374.4 g ha^{-1}), and lastly the upslope pasture (-1328.0 ± 89.0 g ha^{-1}). Cumulative soil CO_2 fluxes as affected by the treatments followed the descending order: woodland riparian buffer; 11927.8 ± 1987.9 kg ha^{-1} > no buffer control; 11101.3 ± 3700.4 kg ha^{-1} > grass riparian buffer; 10826.4 ± 2551.8 kg ha^{-1} > upslope pasture; 10554.6 ± 879.5 kg ha^{-1} > willow riparian buffer; 9294.9 ± 1549.2 5 kg ha^{-1}. There was, however, no evidence of significant differences in cumulative CO_2 amongst all treatments of the current study. Despite the lack of significant differences, the results showed that the woodland riparian buffer might emit the larger soil CO_2 compared to the remainder of the other riparian buffers as well as the upslope pasture it serves.

After the upslope area was converted from permanent pasture to maize (riparian buffers left untouched), the N_2O, CH_4, and CO_2 measurements done between May and October 2019 showed that the no-buffer control generated the largest cumulative N_2O emissions of 18 929 g N ha^{-1} (95% confidence intervals: 524.1 - 63 643) while the maize crop upslope generated the largest cumulative CH_4 emissions of

5 050 ± 875 g ha^{-1}. On the other hand, the woodland (322.9 ± 3.1 kg ha^{-1}) and grass (285 ± 2.7 kg ha^{-1}) riparian buffer treatments (not significant to each other) generated significantly (*p =<0.0001*) the largest CO_2 compared to the rest of the treatments.

A laboratory incubation experiment of the soils sourced from cropland, grass riparian buffer, willow riparian, and woodland riparian buffer using a specialized Denitrification System (DENIS) showed that the grass riparian buffer soils had the highest potential for emissions of NO (2.9 ± 0.31 mg m^{-2}), and N_2O (1413.4 ± 448.3 mg m^{-2}), and the willow riparian buffer treatment showed the highest potential for N_2 (698.1 ± 270.3 mg N m^{-2}), and CO_2 (27558.3 ± 128.9 mg m^{-2}) emissions.

The results on permanent pasture show that the grass riparian buffer may be an N_2O sink, and on the other hand, the willow riparian buffer may be a larger sink for CH_4 and emit lower CO_2 when introduced for water quality protection measures in an ungrazed permanent pasture. On the other hand, the results of the fodder maize experiments suggest that fodder maize production in general, and situations where such cropping is not undertaken in tandem with a riparian buffer strip, result in atmospheric CH_4 and N_2O concerns. Also, the woodland and grass riparian buffers serving a maize crop may pose a CO_2 threat. Lastly, the laboratory incubation results show that soils developed under the grass riparian buffer can potentially emit higher NO and N_2O, while soils under willow riparian buffers can potentially emit larger N_2 and CO_2.

The results of the study point to the need to take into consideration the disbenefits of greenhouse gas emissions by mitigation measures conventionally implemented for improving the sustainability of water resources. Further experiments are suggested particularly with different crops under varying soils and environmental settings to validate the findings of the current study.

Keywords: permanent pasture, fodder maize, riparian buffers, grass, willow, woodland.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ACRONYMS AND ABBREVIATIONS

°C	Degrees Celsius
^{15}N	N isotope natural abundance
BD	Bulk density
C	Carbon
CO_2	Carbon dioxide
CH_3OH	Methanol
CH_4	Methane
DENIS	Denitrification System
DNDC	Denitrification-Decomposition
ECD	Electron capture detector
FID	Flame ionization detector
FWMC	Flow weighted mean concentration
GAEC	Good agricultural and environmental conditions
GHG's	Greenhouse gases
GLM	General linear model
GPS	Global positioning system
GWP	Global warming potential
IPCC	Intergovernmental Panel for Climate Change
KNO_3^-	Potassium nitrate
LMM	Linear mixed model
LSD	Least significant difference
MAP	Mean annual precipitation
MAT	Mean annual temperature

MMF-TWI	Morgan-Morgan-Finney topographic wetness index
MOB	Methane oxidizing bacteria
N	Nitrogen
NO	Nitric oxide
N_2	Nitrogen gas
N_2O	Nitrous oxide
NH_4^+-N	Ammonium nitrogen
NO_2^-	Nitrite
$NO_3^{--}N$	Nitrate nitrogen
NPS	Non-point source
O_2	Oxygen
O_3	Ozone
OM	Organic matter
PVC	Polyvinyl chloride
Ppm	Parts per million
Ppb	Parts per billion
REMM	Riparian Ecosystem Management Model
TON	Total oxidized nitrogen
SWAT	Soil and Water Assessment Tool
%WFPS	Water filled pore spaces

CHAPTER 1.0

GENERAL INTRODUCTION

1.1 Background Information

Worldwide, water quality problems are associated with non-point source (NPS) pollutants, including nitrogen (N) and phosphorus (P) (Carpenter *et al.*, 1998; Valkama *et al.*, 2019; Xia *et al.*, 2020), as well as herbicides and pesticides (Duda, 1993; Tonderski, 1996). The Water Framework Directive was launched across the European Member States in 2000 to ensure that water bodies achieve 'good ecological status.' According to Scheure and Naus (2010), installing riparian buffer strips is essential for some waterbodies to help achieve such status.

Vegetated riparian buffer strips (Figure 1.1), defined as transitionary boundaries disconnecting direct interaction between freshwater ecosystems and utilized agricultural land (Naiman *et al.*, 2010), may include various vegetation types, including single species or a combination of shrubs, trees, grasses, and forbs (Schultz *et al.*, 2004) (Figure 1.2). Riparian buffer strips are commonly seen as practical interventions for soil and water resource conservation in agroecosystems (Lowrance *et al.*, 2002) (Figure 1.1). Numerous studies, particularly Hubbard *et al.* (2004), Mitsch *et al.* (2001), and Sabater *et al.* (2003), have advocated for riparian buffer strips as practical tools to effectively control NPS pollution.

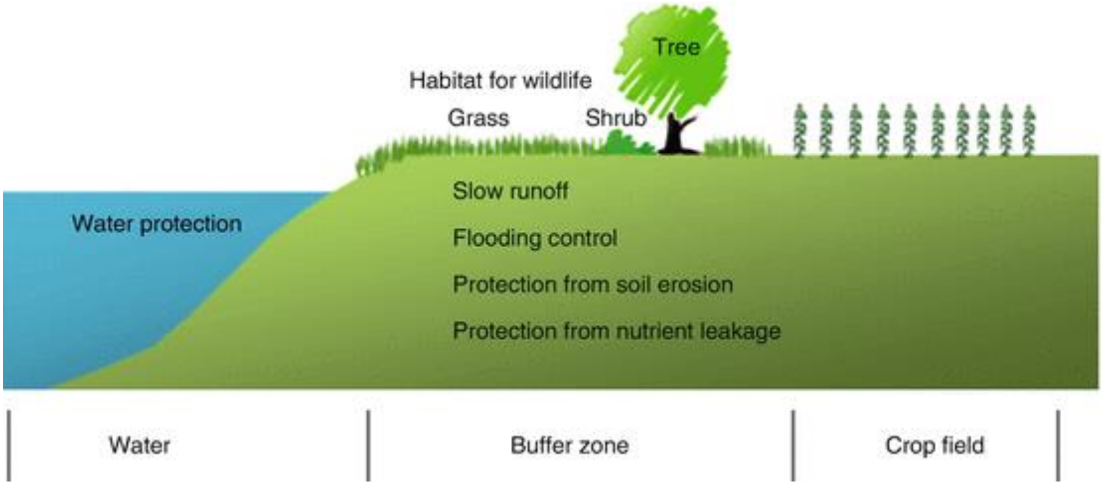

Figure 1. 1: An illustration of a riparian buffer strip between a cropland and a freshwater ecosystem (Ma, 2016).

The inclusion of riparian buffer strips into agroecosystems has been shown to improve carbon (C) sequestration, water quality, and soil's physical, chemical, and biological properties (Paudel *et al.*, 2011; Udawatta *et al.*, 2009) (Figure 1.1). Previous studies have shown that riparian buffer strips can reduce N fluxes by up to 90% through a range of processes (Dukes *et al.*, 2002; Kuusemets *et al.*, 2001; Zhao *et al.*, 2009), including plant uptake, denitrification, storage, immobilization, and other transformation mechanisms (Figure 1.2) impacting on the chemical inputs from utilized agricultural land (Gundersen *et al.*, 2010; Jaynes and Isenhart, 2014; Schultz *et al.*, 2000).

Riparian buffer strips are often flooded given their juxtaposition to watercourses, sustain high moisture contents from high water tables, and recycle organic matter elevating soil organic C concentrations (Tufekcioglu *et al.*, 2001) (Figure 1.2). These conditions all of which promote microbial processes that produce some gases, i.e., denitrification; nitric oxide (NO), nitrous oxide (N_2O), and carbon dioxide (CO_2), and methanogenesis; methane (CH_4), some of which are environmentally harmful GHGs.

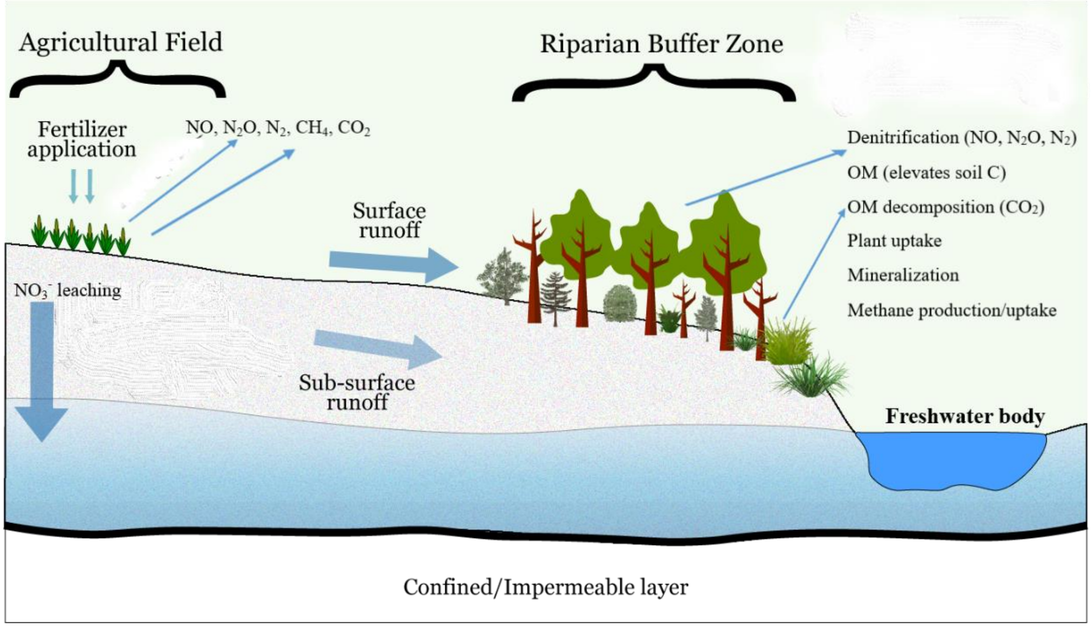

Figure 1. 2: Schematic representation of N and C flows and gas-producing processes in a riparian buffer and an immediately adjacent cropland (Dlamini, 2022).

Utilized agricultural land can be a significant source of nitrate (NO_3^-) in rivers and estuaries (Figure 1.2) (Howarth *et al.*, 2012; Schultz *et al.*, 2000; Zhang *et al.*, 2014). On the other hand, vegetated riparian buffer strips can help to intercept and process NO_3^--rich surface run-off and subsurface lateral flow from utilized agricultural land (Groffman *et al.*, 1998; Hefting *et al.*, 2003; Mitsch *et al.*, 2001; Reay *et al.*, 2012), which would otherwise enter freshwaters. Denitrification has been shown to increase following increases in soil organic C and N since they are an energy source and substrate for microbial reactions, respectively (Choi *et al.*, 2006; Dlamini *et al.*, 2020; Garcia and Tiedje, 1982).

Denitrification is a bacterially-mediated process whereby NO_3^- is transformed to nitrite (NO_2^-), NO, N_2O, and finally nitrogen gas (N_2) (Figure 1.2 & 1.3), under limited oxygen (O_2) by facultative anaerobes (Lowrance, 1992; Robertson and Groffman, 2007). It is an effective mechanism for NO_3^- removal in riparian buffer strips, with rates ranging between 2 and 7 g N m^{-2} $year^{-1}$ (Groffman and Hanson, 1997; Kim *et al.*, 2009a; Watts and Seitzinger, 2000). Currently, N_2O emissions from agroecosystems represent about 60% of all anthropogenic-derived N_2O emissions (Smith *et al.*, 2007). As soils become anoxic, a significant fraction of N_2O produced via denitrification is further reduced into N_2 before leaving the soil, which is a good thing as N_2 is not a GHG (Davidson, 2009; Robertson and Groffman, 2007).

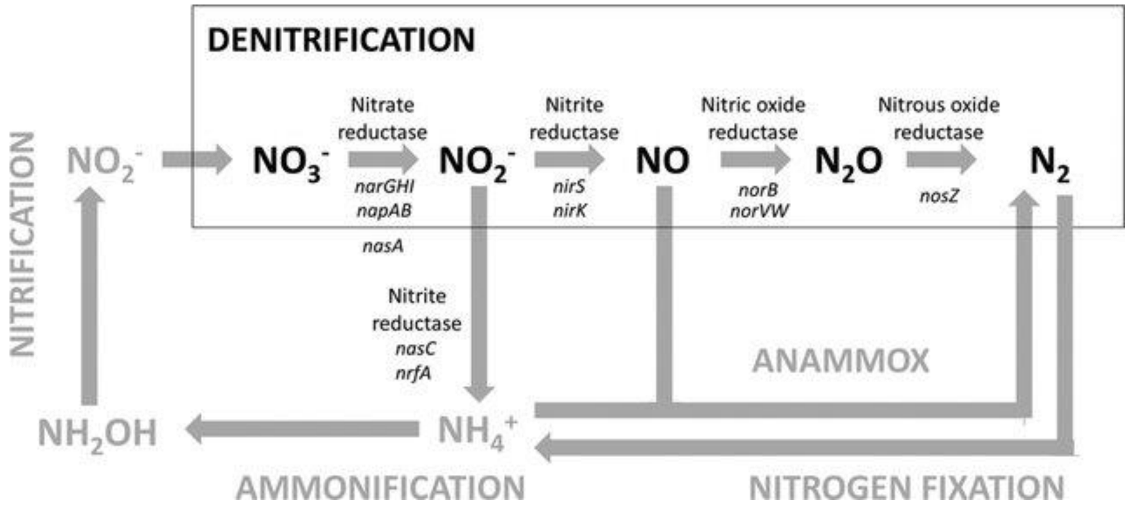

Figure 1. 3: An illustration of the denitrification and nitrification processes in the soil (Alvarez *et al.*, 2014).

Most denitrifying bacteria couple NO_3^- reduction with organic C oxidation to gain energy, making C-supply a usual requirement for denitrification to occur, a process which further produces carbon dioxide (CO_2) (Beauchamp *et al.*, 1989; Knowles, 1982). On the other hand, riparian buffers recycle high organic matter and consequently elevate C, which may have highly labile fractions, resulting in higher CO_2 emissions (Groh *et al.*, 2015; Jacinthe *et al.*, 2015). Methane is formed through the breakdown of organic compounds strictly under anaerobic conditions at a very low redox potential in a process called methanogenesis (Smith *et al.*, 2018). Therefore, large CH_4 fluxes are typical in environments where anoxic fermentation is favoured. The aforementioned conditions are prevailing in riparian buffer areas since they are often flooded and have a seasonally high water tables (Groh *et al.*, 2015; Jacinthe *et al.*, 2015).

Some of the gases produced through denitrification and other processes dominant in riparian buffers areas, i.e., NO, N_2O, CH_4, and CO_2 are of great environmental concern (Kulkarni *et al.*, 2008). Annual global NO emissions from soils are in the order of 10 Tg NO-N (Davidson and Kingerlee, 1997). Besides fossil fuel combustion, biomass burning, and lightning, NO is mainly produced in soils (Laville *et al.*, 2011). Nitric oxide is a precursor of tropospheric ozone (O_3) contributing to global warming (IPCC, 2007b). Globally, N_2O has been increasing at a rate of 3.8 - 5.1% per annum since the 1990s, and it is the most ozone-depleting substance of the 21st century (Ravishankara *et al.*, 2009; Reay *et al.*, 2012). Nitrous oxide is a potent greenhouse gas (GHG) with a global warming potential (GWP) 298-times that of CO_2 over a 100-year timescale (IPCC, 2007a).

Carbon dioxide is one of the most critical GHGs emitted from soils (Xiong and Khalil, 2009), and atmospheric concentrations increased from a pre-industrial value of 280 ppm to 379 ppm in 2005 (IPCC, 2007a). Soil processes are the largest source of CO_2 additions into the atmosphere, contributing considerably to the greenhouse effect (Paustian *et al.*, 2000; Raich and Potter, 1995). Human activities have resulted in an increase in atmospheric CH_4 concentrations compared to pre-industrial values (700ppb in 1750 to 1782ppb in 2006) (Borrel *et al.*, 2011), with about 40% of CH_4 fluxes to the atmosphere originating in soils (Prather, 1995). Generally, CH_4 is emitted in smaller quantities than CO_2, but, over a 100-year period, 1-kg of CH_4 has a GWP 28-times than CO_2 (IPCC, 2014).

Considering that NO is a precursor of tropospheric O_3 contributing to global warming (IPCC, 2007b), the role of N_2O, CH_4, and CO_2 in ozone depletion and global warming (Ravishankara *et al.*, 2009) as well as the importance of riparian buffer areas in the production (Bradley *et al.*, 2011; Fisher *et al.*, 2014) and subsequent emissions of the aforementioned gases may result in unintended trade-offs between emissions to water and air (Groffman *et al.*, 2000; Groffman *et al.*, 1998). Therefore, it is critical to evaluate, compare, and understand the extent of the emissions of these gases from riparian buffer strips and utilized agricultural land through a replicated field and laboratory-based experimental measurements. The findings of the current theses may further be helpful in the assessment of full riparian buffer vegetation GHG (particularly N_2O and CH_4) budgets, which remain critically scant.

1.2 Thesis Problem Statement

Riparian buffer areas represent a valuable practice for conserving water and soil resources (Lowrance *et al.*, 2002), especially NPS pollution associated with N fluxes (Kuusemets *et al.*, 2001; Zhao *et al.*, 2009). Nitrogen and C transformations within buffers receiving high NO_3^- loads from utilized upslope agricultural lands consequently result in significant GHG emissions (Fisher *et al.*, 2014; Groffman *et al.*, 1998). However, there is limited literature on the influence of downslope buffers on the total GHG emissions (Groffman *et al.*, 1991; Kim *et al.*, 2009b) compared to the utilized agricultural lands. Also, Groffman *et al.* (2002) suggested that the IPCC's inventory might be improved by including additional measurements from riparian buffers. Thus, it is critical to determine, through measurements, if they are relevant currently and further explore their potential for further emissions if they are widely implemented.

1.3 Thesis Aim and Objectives

1.3.1 Overall aim

To quantify N and C losses to air and water from fertilized croplands in a temperate climate and their potential for emissions of NO, N_2O, N_2, CH_4, and CO_2 as well as in downslope riparian buffers with varying vegetation (grass, willow, and woodland).

1.3.2 Objectives

i. To measure N_2O emissions and their soil and environmental controls from a cropland with permanent upslope pasture and downslope riparian buffer strips with varying vegetation.

ii. To investigate the extent of CH_4 fluxes from a cropland with a permanent upslope pasture and downslope riparian buffers.

iii. To quantify CO_2 fluxes from a cropland with a permanent upslope pasture and downslope riparian buffers.

iv. To understand N_2O and CH_4 emissions and their global warming potential in conjunction with fodder maize production with and without riparian buffer strips of differing vegetation.

v. To investigate the dynamics of soil CO_2 fluxes in fodder maize production with and without riparian buffer strips of varying vegetation.

vi. To estimate the potential of NO, N_2O, N_2, and CO_2 emissions in soils sourced from the cropland and downslope riparian buffers with varying vegetation.

1.4 Thesis Outline and Chapter Details

This thesis comprises nine chapters, six of which (chapters 2, and 4 to 8) are prepared and presented as journal article manuscripts, with the authorship and progress (*prepared*, *submitted*, *under review*, *accepted*, or *published*) provided on the title page of each chapter.

Chapter 2: *"Nitrous oxide emissions from croplands and their adjacent riparian buffer areas: A global meta-analysis."* This chapter reviews current global research regarding (i) Soil and environmental controls of N_2O emissions from cereal croplands and their adjacent vegetated riparian buffer areas, and (ii) Comparison of the N_2O emitted from the croplands and their adjacent riparian buffer areas, and (iii) Exploring knowledge gaps in the understanding of N_2O emissions from such agro systems.

Chapter 3: Materials and Methods. This chapter details the materials and methods used to carry-out the experiments whose results are reported in the different chapters.

Chapter 4: *"Buffer strips influence nitrogen losses as nitrous oxide and leached N from permanent grassland."* This chapter explores N_2O and run-off N dynamics in upslope pasture and downslope riparian buffers with varying vegetation. It maps the interaction between permanent upslope pasture and downslope riparian buffers with respect N_2O emissions and run-off N.

Chapter 5: *"Soil methane (CH_4) fluxes in a cropland with a permanent pasture and riparian buffer strips with different vegetation".* This chapter interrogates the controls of CH_4 fluxes in upslope permanent pasture in comparison with downslope riparian buffers areas with different vegetation.

Chapter 6: *"Soil CO_2 fluxes in a cropland with permanent pasture and riparian buffer strips with different vegetation".* This chapter interrogates the controls of CH_4 fluxes in upslope permanent and downslope riparian buffers areas with different vegetation.

Chapter 7: "*Soil N_2O and CH_4 in fodder maize production with and without riparian buffer strips of varying vegetation".* This chapter explores the unintended N_2O and CH_4 consequences and their global warming potential in fodder maize with and without riparian buffers of varying vegetation primarily introduced for water quality purposes.

Chapter 8: *"Soil CO_2 in fodder maize production with and without riparian buffer strips of varying vegetation".* This chapter investigates the dynamics and soil and environmental controls of soil CO_2 fluxes in fodder maize with and without riparian buffer strips of varying vegetation.

Chapter 9: *"Emissions of NO, N_2O, N_2, and CO_2 from soils sourced from a cropland and riparian buffer soils with different vegetation".* This chapter explores the potential of denitrification to produce NO, N_2O, N_2, and CO_2 in soils sourced from the upslope cropland and downslope riparian buffer with different vegetation. A specialized Denitrification System (DENIS) that enables the incubation of different amended soils was used for the current chapter's experiments.

Chapter 10: *"Synthesis and recommendations."* This chapter synthesizes the findings of the thesis, provides general conclusions on the set objectives and provides recommendations for future research.

1.5 References

Alvarez, L., Bricio C., Blesa A., Hidalgo A., Berenguer J., 2014. Transferable denitrification capability of Thermus thermophilus. *Applied & Environmental Microbiology*, 80:19-28.

Beauchamp, E.G., Trevors J.T., Paul J.W., 1989. Carbon Sources for Bacterial Denitrification, In: BA Stewart (Ed.), Advances in Soil Science, Springer., New York. pp. 113-142.

Borrel, G., Jézéquel D., Biderre-Petit C., Morel-Desrosiers N., Morel J.-P., Peyret P., Fonty G., Lehours A.-C., 2011. Production and consumption of methane in freshwater lake ecosystems. *Research in Microbiology*, 162:832-847.

Bradley, R., Whalen J., Chagnon P.-L., Lanoix M., Alves M., 2011. Nitrous oxide production and potential denitrification in soils from riparian buffer strips: influence of earthworms and plant litter. *Applied Soil Ecology*, 47:6-13.

Carpenter, S.R., Caraco N.F., Correll D.L., Howarth R.W., Sharpley A.N., Smith V.H., 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecological Applications*, 8:559-568.

Choi, W.-J., Lee S.-M., Han G.-H., Yoon K.-S., Jung J.-W., Lim S.-S., Kwak J.-H., 2006. Available organic carbon controls nitrification and immobilization of ammonium in an acid loam-textured soil. *Journal of Applied Biological Chemistry*, 49:28-32.

Davidson, E.A., 2009. Microbial processes of production and consumption of nitric oxide, nitrous oxide and methane, In: PA Matson and RC HArris (Eds.), Biogenic Trace Gases : Measuring Emisions from Soil and Water, Wiley-Blackwell, Oxford.

Davidson, E.A., Kingerlee W., 1997. A global inventory of nitric oxide emissions from soils. *Nutrient Cycling in Agroecosystems*, 48:37-50.

Dlamini, J., Chadwick D., Hawkins J., Martinez J., Scholefield D., Ma Y., Cárdenas L., 2020. Evaluating the potential of different carbon sources to promote denitrification. *Journal of Agricultural Science*, 158:194-205.

Duda, A.M., 1993. Addressing nonpoint sources of water pollution must become an international priority. *Water Science & Technology*, 28:1-11.

Dukes, M., Evans R., Gilliam J., Kunickis S., 2002. Effect of riparian buffer width and vegetation type on shallow groundwater quality in the Middle Coastal Plain of North Carolina. *Transactions of the ASAE*, 45:327.

Fisher, K., Jacinthe P., Vidon P., Liu X., Baker M., 2014. Nitrous oxide emission from cropland and adjacent riparian buffers in contrasting hydrogeomorphic settings. *Journal of Environmental Quality*, 43:338-348.

Garcia, J.-L., Tiedje J., 1982. Denitrification in rice soils, In: D YR and H Diem (Eds.), Microbiology of Tropical Soils and Plant Productivity, Springer, London. pp. 187-208.

Groffman, P.M., Axelrod E.A., Lemunyon J.L., Sullivan W.M., 1991. Denitrification in grass and forest vegetated filter strips. *Journal of Environmental Quality*, 20:671-674.

Groffman, P.M., Gold A., Kellog D., Addy K., 2002. Mechanisms, rates and assessment of N_2O in groundwater, riparian zones and rivers, Non-CO_2 Greenhouse Gases: Scientific Understanding, Control Options and Policy Aspects. Proceedings of the Third International Symposium, Maastricht, The Netherlands. pp. 159-166.

Groffman, P.M., Gold A.J., Addy K., 2000. Nitrous oxide production in riparian zones and its importance to national emission inventories. *Chemosphere-Global Change Science*, 2:291-299.

Groffman, P.M., Gold A.J., Jacinthe P.-A., 1998. Nitrous oxide production in riparian zones and groundwater. *Nutrient Cycling in Agroecosystems*, 52:179-186.

Groffman, P.M., Hanson G.C., 1997. Wetland denitrification: influence of site quality and relationships with wetland delineation protocols. *Soil Science Society of America Journal,* 61:323-329.

Groh, T.A., Gentry L.E., David M.B., 2015. Nitrogen removal and greenhouse gas emissions from constructed wetlands receiving tile drainage water. *Journal of Environmental Quality,* 44:1001-1010.

Gundersen, P., Laurén A., Finér L., Ring E., Koivusalo H., Sætersdal M., Weslien J.-O., Sigurdsson B.D., Högbom L., Laine J., 2010. Environmental services provided from riparian forests in the Nordic countries. *Ambio*, 39:555-566.

Hefting, M.M., Bobbink R., de Caluwe H., 2003. Nitrous oxide emission and denitrification in chronically nitrate-loaded riparian buffer zones. *Journal of Environmental Quality*, 32:1194-1203.

Howarth, R., Swaney D., Billen G., Garnier J., Hong B., Humborg C., Johnes P., Mörth C.-M., Marino R., 2012. Nitrogen fluxes from the landscape are controlled by net anthropogenic nitrogen inputs and by climate. *Frontiers in Ecology & the Environment,* 10:37-43.

Hubbard, R.K., Sheridan J.M., Lowrance R., Bosch D.D., Vellidis G., 2004. Fate of nitrogen from agriculture in the southeastern Coastal Plain. *Journal of Soil & Water Conservation,* 59:72-86.

IPCC, 2007a. Changes in atmospheric constituents and in radiative forcing. Chapter 2, Climate Change 2007. The Physical Science Basis.

IPCC, 2007b. The fourth assessment report-work group I, chapter 7: couplings between changes in the climate system and biogeochemistry, New York: Intergovernmental Panel on Climate Change (IPCC), 2007: 499-588.

IPCC, 2014. Climate change 2014: synthesis report. Contribution of Working Groups I, II and III to the fifth assessment report of the Intergovernmental Panel on Climate Change IPCC.

Jacinthe, P.-A., Vidon P., Fisher K., Liu X., Baker M., 2015. Soil methane and carbon dioxide fluxes from cropland and riparian buffers in different hydrogeomorphic settings. *Journal of Environmental Quality,* 44:1080-1090.

Jaynes, D.B., Isenhart T.M., 2014. Reconnecting tile drainage to riparian buffer hydrology for enhanced nitrate removal. *Journal of Environmental Quality*, 43:631-638.

Kim, D.-G., Isenhart T., Parkin T., Schultz R., Loynachan T., 2009a. Nitrate and dissolved nitrous oxide in groundwater within cropped fields and riparian buffers. *Biogeosciences Discussions*, 6:651-685.

Kim, D., Isenhart T.M., Parkin T.B., Schultz R.C., Loynachan T.E., Raich J.W., 2009b. Nitrous oxide emissions from riparian forest buffers, warm-season and cool-season grass filters, and crop fields. *Biogeosciences Discussions*, 6:607.

Knowles, R., 1982. Denitrification. *Microbiology Review*, 46:43.

Kulkarni, M.V., Groffman P.M., Yavitt J.B., 2008. Solving the global nitrogen problem: it's a gas! *Frontiers in Ecology & the Environment*, 6:199-206.

Kuusemets, V., Mander Ü., Lohmus K., Ivask M., 2001. Nitrogen and phosphorus variation in shallow groundwater and assimilation in plants in complex riparian buffer zones. *Water Science & Technology*, 44:615-622.

Laville, P., Lehuger S., Loubet B., Chaumartin F., Cellier P., 2011. Effect of management, climate and soil conditions on N_2O and NO emissions from an arable crop rotation using high temporal resolution measurements. *Agricultural & Forest Meteorology*, 151:228-240.

Lowrance, R., 1992. Groundwater nitrate and denitrification in a coastal plain riparian forest. *Journal of Environmental Quality*, 21:401-405.

Lowrance, R., Dabney S., Schultz R., 2002. Improving water and soil quality with conservation buffers. *Journal of Soil & Water Conservation,* 57:36A-43A.

Ma, M., 2016. Riparian buffer zone for wetlands, The Wetland book: 1. Structure and Function, Management, and Methods, Springer.

Mitsch, W.J., Day J.W., Gilliam J.W., Groffman P.M., Hey D.L., Randall G.W., Wang N., 2001. Reducing Nitrogen Loading to the Gulf of Mexico from the Mississippi River Basin: Strategies to Counter a Persistent Ecological Problem: Ecotechnology-the use of natural ecosystems to solve environmental problems-should be a part of efforts to shrink the zone of hypoxia in the Gulf of Mexico. *AIBS Bulletin* 51:373-388.

Naiman, R.J., Decamps H., McClain M.E., 2010. Riparia: ecology, conservation, and management of streamside communities. Elsevier Academic Press, Carlifornia.

Paudel, B.R., Udawatta R.P., Anderson S.H., 2011. Agroforestry and grass buffer effects on soil quality parameters for grazed pasture and row-crop systems. *Applied Soil Ecology*, 48:125-132.

Paustian, K., Six J., Elliott E., Hunt H., 2000. Management options for reducing CO_2 emissions from agricultural soils. *Biogeochemistry*, 48:147-163.

Prather, M., 1995. Other trace gases and atmospheric chemistry. *Climate Change*:77-126.

Raich, J.W., Potter C.S., 1995. Global patterns of carbon dioxide emissions from soils. *Global Biogeochemical Cycles*, 9:23-36.

Ravishankara, A., Daniel J.S., Portmann R.W., 2009. Nitrous oxide (N_2O): the dominant ozone-depleting substance emitted in the 21st century. *Science,* 326:123-125.

Reay, D.S., Davidson E.A., Smith K.A., Smith P., Melillo J.M., Dentener F., Crutzen P.J., 2012. Global agriculture and nitrous oxide emissions. *Nature Climate Change*, 2:410.

Robertson, G.P., Groffman P., 2007. Nitrogen Transformations, In: EA Paul (Ed.), Soil Microbiology, Ecology and Biochemistry, Elsevier, Amsterdam. pp. 341-364.

Sabater, S., Butturini A., Clement J.-C., Burt T., Dowrick D., Hefting M., Matre V., Pinay G., Postolache C., Rzepecki M., 2003. Nitrogen removal by riparian buffers along a European climatic gradient: patterns and factors of variation. *Ecosystems*, 6:0020-0030.

Scheure, S., Naus J., 2010. 10 Years of the Water Framework Directive: A toothless tiger?- A snapshot assessment of EU environmental ambitions., in: J Hontelez (Ed.), Environmental and Energy Policies, European Environmental Bureau, Brussels, Belgium.

Schultz, R., Colletti J., Isenhart T., Marquez C., Simpkins W., Ball C., Schultz O., 2000. Riparian forest buffer practices, In: H Garrett, et al. (Eds.), North American Agroforestry: An Integrated Science and Practice American Society of Agronomy, Madison, Wisconsin. pp. 189-281.

Schultz, R., Isenhart T., Simpkins W., Colletti J., 2004. Riparian forest buffers in agroecosystems–lessons learned from the Bear Creek Watershed, central Iowa, USA. *Agroforestry Systems*, 61:35-50.

Smith, K., Ball T., Conen F., Dobbie K., Massheder J., Rey A., 2018. Exchange of greenhouse gases between soil and atmosphere: interactions of soil physical factors and biological processes. *European Journal of Soil Science*, 69:10-20.

Smith, P., Martino D., Cai Z., Gwary D., Janzen H., Kumar P., McCarl B., Ogle S., O'Mara F., Rice C., 2007. Greenhouse gas mitigation in agriculture. *Philosophical Transactions of the Royal Society B: Biological Sciences*, 363:789-813.

Tonderski, A., 1996. Landuse-based nonpoint source pollution. A threat to water resources in developing countries. *Water Science & Technology*, 33:53-61.

Tufekcioglu, A., Raich J.W., Isenhart T.M., Schultz R.C., 2001. Soil respiration within riparian buffers and adjacent crop fields. *Plant & Soil,* 229:117-124.

Udawatta, R.P., Kremer R.J., Garrett H.E., Anderson S.H., 2009. Soil enzyme activities and physical properties in a watershed managed under agroforestry and row-crop systems. *Agriculture, Ecosystems, & Environment,* 131:98-104.

Valkama, E., Usva K., Saarinen M., Uusi-Kämppä J., 2019. A meta-analysis on nitrogen retention by buffer zones. *Journal of Environmental Quality*, 48:270-279.

Watts, S.H., Seitzinger S.P., 2000. Denitrification rates in organic and mineral soils from riparian sites: a comparison of N_2 flux and acetylene inhibition methods. *Soil Biology & Biochemistry*, 32:1383-1392.

Xia, Y., Zhang M., Tsang D.C., Geng N., Lu D., Zhu L., Igalavithana A.D., Dissanayake P.D., Rinklebe J., Yang X., 2020. Recent advances in control technologies for non-point source pollution with nitrogen and phosphorous from agricultural runoff: current practices and future prospects. *Applied Biological Chemistry*, 63:1-13.

Xiong, Z., Khalil M., 2009. Greenhouse Gases from Crop Fields, In: SS (Ed.) (Ed.), Environmental Science and Engineering, Springer Nature, Switzerland. pp. 113.

Zhang, Y., Collins A., Murdoch N., Lee D., Naden P., 2014. Cross sector contributions to river pollution in England and Wales: Updating waterbody scale information to support policy delivery for the Water Framework Directive. *Environmental Science & Policy,* 42:16-32.

Zhao, T., Xu H., He Y., Tai C., Meng H., Zeng F., Xing M., 2009. Agricultural non-point nitrogen pollution control function of different vegetation types in riparian wetlands: A case study in the Yellow River wetland in China. *Journal of Environmental Sciences*, 21:933-939.

CHAPTER 2.0

NITROUS OXIDE EMISSIONS FROM CROPLANDS AND ADJACENT RIPARIAN BUFFERS: A GLOBAL META-ANALYSIS

This chapter is *prepared* for submission in the journal “**Journal of Environmental Quality**” as:

Dlamini JC, Tesfamariam EH, Dlamini P, Evans J, Collins AL, Cardenas LM. Nitrous oxide emissions from croplands and adjacent riparian buffers: a global meta-analysis.

Corresponding author: JCD

Author contributions:

JCD, JE, EHT, LMC, PD, ALC: Conceptualization, Methodology, Software. **JCD:** Data curation, Writing- Original draft preparation. **JCD, JE:** Visualization, Investigation. **EHT, LMC:** Supervision. **JCD, JE:** Software, Validation. **EHT, LMC, PD, ALC:** Reviewing and Editing.

Abstract

Riparian buffer strips, transitionary boundaries between utilized agricultural land and water bodies, are widely used to intercept, and process surface and subsurface NPS including N run-off. The N-processing in riparian buffers may result in increased production of environmentally harmful greenhouse gases including N_2O. In 2006, the IPCC advised that GHG inventories for agricultural lands could be improved by including additional measurements from riparian buffers to help identify key controls and the extent and magnitude of these emissions from riparian buffers. Here, a meta-analysis of studies was conducted comparing N_2O emissions from riparian buffers and their adjacent utilized agricultural land they serve and further explored the controlling factors. It was identified that while there is growing literature quantifying N_2O emissions from different land uses, comparative assessments of N_2O emissions from riparian buffers and adjacent croplands remain limited. This was evident in our literature database that synthesized data from 13 studies published between 1980-2021: 44 data points with $n = 22$ from croplands and $n = 22$ for riparian buffers. The results of the meta-analysis showed that croplands generated significantly higher N_2O emissions compared to the riparian buffers. The emissions of N_2O were driven by elevation ($p = 0.029$), land use ($p < 0.0001$), soil texture ($p = 0.018$), soil bulk density (BD) ($p < 0.0001$), total carbon (C) ($p < 0.0001$), C: N ratio ($p < 0.0001$), and ammonium N (NH_4^+-N) ($p < 0.0001$). Although lower than in the croplands, the extent of the N_2O emissions in the riparian buffers (32% of the croplands N_2O) shows that riparian buffers may require attention when accounting for N_2O budgets from agricultural land.

2.1 Introduction

Riparian buffers are transitionary areas disconnecting utilized agricultural land and water bodies (Naiman *et al.*, 2010). They deliver a wide range of ecosystem services, including regulation of erosion and water quality, and serve as important habitats in support of biodiversity; thus, they are common features in most agroecosystems worldwide especially since agricultural policy instruments in many countries have driven their installation (Gundersen *et al.*, 2010; Naiman *et al.*, 2010). The unique location of riparian buffers in the landscape (usually in the foot slope between utilized agricultural land and freshwater) is critical for their capacity to moderate the delivery of pollutants such as N, P (O'donnell and Jones, 2006) and pesticides (Tonderski, 1996) derived from upslope agricultural land to freshwater ecosystems (Hubbard *et al.*, 2004).

Some studies have advocated riparian buffers as practical tools for effectively controlling NPS pollution (Mitsch *et al.*, 2001) and have underscored the use of buffers as an effective intervention for soil and water resource conservation (Lowrance *et al.*, 2002). Riparian buffers can moderate chemical inputs from adjacent utilized agricultural land through storage, immobilization, transformation, and filtration, and by retention of sediments before they reach freshwater ecosystems (Schultz *et al.*, 2000). Soil properties (i.e., reported in the meta-analysis herein) such as soil bulk density, soil organic and mineral N, and C developing under the riparian buffer vegetation have been reported to play a significant role in facilitating these regulatory functions (Groffman *et al.*, 1998; Seobi *et al.*, 2005; Tufekcioglu *et al.*, 2001).

The impacts of riparian buffers on water quality and soil conservation have been studied extensively (Sabater *et al.*, 2003), but their quantitative role in total GHG emissions, including N_2O, is still not well understood (Gundersen *et al.*, 2010; Hefting *et al.*, 2003; Soosaar *et al.*, 2011; Teiter and Mander, 2005) and, in particular, comparisons with emissions from immediately adjacent croplands remain especially scant (Kim *et al.*, 2009).

Seasonally variable water tables are an important characteristic of riparian buffer ecosystems, which through constant contact with different soil layers, may influence biological activities that stimulate N_2O production (Jacinthe *et al.*, 2015; McLain and Martens, 2006). During wet seasons, riparian buffers are subject to constant nutrient replenishment due to surface and subsurface run-off and leaching from adjacent agricultural land (Fisher *et al.*, 2014). Compared to utilized agricultural land, riparian buffer vegetation may influence some soil properties suitable for the production of N_2O (Berglund and Berglund, 2011; Mukherjee *et al.*, 2014). For instance, riparian buffer vegetation recycles organic matter, elevating soil C, which, together with the commonplace significant NO_3^- loads from adjacent utilized agricultural fields, stimulates N_2O emissions from such riparian buffer areas (Groffman *et al.*, 1998; Mitsch *et al.*, 2001).

Nitrous oxide is a radiative air pollutant of primary environmental concern, with agriculture representing about 60% of total global anthropogenic N_2O emissions (Syakila and Kroeze, 2011). Atmospheric N_2O plays a pivotal role as a precursor in ozone layer depletion and contributes to the greenhouse effect (IPCC, 2008; 2014). Although N_2O is emitted in relatively smaller amounts than CO_2, it has a high GWP; i.e., 298-times more powerful than that of CO_2 over a 100-year horizon (Forster *et al.*, 2007; IPCC, 2006). Given that riparian buffers may be hotspots for environmentally harmful gases such as N_2O, it is evident that trade-offs may counter their benefits for water quality protection for atmospheric emissions (Groffman *et al.*, 2000). Further, Groffman *et al.* (2002) recommended that N_2O inventories might be improved by including additional measurements from riparian buffers to identify the extent of such emissions and their key controlling factors. Accordingly, the objectives of this study were to: (i) compare the extent of N_2O emissions for croplands and their adjacent riparian buffers, and (ii) distinguish biophysical factors controlling N_2O in both croplands and riparian buffers through a meta-analysis of available global data.

2.2 Materials and Methods

2.2.1 The database

The literature search on the Web of Science (https://webofknowledge.com/), Scopus, and Science Direct, only included studies conducted and published between 1980 and 2021. The search was performed using the keywords: "agricultural land, OR, cropland AND, nitrous oxide, OR N_2O*, AND, grass riparian buffer, OR woodland riparian buffer, OR willow riparian buffer, OR riparian filter strips". A total of 61 manuscripts, of which only 13 manuscripts compared N_2O emissions between croplands and their adjacent riparian buffers. From these studies 44 observations (*n = 22* for both croplands and riparian buffers) were obtained.

To be included in the database, the study had to meet the following criteria:

i. A study where the source of N-pollutants intercepted by the riparian buffer vegetation was an adjacent agricultural field planted with cereal crops and non-grazed fodder pastures.
ii. The study assessed N_2O emissions in both the utilized cropland and its adjacent riparian buffers.
iii. The study had appropriate vegetation in the buffer areas: e.g., (a) grassland riparian buffer and (b) forest riparian buffer.

iv. Values of N_2O were recorded as either original data for each year of experimentation, or as sample replicates, or as a mean of each treatment (e.g., for grassland riparian buffer) with sample size and standard deviation (SD) or standard error (SE).

v. The riparian buffer was not fertilized directly.

2.2.2 Objective of the meta-analysis

The objectives of the meta-analysis are to: (i) combine information from different studies to identify explanatory variables that showed evidence of relationships with N_2O. Moreover, (ii) to fit a meta-regression model and further use it to estimate expected N_2O for each level of the different explanatory variables, particularly to determine if there were differences as influenced by land use.

2.2.3 Explanatory variables

The explanatory variables considered were: (i) number of experimental years, (ii) Köppen climate classification, (iii) latitude, (iv) longitude, (v) elevation, (vi) mean annual precipitation (MAP), (vii) mean annual temperature (MAT), (viii) land use in the upslope of the riparian buffers, (ix) vegetation type, and (x) soil texture. The other explanatory variables considered were soil pH, bulk density (BD), total C, total N, C: N ratio, NO_3^--N, and NH_4^+-N. Variables including microbial biomass N and C, fertilizer type and rates used in the croplands, dissolved organic C, N and C mineralization, soil temperature, and water-filled pore spaces or soil moisture were only reported by some studies and thus were discarded from the meta-analysis.

2.2.4 Data processing and analysis

R version 4.0.2. (https://www.r-project.org/) was used to perform all statistical analysis.

2.2.4.1 Model details

The metafor package was used to fit weighted linear regression models, with a random structure *(Ref/ob)* accounting for variation between studies that were not accounted for by the variables included in the fixed structure of the model and accounting for paired observations (i.e., cropland and riparian buffer from the same study). For each model mentioned below, the response variable was *Log*(N_2O) – N_2O was log-transformed to satisfy the assumptions of the analysis. The fixed structure of each model included one or more of the explanatory variables (a different subset for each model considered) as detailed in the model outputs below. Each observation was weighted by the inverse of its standard error – meaning that observations with substantial uncertainty (sizeable standard error) had a lower contribution to fitted models than those with less uncertainty (minor standard errors).

2.2.4.2 Simple analyses of each variable

In the initial step of the analysis, each explanatory variable was considered separately; thus, each model contained only one explanatory variable. For each model, *p*-values of the test of moderators were used to indicate whether each explanatory variable displayed a relationship with *log* (N_2O).

2.2.4.3 Main analysis-combined model for significant variables

The main analysis aimed to build a model containing multiple explanatory variables that could predict the value of *log* (N_2O) for values of each variable. Variables showing evidence of a relationship in the above step were included in the model selection process, and interactions between variables were considered. The model was selected based on an exhaustive search using bias-corrected Akaike's information criterion (AICc) (Fitzmaurice *et al.*, 2012). There was evidence that including an interaction between elevation and land use was beneficial (AICc decreased from 152.5

to 149.5). However, one study had an extremely high elevation value, which may have significantly influenced the fitted model. When this extreme value was excluded, the effect of elevation was no longer statistically significant, and the best model included land use, soil texture, and interaction. This was also the best model if the elevation was excluded from the selection procedure. Therefore, the final model presented was *Log* (N_2O) *~ Land use + texture + Land use: texture.*

2.2.4.4 Supplementary analyses of excluded variables

Each excluded explanatory variable (mentioned in section 2.2.4.3) was considered separately (where possible) using the same model form as detailed in section 2.2.4.2. The *p*–values from the test of moderator variables indicated whether each variable showed evidence of a relationship with *log* (N_2O). Since these variables had some missing values, these models were fitted to smaller datasets and are less reliable. Therefore, more evidence is required to support any of the relationships indicated.

2.3 Results

2.3.1 Data availability

Only 21.3% of the 61 observations found in the literature were used for analysis, and the remainder were discarded on the basis that they did not compare N_2O emissions between croplands and adjacent riparian buffers but, instead, compared emissions amongst different riparian buffer vegetation (77%) or were compromised for the purposes of our meta-analysis by missing information including the standard error of the mean (SEM) (2%). Table 2.1 shows a list of publications used in the meta-analysis. Of all the campaigns, 46% were from the USA, 23% from Canada, 8% from Chile, 8% from the Netherlands, 8% from Thailand, and 8% from France.

Table 2. 1: Publications (1980-2021; n=13) gathered for the systematic review and passed the screening criteria for data extraction.

Author	Year	Country	Journal	Volume	Pages
Baskerville et al.	2021	Canada	EM	67	371-383
Bradley et al.	2008	Canada	ASE	47	6-13
Cuevas et al.	2020	Chile	JSSPN	20	1859-1879
Davis et al.	2019	USA	JEQ	48	261-269
Fisher et al.	2014	USA	JEQ	43	338-348
Groh et al.	2015	USA	JEQ	44	1001-1010
Hefting et al.	2003	Netherlands	JEQ	32	1194-1203
Iqbal et al.	2015	USA	SSSAJ	79	239-250
Kachenchart et al.	2012	Thailand	AEE	158	15-30
Kim et al.	2009	USA	BD	6	607-650
Mafa-Attoye et al.	2020	Canada	STOTEN	724	138-148
Salehin et al.	2020	USA	S	12	6014
Vilain et al.	2010	France	AFM	150	1192-1202

Note: *EM (Environmental Management: n= 1); ASE (Applied Soil Ecology: n = 1); JSSPN (Journal of Soil Science and Plant Nutrition: n= 1); JEQ (Journal of Environmental Quality: n= 3); SSSAJ (Soil Science Society of America Journal: N=1); AEE (Agriculture, Ecosystem and Environment: n=1); BD (Biogeosciences Discussions: n=1); STOTEN (Science of the Total Environment: n=1); S (Sustainability: n=1); AFM (Agricultural and Forest Meteorology: n=1).*

2.3.2 N_2O range and proxy measurements

In the croplands, soil N_2O emissions ranged from 1.16 (Baskerville *et al.*, 2021) to 24.0 kg ha^{-1} $year^{-1}$ (Kim *et al.*, 2009). On the other hand, in the riparian buffers, N_2O emissions ranged from 0.08 (Mafa-Attoye *et al.*, 2020) to 9.3 kg ha^{-1} $year^{-1}$(Bradley *et al.*, 2011) (Figure 2.1). Table 2.2 shows that soil pH ranged from 5.7 (Cuevas *et al.*, 2020) to 7.8 (Salehin *et al.*, 2020) in the croplands and from 5.1 (Cuevas *et al.*, 2020) to 7.8 (Mafa-Attoye *et al.*, 2020) in the riparian buffers. Soil BD ranged from 0.7 (Cuevas *et al.*, 2020) to 1.7 (Kim *et al.*, 2009) g cm^{-3} in the croplands and from 0.6 (Baskerville *et al.*, 2021) to 1.4 (Kachenchart *et al.*, 2012) g cm^{-3} in the riparian buffers. Total C ranged from 12.5 (Vilain *et al.*, 2010) to 62 (Cuevas *et al.*, 2020) g kg^{-1} in the croplands and from 16.9 (Vilain *et al.*, 2010) to 91 (Cuevas *et al.*, 2020) g kg^{-1} in the riparian buffers. Total N ranged from 0.9 (Kachenchart *et al.*, 2012) to 29.7 (Mafa-Attoye *et al.*, 2020) g kg^{-1} in the croplands and from 1.2 (Kachenchart *et al.*, 2012) to 19.6 (Mafa-Attoye *et al.*, 2020) g kg^{-1} in the riparian buffers. In the croplands, the soil

C: N ratio ranged from 1.5 (Mafa-Attoye *et al.*, 2020) to 20.5 (Cuevas *et al.*, 2020), while in the riparian buffers, ratios ranged from 2.2 (Mafa-Attoye *et al.*, 2020) to 18.5 (Cuevas *et al.*, 2020). Soil NO_3^- ranged from 1.2 (Kim *et al.*, 2009) to 53.8 (Mafa-Attoye *et al.*, 2020) mg kg^{-1} in the croplands and from 0.2 (Kim *et al.*, 2009) to 46.4 (Baskerville *et al.*, 2021) mg kg^{-1} in the riparian buffers. Soil NH_4^+-N ranged from 1.7 (Kim *et al.*, 2009) to 11.1 (Iqbal *et al.*, 2015) mg kg^{-1} in the croplands and from 3.1 (Bradley *et al.*, 2011) to 8.7 (Iqbal *et al.*, 2015) in the riparian buffers.

Table 2. 2: Descriptive statistics of the soil variables whose relationships were tested against *log* (N_2O)

	Cropland			Riparian Buffer		
Variable	**Mean**	**Min.**	**Max.**	**Mean**	**Min.**	**Max.**
pH	6.7	5.7	7.8	6.9	5.1	7.8
BD (g cm^{-3})	1.4	0.7	1.7	1.04	0.6	1.4
Total C (g kg^{-1})	28.8	12.5	62	45.4	16.9	91
Total N (g kg^{-1})	6.9	0.9	29.7	6.1	1.2	19.6
C:N	10.9	1.5	20.5	11.1	2.2	18.5
NO_3^- -N (mg kg^{-1})	21.6	1.2	53.8	11.6	0.2	46.4
NH_4^+-N (mg kg^{-1})	5.1	1.7	11.1	5.8	3.11	8.7

Soil N_2O was shown to be influenced by loamy soils in both the croplands and riparian buffers compared to sandy and clayey soils (Figure 2.1).

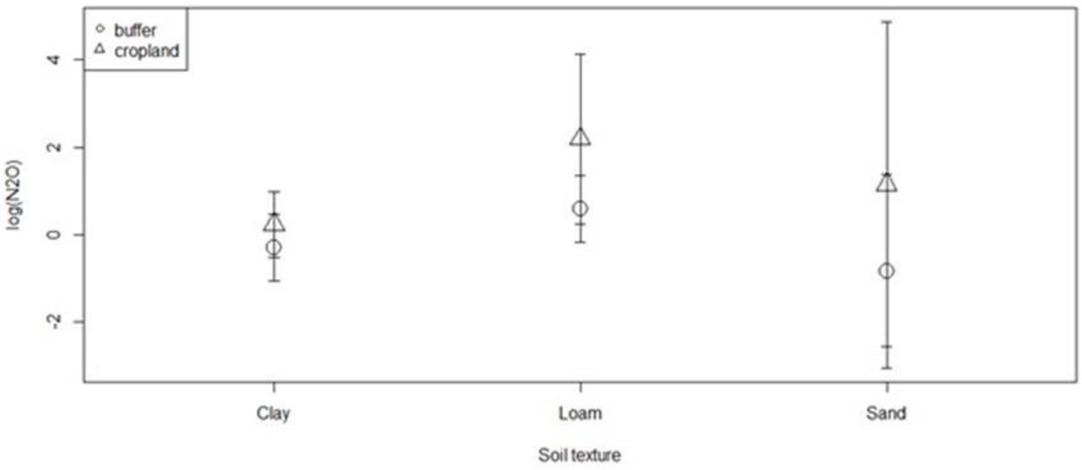

Figure 2. 1: Predicted soil texture influences on *log* (N_2O) in the cropland and the riparian buffers with 95% confidence intervals.

The mean soil N_2O from the croplands was 7.8 ± 1.6 kg N ha^{-1} $year^{-1}$, while the corresponding mean from the riparian buffers was 2.5 ± 0.5 kg N ha^{-1} $year^{-1}$ (Figure 2.2).

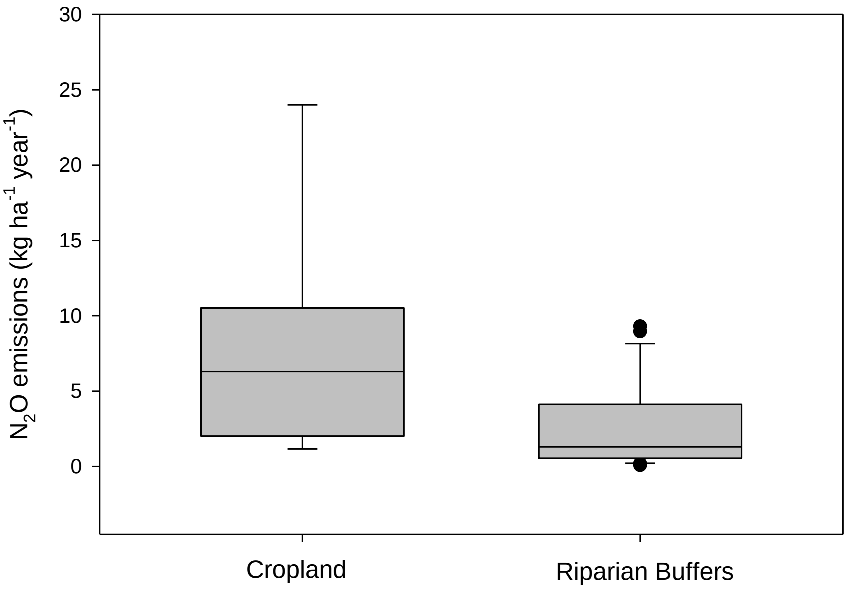

Figure 2. 2: Land use effects on observed N_2O emissions in the croplands (*n*=22) and the riparian buffers (*n*=22). Whiskers denote 95% confidence interval and dots denote outliers.

2.3.3 Initial single moderator models and model selection

Table 2.3 shows the results of the initial single moderator model. Only three variables exhibited statistically significant effects at a 5% significance level from all the factors analysed. These were elevation ($p = 0.029$), land use ($p <0.0001$) and soil texture ($p = 0.018$).

Table 2. 3: *p*-values indicating evidence of relationships for explanatory variables with *log* (N_2O) in simple models described in section 2.2.4.2.

Explanatory variables	*p*-value for test of moderator model
Number of experiment years	0.4904
Köppen Geiger climate class	0.0649
Latitude	0.6042
Longitude	0.9867
Elevation	**0.0286**[†]
MAP	0.3196
MAT	0.9756
Land use	**<0.0001**
Buffer type	0.9841
Soil texture	**0.0182**

[†]Bold explanatory variables and their values are significant

Table 2.4 shows the supplementary simple analysis results for the variables excluded from the main analysis, and of all the collected variables, only four factors were significant at the 5% significance level. These were soil BD ($p <0.0001$), total C ($p < 0.0001$), C: N ratio ($p <0.0001$) and NH_4^+-N ($p <0.0001$).

Table 2. 4: *p*-values from models described in section 2.2.4.4 indicating soil explanatory variables' relationship with *log* (N_2O).

Soil explanatory variables	***p*-values**
pH	0.5819
BD	**<0.0001†**
Total C	**<0.0001**
Total N	0.3881
C: N	**<0.0001**
NO_3^- -N	0.0771
NH_4^+ -N	**<0.0001**

†Bold explanatory variables and their values are significant

2.4 Discussion

2.4.1 Limitations in reported data

Although all the publications used in the current meta-analysis reported soil N_2O emissions from croplands and adjacent riparian buffers, some essential soil and environmental variables were often lacking in some of the studies. All studies described factors including climate, elevation, MAP, MAT, land use type, and soil texture, but not all the studies considered critical factors such as soil BD, total C, and N, NO_3^--N, and NH_4^+-N. Only a few studies reported microbial biomass N and C, fertilizer type and rates used in the croplands, dissolved organic C, N and C mineralization, soil temperature, and water-filled pore space or soil moisture; hence these variables were excluded from the meta-analysis.

2.4.2 Reported N_2O and its drivers within the different land-uses

Elevation directly influences soil N_2O emissions (Martinson *et al.*, 2013; Sousa Neto *et al.*, 2011; Teh *et al.*, 2014). Elevation was significantly correlated with soil N_2O emissions in the current meta-analysis; however, this was driven by one extreme study, so more evidence is needed to confirm this effect (Table 2.3). For instance, the aforementioned authors observed that lower soil elevations increased plant litter fall input (increasing N and C for microbial reactions), maintained higher soil temperature, and had more significant soil moisture contents, promoting denitrification and, consequently, higher N_2O emissions; all of which declined with increasing altitudes.

Land use has been recognized to influence soil N_2O emissions by numerous authors, particularly Kachenchart *et al.* (2012), Álvaro-Fuentes *et al.* (2017), and Leifeld (2018). Similar to these previous studies, the current meta-analysis found a significant effect of different land-uses on soil N_2O (Table 2.3). The previous studies reported that soil properties prevailing under different land uses were significant drivers of soil N_2O. For instance, Álvaro-Fuentes *et al.* (2017) credited the direct application of N fertilizer to cropland as one of the primary drivers of the high N_2O emissions compared to unfertilized abandoned and afforested lands in riparian zones which had lower emissions. Like the previous author, Leifeld (2018) also reported higher N_2O emissions in cropland compared to both a forest and grassland, crediting the higher N_2O in the cropland to the application of N fertilizer. Contrary to the previous authors, however, Kachenchart *et al.* (2012) reported significantly high N_2O emissions from leguminous afforestation compared to a fertilized maize crop and credited high soil moisture, increased denitrification, and microbial biomass C, but not nitrification as drivers of the high N_2O in the leguminous afforestation. This highlights that N-fertilized croplands may emit more N_2O than unfertilized lands, but some prevailing conditions in the non-directly fertilized riparian lands may promote processes such as denitrification, which elevate N_2O emissions.

Several authors, including Skiba and Ball (2002), Harrison-Kirk *et al.* (2013), and Yu *et al.* (2019), have studied soil texture as one of the drivers of soil N_2O. Similar to these authors, the current meta-analysis showed that loamy soils significantly elevated N_2O losses, leading to higher emissions than from clayey and sandy soils in both the croplands and the riparian buffers (Figure 2.1). Also, the meta-analysis revealed a significant relationship between soil texture and N_2O (Table 2.3). For instance, Yu *et al.* (2019) reported higher N_2O emissions from a sandy clay loam and credited it to enhanced N mineralization and fungal denitrification rates and comparatively lower N_2O in silty clay loam soils. Harrison-Kirk *et al.* (2013) reported that higher N_2O emissions from a clay loam soil compared with a silt loam resulted from available C (i.e., high organic matter content) and sufficiently high soil moisture content for microbial processes.

Soil BD showed a significant relationship with soil N_2O, which shows that soil BD was one of the significant drivers of N_2O across the different land uses (Table 2.4), similar to observations reported by Šimek *et al.* (2006) and Klefoth *et al.* (2014). The aforementioned authors observed that low soil BD improved soil gas diffusivity from production microsites to the soil surface, whilst higher soil BD impeded soil gas diffusivity, which further reduced N_2O to N_2 before it could reach the soil surface. Contrary to the observations of the previous authors, however, the current meta-analysis showed that the croplands, which had a higher range and mean soil BD, exhibited significantly higher soil N_2O emissions than the riparian buffers, which had a lower range and mean soil BD (Table 2.2 and Figure 2.2). This signifies that other soil variables and factors could have masked the role of soil BD in influencing soil N_2O emissions, as reported by Wang *et al.* (2018) and Mazzetto *et al.* (2020), who recognized soil pH and N fertilizer, respectively, to be chief modifiers of soil N_2O.

Denitrification is one of the significant N_2O-producing microbial reactions; it is carried out by facultative anaerobes and involves an electron transfer between N and C, thus making a supply of C a usual requirement for the process (Hume *et al.*, 2002; Mitchell *et al.*, 2013). In the current meta-analysis, significant relationships were found between total C and N_2O emissions (Table 2.4). For instance, (Mitchell *et al.*, 2013) reported that C, especially with a highly labile fraction, was an essential control for N_2O emissions in soils. To further reiterate the role of C in N_2O emissions, Li *et al.* (2005) observed that C sequestration in arable soils increased soil N_2O, thus counteracting the effort to reduce radiative forcing from arable systems. On the contrary to these authors, however, in the current meta-analysis, the riparian buffers had a higher range and mean total C than the croplands, but the latter generated higher N_2O emissions. This could mean that the croplands recycled highly labile C, which promoted N_2O-producing reactions, including denitrification, similar to Dlamini *et al.* (2020), but the information on C fractions was not available from the reviewed studies to confirm this in the current meta-analysis.

Low soil C: N ratios have been recognized to increase soil N_2O emissions in several studies including, for example, Huang *et al*. 2004; Ernfors *et al.* (2007), Chen *et al.* (2013) and Shan and Yan (2013). The findings of the current meta-analysis were in line with the findings of these specific studies, since the croplands, which had a lower mean C: N ratio (10.9), exhibited a significantly higher N_2O emission compared to the riparian buffers, which had a higher mean C: N ratio (11.1) (Table 2.2 and Figure 2.2). A low C: N ratio in the soil suggests that N-rich substrates are found in the soil for N_2O-producing microbial reactions; i.e., denitrification and nitrification (Baggs *et al.*, 2000; Millar and Baggs, 2005), hence the resultant increase in N_2O emissions. These relationships have been further attested to negative correlations between soil N_2O emissions and C: N ratios in many studies (Huang *et al.*, 2004; Toma and Hatano, 2007).

Soil N_2O was found to be significantly related to soil NH_4^+-N (Table 2.4), similar to other studies including, for instance, Singh *et al.* (2013) and Harty *et al.* (2016). These authors observed that NH_4^+-N increased N_2O emissions in soils, especially when other factors, i.e., soil moisture, were not limiting to the N_2O-producing processes. From the current analysis, the cropland with a more extensive range and mean soil NH_4^+-N generated significantly higher N_2O emissions than the riparian buffers, which had a lower range and mean soil NH_4^+-N. The findings of the current meta-analysis are in line with the work of other authors, including Venterea *et al.* (2005) and Hink *et al.* (2018), who credited greater N_2O emissions to high soil NH_4^+-N supply. Soil NH_4^+-N is one of the major substrates for N_2O-producing microbes, i.e., denitrifiers and nitrifiers; hence its increase in soils stimulates soil N_2O emissions (Harty *et al.*, 2016; Webb *et al.*, 2014).

2.4.3 Implications for N_2O inventories of croplands

In order to be considered an air quality threat, riparian buffers must emit significantly greater N_2O emissions than adjacent croplands (Fisher *et al.*, 2014). The current review revealed that riparian buffers are generally a less important air quality threat compared to adjacent croplands. However, considering that riparian buffers are not directly N-fertilized they still emitted ~32% of the total N_2O obtained from the N-fertilized croplands. This signifies that although N_2O emissions from riparian buffers are generally lower than in croplands, they have the potential to contribute significantly to the total N_2O budgets for agricultural land, especially where they are introduced extensively for protecting water quality and other ecosystem services. Overall, despite emitting significantly less N_2O compared to adjacent croplands, this review shows that N_2O emissions from riparian buffers are relevant, and that their emissions should be taken into account where they are implemented extensively (Figure 2.2). This supports the recommendation of the IPCC (2006).

2.5 Conclusion

The findings of the meta-analysis showed that elevation, land-use differences, total C, C: N ratio, and NH_4^+ N were major drivers of N_2O emissions from both the croplands and riparian buffers. The results of the meta-analysis further revealed that croplands generate significantly higher N_2O emissions compared to the adjacent riparian buffers. Despite being characterized by lower N_2O emissions, the analysis shows that further attention must be given to including values from riparian buffers when accounting for N_2O budgets from agricultural land to improve existing inventories.

2.6 References

Álvaro-Fuentes, J., Arrúe J.L., Bielsa A., Cantero-Martínez C., Plaza-Bonilla D., Paustian K., 2017. Simulating climate change and land use effects on soil nitrous oxide emissions in Mediterranean conditions using the Daycent model. *Agricultre, Ecosystems, & Environment,* 238:78-88.

Baggs, E., Rees R., Smith K., Vinten A., 2000. Nitrous oxide emission from soils after incorporating crop residues. *Soil Use & Management*, 16:82-87.

Baskerville, M., Reddy N., Ofosu E., Thevathasan N., Oelbermann M., 2021. Vegetation Type Does not Affect Nitrous Oxide Emissions from Riparian Zones in Agricultural Landscapes. *Environmental Management,* 67:371-383.

Berglund, Ö., Berglund K., 2011. Influence of water table level and soil properties on emissions of greenhouse gases from cultivated peat soil. *Soil Biology & Biochemistry*, 43:923-931.

Bradley, R., Whalen J., Chagnon P.-L., Lanoix M., Alves M., 2011. Nitrous oxide production and potential denitrification in soils from riparian buffer strips: influence of earthworms and plant litter. *Applied Soil Ecology*, 47:6-13.

Chen, H., Li X., Hu F., Shi W., 2013. Soil nitrous oxide emissions following crop residue addition: a meta-analysis. *Global Change Biology*, 19:2956-2964.

Cuevas, J.G., Paulino L., Dörner J., 2020. Pathways for Nitrous Oxide Generation in Forested and Agricultural Zones Growing on Volcanic Ash Soils. *Journal of Soil Science & Plant Nutrition*, 20:1859-1871.

Dlamini, J., Chadwick D., Hawkins J., Martinez J., Scholefield D., Ma Y., Cárdenas L., 2020. Evaluating the potential of different carbon sources to promote denitrification. *Journal of Agricultural Sciences*, 158:194-205.

Ernfors, M., von Arnold K., Stendahl J., Olsson M., Klemedtsson L., 2007. Nitrous oxide emissions from drained organic forest soils—an up-scaling based on C: N ratios. *Biogeochemistry*, 84:219-231.

Fisher, K., Jacinthe P., Vidon P., Liu X., Baker M., 2014. Nitrous oxide emission from cropland and adjacent riparian buffers in contrasting hydrogeomorphic settings. *Journal of Environmental Quality*, 43:338-348.

Fitzmaurice, G.M., Laird N.M., Ware J.H., 2012. Applied longitudinal analysis John Wiley & Sons.

Forster, P., Ramaswamy V., Artaxo P., Berntsen T., Betts R., Fahey D.W., Haywood J., Lean J., Lowe D.C., Myhre G., 2007. Changes in atmospheric constituents and in radiative forcing. Chapter 2, Climate Change 2007. The Physical Science Basis.

Groffman, P.M., Gold A., Kellog D., Addy K., 2002. Mechanisms, rates and assessment of N_2O in groundwater, riparian zones and rivers, Proceedings of the third International Symposium on Non-CO. pp. 159-166.

Groffman, P.M., Gold A.J., Addy K., 2000. Nitrous oxide production in riparian zones and its importance to national emission inventories. *Chemosphere-Global Change Science*, 2:291-299.

Groffman, P.M., Gold A.J., Jacinthe P.-A., 1998. Nitrous oxide production in riparian zones and groundwater. *Nutrient Cycling in Agroecosystems*, 52:179-186.

Gundersen, P., Laurén A., Finér L., Ring E., Koivusalo H., Sætersdal M., Weslien J.-O., Sigurdsson B.D., Högbom L., Laine J., 2010. Environmental services provided from riparian forests in the Nordic countries. *Ambio*, 39:555-566.

Harrison-Kirk, T., Beare M., Meenken E., Condron L., 2013. Soil organic matter and texture affect responses to dry/wet cycles: Effects on carbon dioxide and nitrous oxide emissions. *Soil Biology & Biochemistry*, 57:43-55.

Harty, M.A., Forrestal P.J., Watson C., McGeough K., Carolan R., Elliot C., Krol D., Laughlin R.J., Richards K.G., Lanigan G., 2016. Reducing nitrous oxide emissions by changing N fertiliser use from calcium ammonium nitrate (CAN) to urea based formulations. *Science of the Total Environment*, 563:576-586.

Hefting, M.M., Bobbink R., de Caluwe H., 2003. Nitrous oxide emission and denitrification in chronically nitrate-loaded riparian buffer zones. *Journal of Environmental Quality*, 32:1194-1203.

Hink, L., Gubry-Rangin C., Nicol G.W., Prosser J.I., 2018. The consequences of niche and physiological differentiation of archaeal and bacterial ammonia oxidisers for nitrous oxide emissions. *The ISME Journal*,12:1084-1093.

Huang, Y., Zou J., Zheng X., Wang Y., Xu X., 2004. Nitrous oxide emissions as influenced by amendment of plant residues with different C: N ratios. *Soil Biology & Biochemistry*, 36:973-981.

Hubbard, R.K., Sheridan J.M., Lowrance R., Bosch D.D., Vellidis G., 2004. Fate of nitrogen from agriculture in the southeastern Coastal Plain. *Journal of Soil & Water Conservation*, 59:72-86.

Hume, N.P., Fleming M.S., Horne A.J., 2002. Denitrification potential and carbon quality of four aquatic plants in wetland microcosms. *Soil Science Society of America Journal*, 66:1706-1712.

IPCC, 2006. 2006 IPCC guidelines for national greenhouse gas inventories Institute for Global Environmental Strategies Hayama, Japan.

IPCC, 2008. IPCC, 2007: climate change 2007: synthesis report, IPCC.

IPCC, 2014. Climate change 2014: synthesis report. Contribution of Working Groups I, II and III to the fifth assessment report of the Intergovernmental Panel on Climate Change IPCC.

Iqbal, J., Parkin T.B., Helmers M.J., Zhou X., Castellano M.J., 2015. Denitrification and nitrous oxide emissions in annual croplands, perennial grass buffers, and restored perennial grasslands. *Soil Science Society of America Journal*, 79:239-250.

Jacinthe, P.-A., Vidon P., Fisher K., Liu X., Baker M., 2015. Soil methane and carbon dioxide fluxes from cropland and riparian buffers in different hydrogeomorphic settings. *Journal Environmental Quality*, 44:1080-1090.

Kachenchart, B., Jones D.L., Gajaseni N., Edwards-Jones G., Limsakul A., 2012. Seasonal nitrous oxide emissions from different land uses and their controlling factors in a tropical riparian ecosystem. *Agriculture, Ecosystems, & Environment*, 158:15-30.

Kim, D., Isenhart T.M., Parkin T.B., Schultz R.C., Loynachan T.E., Raich J.W., 2009. Nitrous oxide emissions from riparian forest buffers, warm-season and cool-season grass filters, and crop fields. *Biogeosciences Discussions,* 6:607.

Klefoth, R.R., Clough T.J., Oenema O., Van Groenigen J.-W., 2014. Soil bulk density and moisture content influence relative gas diffusivity and the reduction of nitrogen-15 nitrous oxide. *Vadose Zone Journal*, 13:vzj2014. 07.0089.

Leifeld, J., 2018. Distribution of nitrous oxide emissions from managed organic soils under different land uses estimated by the peat C/N ratio to improve national GHG inventories. *Science of the Total Environment*, 631:23-26.

Li, C., Frolking S., Butterbach-Bahl K., 2005. Carbon sequestration in arable soils is likely to increase nitrous oxide emissions, offsetting reductions in climate radiative forcing. *Climate Change*, 72:321-338.

Lowrance, R., Dabney S., Schultz R., 2002. Improving water and soil quality with conservation buffers. *Journal of Soil & Water Conservation*, 57:36A-43A.

Mafa-Attoye, T.G., Baskerville M.A., Ofosu E., Oelbermann M., Thevathasan N.V., Dunfield K.E., 2020. Riparian land-use systems impact soil microbial communities and nitrous oxide emissions in an agro-ecosystem. *Science of The Total Environment*, 724:138148.

Martinson, G.O., Corre M.D., Veldkamp E., 2013. Responses of nitrous oxide fluxes and soil nitrogen cycling to nutrient additions in montane forests along an elevation gradient in southern Ecuador. *Biogeochemistry*, 112:625-636.

Mazzetto, A.M., Styles D., Gibbons J., Arndt C., Misselbrook T., Chadwick D., 2020. Region-specific emission factors for Brazil increase the estimate of nitrous oxide emissions from nitrogen fertiliser application by 21%. *Atmospheric Environment*, 230:117506.

McLain, J.E., Martens D.A., 2006. Moisture controls on trace gas fluxes in semiarid riparian soils. *Soil Science Society of America Journal*, 70:367-377.

Millar, N., Baggs E., 2005. Relationships between N_2O emissions and water-soluble C and N contents of agroforestry residues after their addition to soil. *Soil Biology & Biochemistry*, 37:605-608.

Mitchell, D.C., Castellano M.J., Sawyer J.E., Pantoja J., 2013. Cover crop effects on nitrous oxide emissions: role of mineralizable carbon. *Soil Science Society of America Journal,* 77:1765.

Mitsch, W.J., Day J.W., Gilliam J.W., Groffman P.M., Hey D.L., Randall G.W., Wang N., 2001. Reducing Nitrogen Loading to the Gulf of Mexico from the Mississippi River Basin: Strategies to Counter a Persistent Ecological Problem: Ecotechnology—the use of natural ecosystems to solve environmental problems—should be a part of efforts to shrink the zone of hypoxia in the Gulf of Mexico. *AIBS Bulletin*, 51:373-388.

Mukherjee, A., Lal R., Zimmerman A., 2014. Effects of biochar and other amendments on the physical properties and greenhouse gas emissions of an artificially degraded soil. *Science of Total Environment*, 487:26-36.

Musfiq-Us-Salehin, S., Ghimire R., Angadi S.V., Idowu O.J., 2020. Grass buffer strips improve soil health and mitigate greenhouse gas emissions in center-pivot irrigated cropping systems. *Sustainability*, 12:6014.

Naiman, R.J., Decamps H., McClain M.E., 2010. Riparia: ecology, conservation, and management of streamside communities Elsevier Academic Press, Carlifornia.

O'donnell, J., Jones J., 2006. Nitrogen retention in the riparian zone of catchments underlain by discontinuous permafrost. *Freshwater Biology*, 51:854-864.

Sabater, S., Butturini A., Clement J.-C., Burt T., Dowrick D., Hefting M., Matre V., Pinay G., Postolache C., Rzepecki M., 2003. Nitrogen removal by riparian buffers along a European climatic gradient: patterns and factors of variation. *Ecosystems*, 6:0020-0030.

Schultz, R., Colletti J., Isenhart T., Marquez C., Simpkins W., Ball C., Schultz O., 2000. Riparian forest buffer practices, In: WRaRF HE Garrett (Ed.), North American

Agroforestry: an Integrated Science and Practice. Eds. , America Society of Agronomy, Madison, Wisconsin. pp. 189-281.

Seobi, T., Anderson S., Udawatta R., Gantzer C., 2005. Influence of grass and agroforestry buffer strips on soil hydraulic properties for an Albaqualf. *Soil Science Society of America Journal*, 69:893-901.

Shan, J., Yan X., 2013. Effects of crop residue returning on nitrous oxide emissions in agricultural soils. *Atmospheric Environment*, 71:170-175.

Šimek, M., Brůček P., Hynšt J., Uhlířová E., Petersen S.O., 2006. Effects of excretal returns and soil compaction on nitrous oxide emissions from a cattle overwintering area. *Agriculture, Ecosystems, & Environment*, 112:186-191.

Singh, J., Kunhikrishnan A., Bolan N., Saggar S., 2013. Impact of urease inhibitor on ammonia and nitrous oxide emissions from temperate pasture soil cores receiving urea fertilizer and cattle urine. *Science of the Total Environment*, 465:56-63.

Skiba, U., Ball B., 2002. The effect of soil texture and soil drainage on emissions of nitric oxide and nitrous oxide. *Soil Use & Management*, 18:56-60.

Soosaar, K., Mander Ü., Maddison M., Kanal A., Kull A., Lõhmus K., Truu J., Augustin J., 2011. Dynamics of gaseous nitrogen and carbon fluxes in riparian alder forests. *Ecological Engineering,* 37:40-53.

Sousa Neto, E., Carmo J., Keller M., Martins S., Alves L., Vieira S., Piccolo M., Camargo P., Couto H., Joly C., 2011. Soil-atmosphere exchange of nitrous oxide, methane and carbon dioxide in a gradient of elevation in the coastal Brazilian Atlantic forest. *Biogeosciences*, 8:733-742.

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

Teh, Y., Diem T., Jones S., Huaraca Quispe L.P., Baggs E., Morley N., Richards M., Smith P., Meir P., 2014. Methane and nitrous oxide fluxes across an elevation gradient in the tropical Peruvian Andes. *Biogeosciences*, 11:2325-2339.

Teiter, S., Mander Ü., 2005. Emission of N_2O, N_2, CH_4, and CO_2 from constructed wetlands for wastewater treatment and from riparian buffer zones. *Ecological Engineering*, 25:528-541.

Toma, Y., Hatano R., 2007. Effect of crop residue C: N ratio on N_2O emissions from Gray Lowland soil in Mikasa, Hokkaido, Japan. *Journal Soil Science & Plant Nutrition*, 53:198-205.

Tonderski, A., 1996. Landuse-based nonpoint source pollution. A threat to water resources in developing countries. *Water Science & Technology*, 33:53-61.

Tufekcioglu, A., Raich J.W., Isenhart T.M., Schultz R.C., 2001. Soil respiration within riparian buffers and adjacent crop fields. *Plant & Soil*, 229:117-124.

Venterea, R.T., Burger M., Spokas K.A., 2005. Nitrogen oxide and methane emissions under varying tillage and fertilizer management. *Journal of Environmental Quality*, 34:1467-1477.

Vilain, G., Garnier J., Tallec G., Cellier P., 2010. Effect of slope position and land use on nitrous oxide (N_2O) emissions (Seine Basin, France). *Agricultural & Forest Meteorology*, 150:1192-1202.

Wang, Y., Guo J., Vogt R.D., Mulder J., Wang J., Zhang X., 2018. Soil pH as the chief modifier for regional nitrous oxide emissions: new evidence and implications for global estimates and mitigation. *Global Change Biology*, 24:e617-e626.

Webb, J., Thorman R., Fernanda-Aller M., Jackson D., 2014. Emission factors for ammonia and nitrous oxide emissions following immediate manure incorporation on two contrasting soil types. *Atmospheric Environment*, 82:280-287.

Yu, Y., Zhao C., Zheng N., Jia H., Yao H., 2019. Interactive effects of soil texture and salinity on nitrous oxide emissions following crop residue amendment. *Geoderma*, 337:1146-1154.

CHAPTER 3.0

MATERIALS AND METHODS

3.1 Study Site Description

The replicated bounded plots used in this experiment are located at Rothamsted Research, North Wyke, Devon, United Kingdom (50°46´ 10´´N, 3° 54´05´´E). The facility is situated at an altitude of 177 m above sea level, has a 36-year (from 1982 to 2018) mean annual precipitation (MAP) of 1033 mm and a mean annual temperature (MAT) of 10.1°C (Orr *et al.*, 2016). The slope is 8°, and soils primarily belong to the Hallsworth series (Clayden and Hollis, 1985), but with dystric gleysols (FAO, 2006); a stony clay loam topsoil comprising 15.7% sand, 47.7% clay, and 36.6% silt (Armstrong and Garwood, 1991), overlying a mottled stony clay, derived from Carboniferous Culm rocks. Below the topsoil layer, the subsoil is impermeable to water and is seasonally waterlogged; most excess water moves by surface and sub-surface lateral flow across the clay layer (Orr *et al.*, 2016), which made the site suitable for the current experiments. Some soil parameters at the commencement of the current experiment in June 2018, are shown in Table 3.1. This experiment forms part of a project investigating the environmental and economic efficiency of diverse types of vegetated buffer strips. The treatments were established in 2016.

3.2 Experimental Design and Treatments

The experiment was laid out as three blocks of four plots, with four treatments replicated three times on the twelve plots (Figure 3.1). The four treatments comprised three different riparian buffer strip vegetation (grass, willow, and woodland, riparian buffers) and a no-buffer control, each with a permanent upslope pasture (Figure 3.1). Each plot consisted of the main crop area and a control (no buffer) area or a buffer (sown with one of three riparian buffer vegetation covers) area. Each plot was 46-m in length and 10 m wide; the main upslope pasture (area ‘a’ in Figure 3.1) being 34 m in length (340-m^2) and the buffer strip being 12-m (120-m^2) (areas ‘b’ and ‘c’ in Figure 3.1, see description below). Area “b” was planted with three different riparian buffer vegetation types (10-m x 10-m). Area “c” was an untouched strip of existing vegetation measuring 2-m x 10-m.

Figure 3. 1: Schematic of the replicated plot, treatment, and chamber layout, and their location at NorthWyke, United Kingdom.

In order to hydrologically isolate each plot, a plastic-lined and gravel-filled trench was installed to a depth of 1.40m to avoid the lateral flow of water and associated pollutants, including nutrients (Figure 3.1). The upslope plot was managed as a three-cut silage crop, with a permanent pasture dominated by ryegrass (*Lolium perenne* L.), Yorkshire fog (Hol*cus lanatus* L.), and creeping bentgrass (*Agrostis stolonifera* L.). Fertilizer N (as NH_4^+-N; Nitram), P (as P_2O_5, triple superphosphate), and potassium (K; as K_2O; muriate of potash) were previously split-applied into three silage cutting events, with annual rates of 180 (split: 80, 50, 50), 140 (split: 100, 25, and 15) and 290 (split: 80, 100, and 80 and autumn: 30) kg ha^{-1}, respectively. During the current study, fertilizer was applied all at once in the upslope pasture at 50, 15, and 80 kg ha^{-1} for N, P, and K, respectively, which were initially recommended by routine soil analysis. Fertilizers were only applied to the upslope pasture and no buffer control areas, with no fertilizer application occurring in the three vegetated riparian buffer strips. Further details for the treatments are listed below:

i) No-Buffer control: plots with no-buffer strip at the base of the hydrologically isolated slope. The area of land described as a no-buffer control was always managed in exactly the same way as what is described for the areas used for the upslope permanent pasture.

ii) Grass Buffer: Novel grass buffer (*Festulolium loliaceum* cv. Prior) - The novel grass was planted at the end of 2016 at a seeding rate of 5 kg ha^{-1}; a recommended seeding rate for the species for the Devon area. The novel grass hybrid was developed to be a dual-use grass species that provides efficient forage production and could help mitigate flooding by increasing water infiltration (Macleod *et al.*, 2013). During the current study, the 3-year-old hybrid grass was about 80-cm tall and had never been cut since planting in 2016.

iii) Woodland Buffer: Deciduous woodland - Six species, namely Pedunculate oak (*Quercus robur* L.), hazel (*Corylus avellana* L.), Hornbeam (*Carpinus betulus* L.), Small-leaved lime (*Tilia cordata* Mill.), Sweet chestnut (*Castanea sativa* Mill.) and Wych elm (*Ulmus glabra* Huds.) were planted in the woodland buffer strips. Five individual plants (each 40 cm in height and bare rooted) of each species were planted 1.6 m apart in rows 2-m apart in December 2016 in the 10 x 10-m area, with 1.5-m tall protection tubes used to remove risk of browsing by wild herbivores (e.g., deer). Planting was done at a density of 3000 plants ha^{-1}: a recommended planting density for the Devon area. The woodland species were chosen for their ability to respond well to coppicing (where the wood is cut to near ground level and the tree sends out new shoots to form a stool the next growing season). The choice was also based on financial incentives for planting woodland along riparian buffer zones and, as well as it's potential for water quality improvement (Sydes and Grime, 1981). This choice also fitted with the local agri-environment payment scheme available at the time (Countryside Stewardship) for a riparian buffer zone, so it would be something that farmers with watercourses would be able to receive a payment for, in terms of getting money to plant the trees in their riparian areas. During the current experiment, the 3-year-old woodland trees were 1.6 m tall and had never been cut since planting in 2016.

iv) Willow Buffer: Bio-energy crop – Five willow cultivars, namely Cheviot, Mourne, Hambleton, Endurance and Terra Nova (all *Salix* spp.); the first three being newly developed cultivars and the latter being older ones. Whips of willow approximately 30 cm in length were inserted flush into the ground in May of 2016 at a population of 200 plants per 10 m x 10 m area: a recommended planting density for willows in the Devon area. The willow cultivars were chosen from the National Willow Collection based at Rothamsted Research, Harpenden site to be suitable for growing in the wet clay-rich soils of the Devon site. They were also chosen based on their high capacity for pollutant uptake and their use for soil bioremediation (Aronsson and Perttu, 2001). During the current experiment, the 3-year-old willow trees were about 3-m tall and had not been cut since planting in 2016.

Area ‘c’ is a requirement for cross-compliance in England whereby farmers with watercourses must adhere to GAEC (Good Agricultural and Environmental Condition) rule 1; establishment of buffer strips along watercourses (DEFRA, 2019). All the areas within the 10 m x 10 m (10 m length is a GAEC recommended N fertilizer application distance away from surface waters) managed riparian buffer strips were sprayed with glyphosate to remove the existing vegetation in spring 2016. The grass riparian buffer strips were cultivated, and the seed was sown as described above, while the willow and woodland buffers had the trees planted within the swathe of dead grass.

3.2.1 Sampling design

Each plot consisted of the main crop area with one chamber and either a control (no-buffer) area with a single chamber or a buffer area (sown with one of three riparian buffer vegetation covers) that had two chambers (upper and lower). The three no-buffer control plots on the experiment had a chamber box situated at a similar position on the slope to where the buffer strip boxes were, but they were still part of the fertilized crop area (Figure 3.1).

3.3 Measurements

3.3.1 Gas measurement and laboratory analysis

3.3.1.1 Field sampling and laboratory analysis

Nitrous oxide, CH_4, and CO_2 fluxes were measured using the static chamber technique (Chadwick *et al.*, 2014; De Klein and Harvey, 2012). The polyvinyl chloride (PVC) chambers were square frames with lids (40 cm width x 40 cm length x 25 cm height) with an internal base area of 0.16 m^2. Thirty-three chamber collars were inserted to a depth of 5 cm below the soil surface using a steel base, and installation points were marked using a hand-held global positioning system (GPS; Trimble, California, USA) so that they could be reinserted into the same positions after removing them during some agronomic practices i.e., silage cutting, tillage, seed drilling. In the woodland and willow riparian buffers, chambers were installed in-between two rows, while in the no-buffer control, and grass riparian buffer treatments, and the upslope pasture, chambers were installed in pre-determined positions (Figure 3.1). The chambers were installed in the following configuration: (i) in area ‘a’ there was one chamber on the top of the plot (called area “a” top chamber); in the no-buffer control plots there was an additional chamber near the bottom of the plot (called area “a” bottom chamber); (ii) in area ‘b’ there were 2 chambers, one on the top and one on the bottom of the treatment buffer strip (called area ‘b’ top and bottom chambers, respectively).

Gas sampling was conducted periodically from June 2018 to October 2019 (18 sampling events in permanent pasture between June 2018 to March 2019 and 16 sampling events in maize between May and October 2019), between 10:00 and 13:00, using 60-mL syringes and pre-evacuated 22-ml vials fitted with butyl rubber septa. At each sampling occasion, samples were collected at four-time intervals (0, 20, 40, and 60 minutes) from three chambers to account for the non-linear increase in gas concentration with deployment time and to adequately assess the quality of the calculated flux (Grandy *et al.*, 2006; Kaiser *et al.*, 1996). The remaining chambers were sampled terminally at 40 minutes after closure (Chadwick *et al.*, 2014). Additionally, ten ambient gas samples were collected adjacent to the experimental area: five at the start and another five at the end of each sampling event. A Perkin Elmer Clarus 500 gas chromatograph (Perkin Elmer Instruments, Beaconsfield, UK) fitted with a Turbomatrix 110 automated headspace sampler with an electron capture detector (ECD) set at 300^{o}C was used for N_2O analysis and a flame ionization detector (FID) was used for CH_4 and CO_2 analysis, after applying a 5-standard linear regression calibration. Separation was achieved by Perkin Elmer Elite-PLOT mega bore capillary column, 30 m long and 0.53 mm Column Inside Diameter (ID), maintained at 35^{o}C; N_2 was used as a carrier gas (Cardenas *et al.,* 2016).

3.3.1.2 Gas flux determination

As suggested by Conen and Smith (2000), soil gas fluxes were calculated based on the rate of change in concentration (ppm) within the chamber, which was estimated as the slope of a linear regression between concentration and chamber closure time. Gas fluxes were computed using the Livingston and Hutchinson (1995) model (equation 3.1):

$$Fn = \frac{\delta C_n}{\delta_t} \; x \frac{V}{A} \; x \frac{M_n}{V_{mol}} \qquad (Eq. 3.1)$$

Where: $\delta C_n/\delta_t$ is the rate of change in gas concentration (μmol mol^{-1} min^{-1}); V is the chamber headspace volume; M_n is the molecular weight of each measured gas; A is the base area of the chamber, and V_{mol} is the volume of one mole of each measured gas at 20°C (0.024 m^3).

The quality of a calculated flux was adequately assessed using the goodness of fit test and/or by visual inspection; plateauing of gas concentration over time, and data that failed to meet the linearity standards were rejected (Collier *et al.,*2014).

3.3.1.3 Cumulative flux determination and global warming potential (GWP) calculation

Cumulative N_2O, CH_4, and CO_2 fluxes were estimated by calculating the area under the gas flux curve after linear interpolation between sampling points (Mosier *et al.,* 1996). The GWP of CH_4 and N_2O are respectively 28 and 310 times that of CO_2 (IPCC, 2014). Therefore, GWP was estimated by multiplying total CH_4 and N_2O fluxes by 28, and 310, respectively (Del Grosso *et al.,* 2008).

3.3.2 Soil analyses

Soil pH was measured with a pH meter (Jenway, Stafforshire, UK) using a soil suspension (1:2.5 soil: water ratio), and soil organic matter (OM) was determined using the loss-on-ignition (LOI) technique (Wilke, 2005). Composite soil samples (0–10 cm), made up of four random sub-samples, were collected monthly within 1 m of each chamber using a soil corer with a semi-cylindrical gouge auger (2–3 cm diameter) (Poulton *et al.,* 2018). Total oxidized N (TO-N) [nitrite (NO_2^-) and nitrate (NO_3^-)] and ammonium N (NH_4^+) were quantified by extracting field-moist 20 g soil samples using

2 M KCl and a 1:5 soil: extractant ratio; analysis was performed using an AquakemTM analyser (Thermo Fisher Scientific, Finland).

3.3.3 Percent water-filled pore space (% WFPS)

At every gas sampling occasion, composite soil samples (0-10 cm) made of four random sub-samples were collected within 1-m from each chamber using a soil corer for gravimetric soil moisture determination. Dry bulk density was determined at the start of the experiment next to each chamber using the core-cutter method (Amirinejad *et al.*, 2011) and was used to convert the gravimetric moisture determined during each gas sampling event into percent %WFPS using equation 3.2 below:

$$\%WFPS = \frac{VWC}{1 - \frac{BD}{PD}} \; x\;100 \qquad (Eq.\ 3.2)$$

Where, *WFPS* is the water-filled pore spaces (expressed as %); *VWC* is the volumetric water content (expressed as vol. %); *BD* is the soil bulk density (g cm^{-3}); *PD* is the soil particle density (2.65 g cm^{-3}) (Fichtner *et al.*, 2019). The volumetric water content was determined using the following equations 3.3 and 3.4 below:

$$VWC = \emptyset g\ (gg^{-1}) * soil\ BD \qquad (Eq. 3.3)$$

$$\emptyset g\ (gg^{-1}) = {}^{M_w}/_{M_s} \qquad (Eq. 3.4)$$

Where, $\emptyset g$ (gg^{-1}) is the gravimetric moisture content and M_w (g) and Ms (g) are the mass of water lost upon oven drying and the mass of the dry soil, respectively.

3.3.4 Soil temperature

Soil surface temperature was measured using a digital thermometer (Fischer Scientific, UK) during each gas-sampling event.

3.3.5 Meteorological data

Average daily soil temperature at 10 and 30 cm depth, average daily precipitation, minimum and maximum daily temperature, total daily solar radiation, and average daily humidity were calculated from data measured at hourly intervals by an automatic weather station near the replicated plot facility, courtesy of the Environmental Change Network (ECN), at Rowden, Rothamsted Research, North Wyke (Lane, 1997; Rennie *et al.*, 2020).

3.3.6 Flow and water N

Surface run-off and sub-surface lateral flow from each of the hydrologically isolated plots (i.e., combining riparian buffer and upslope pasture) was collected using SampSys autosamplers (ENVITECH, UK) installed at 1.4 m below the soil surface (Figure 3.2) in collection pits. Water samples were collected during storm events and analysed for TON using photometric analysis. Flow-weighted mean N concentrations (FWMC) were calculated by dividing the total N load over the experimental period (concentration x time x flow) by the total flow (Davis *et al.*, 2019; Mueller and Spahr, 2005).

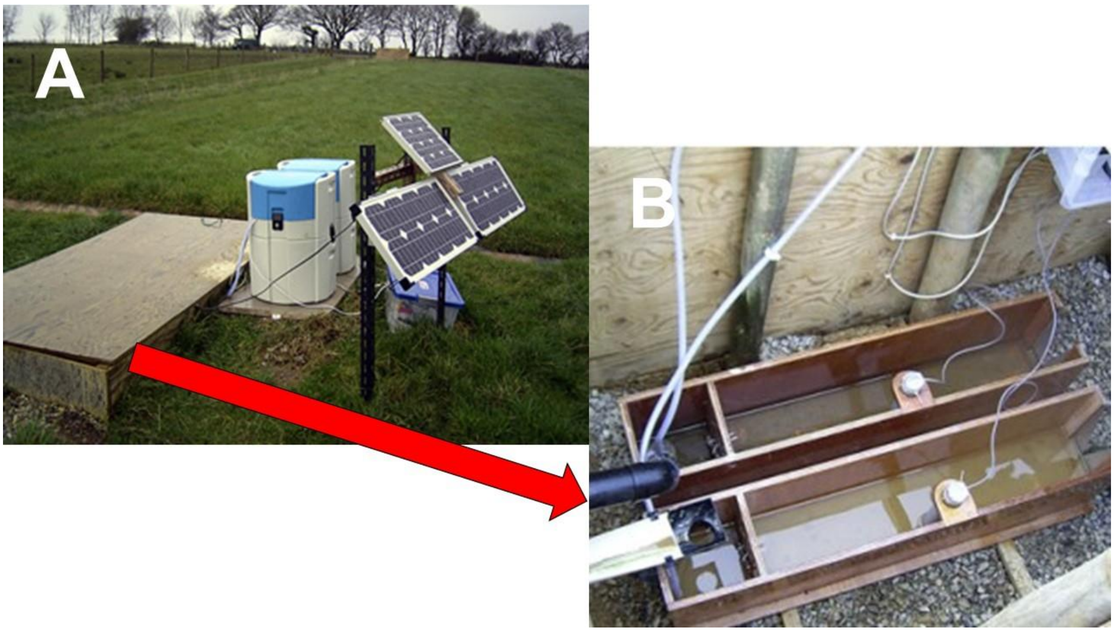

Figure 3. 2: The automated SampSys samplers installed at the end of each replicated plot (A) and the weirs for measuring run-off (B).

3.4 References

Amirinejad, A.A., Kamble K., Aggarwal P., Chakraborty D., Pradhan S., Mittal R.B., 2011. Assessment and mapping of spatial variation of soil physical health in a farm. *Geoderma*, 160:292-303.

Armstrong, A.C., Garwood E., 1991. Hydrological consequences of artificial drainage of grassland. *Hydrological processes*, 5:157-174.

Aronsson, P., Perttu K., 2001. Willow vegetation filters for wastewater treatment and soil remediation combined with biomass production. *Forest Chronicles*, 77:293-299.

Cardenas LM, Misselbrook TM, Hodgson C, Donovan N, Gilhespy S, Smith KA, Dhanoa MS, Chadwick D. 2016. Effect of the application of cattle urine with and without the nitrification inhibitor DCD, and dung on greenhouse gas emissions from a UK grassland soil. *Agriculture, Ecosystems, & Environment*, 235: 229-241.

Clayden, B., Hollis J.M., 1985. Criteria for differentiating soil series, Tech Monograph 17, Harpenden, UK.

Collier SM, Ruark MD, Oates LG, Jokela WE, Dell CJ. 2014. Measurement of greenhouse gas flux from agricultural soils using static chambers. *Journal of Visual Experiments*, 90: 52110.

Davis, M.P., Groh T.A., Jaynes D.B., Parkin T.B., Isenhart T.M., 2019. Nitrous oxide emissions from saturated riparian buffers: Are we trading a water quality problem for an air quality problem? *Journal of Environmental Quality*, 48:261-269.

DEFRA, 2019. The guide to cross compliance in England 2019, in: FaRA Department for Environment (Ed.), United Kingdom.

FAO, 2006. Guidelines for soil description Rome, Italy: Food and Agricultural Organisation of the United Nations.

Fichtner, T., Goersmeyer N., Stefan C., 2019. Influence of soil pore system properties on the degradation rates of organic substances during soil aquifer treatment (SAT). *Applied Sciences,* 9:496.

Grandy, A.S., Loecke T.D., Parr S., Robertson G.P., 2006. Long-term trends in nitrous oxide emissions, soil nitrogen, and crop yields of till and no-till cropping systems. *Journal of Environmental Quality*, 35:1487-1495.

IPCC. 2014. Climate change 2014: synthesis report. Contribution of Working Groups I, II and III to the fifth assessment report of the Intergovernmental Panel on Climate Change IPCC.

Kaiser, E.-A., Munch J.C., Heinemeyer O., 1996. Importance of soil cover box area for the determination of N_2O emissions from arable soils. *Plant & Soil*, 181:185-192.

Lane, A., 1997. The UK environmental change network database: An integrated information resource for long-term monitoring and research. *Journal of Environmental Management*, 51:87-105.

Livingston, G. & Hutchinson, G. (1995). Enclosure-based measurement of trace gas exchange: applications and sources of error. In Matson, P, Harris, RC (eds). *Biogenic Trace Gases: Measuring Emissions from Soil and Water*, pp. 14-51. Massachusetts, USA: Blackwell Publishing.

Macleod, C. J. A., Humphreys, M. W., Whalley, W. R., Turner, L., Binley, A., Watts, C. W., Skøt, L., Joynes, A., Hawkins, S., King, I. P., O'Donovan, S. & Haygarth, P. M. (2013). A novel grass hybrid to reduce flood generation in temperate regions. *Scientific Reports,* 3, 1683.

Mueller, D., Spahr N., 2005. Water-quality, streamflow, and ancillary sata for nutrients in streams and rivers across the Nation, 1992–2001: US Geological Survey Digital Data Series DDS–152.

Orr, R., Murray P., Eyles C., Blackwell M., Cardenas L., Collins A., Dungait J., Goulding K., Griffith B., Gurr S., 2016. The NorthWyke Farm Platform: effect of temperate grassland farming systems on soil moisture contents, runoff and associated water quality dynamics. *European Journal of Soil Science*, 67:374-385.

Poulton, P., Johnston J., Macdonald A., White R., Powlson D., 2018. Major limitations to achieving “4 per 1000” increases in soil organic carbon stock in temperate regions: Evidence from long-term experiments at Rothamsted Research, United Kingdom. *Global Change Biology*, 24:2563-2584.

Rennie, S., Andrews C., Atkinson S., Beaumont D., Benham S., Bowmaker V., Dick J., Dodd B., McKenna C., Pallett D., 2020. The UK Environmental Change Network datasets–integrated and co-located data for long-term environmental research (1993–2015). *Earth System Science Data,* 12:87-107.

Sydes, C., Grime J., 1981. Effects of tree leaf litter on herbaceous vegetation in deciduous woodland: I. Field investigations. *Journal of Ecology*, 237-248.

Wilke B-M (2005) Determination of chemical and physical soil properties, In: A. Varma (Ed.), Monitoring and assessing soil bioremediation, Springer, Berlin Heidelberg. pp. 47-95.

CHAPTER 4.0

RIPARIAN BUFFER STRIPS INFLUENCE NITROGEN LOSSES AS NITROUS OXIDE AND LEACHED N FROM PERMANENT UPSLOPE PASTURE

This chapter is *published* in the journal “**Agriculture, Ecosystems, and Environment**” as:

Dlamini JC, Cardenas LM, Tesfamariam EH, Dunn RM, Loick N, Charteris AF, Cocciaglia L, Vangeli S, Blackwell MSA, Upadhayay HR, Hawkins JMB, Evans J, Collins AL. Riparian buffer strips influence nitrogen losses as nitrous oxide and leached N from upslope permanent pasture. *Agriculture, Ecosystems, & Environment*, 336: 108031. DOI: https://doi.org/10.1016/j.agee.2022.108031

Corresponding author: LMC

Author contribution:

JCD, JE, EHT, LMC, MMSAB, JMBH, RD, ALC: Conceptualization, Methodology, Software. **JCD:** Data curation, Writing- Original draft preparation. **JD, JE:** Visualization, Investigation. **EHT, LMC:** Supervision. **JCD, JE:** Software, Validation. **EHT, LMC, MMSAB, JMBH, RD, ALC, NL, AFC, SV, LC:** Writing- Reviewing and Editing.

Abstract

Riparian buffer strips can significantly reduce N transfers from agricultural land to freshwater primarily via denitrification and plant uptake processes, but an unintended trade-off can be elevated N_2O production. Against this context, a replicated bounded plot scale study investigated N_2O emissions from un-grazed ryegrass pasture served by three types of riparian buffer strips with different vegetation, comprising: (i) novel deep-rooting grass, (ii) willow (establishment phase), and (iii) deciduous woodland (also establishment phase). The experimental control was ryegrass pasture with no buffer strip. Nitrous oxide emissions were measured simultaneously as total oxidized N in run-off, and soil and environmental characteristics in the riparian buffer strips and the upslope permanent pasture between 2018 and 2019. During most sampling days, the no-buffer control showed significantly (p <0.05) greater N_2O fluxes and a resultant cumulative N_2O emissions than the remainder of the treatments. The results of the current study also showed that the grass riparian buffer strip was a sink of N_2O equivalent to -2310.2 g ha^{-1} (95% confidence interval: -535.5-492). Event-based water quality results obtained during storms (12 November 2018 and 11 February 2019) showed that the willow riparian buffer treatment had the highest flow-weighted mean N concentrations (FWMC) of 0.041 ± 0.022 and 0.031 ± 0.015 mg N L^{-1} when compared to the other treatments. Riparian buffer strips with novel deep-rooting grass can therefore potentially address emissions to both water and air.

4.1 Introduction

Vegetated riparian buffer strips situated between agricultural fields and fresh waterbodies are commonly seen as practical interventions for soil and water resource conservation in agroecosystems (Lowrance *et al.*, 2002). Numerous studies have advocated riparian buffer strips as practical tools for controlling NPS pollution effectively (Hubbard *et al.*, 2004; Lowrance *et al.*, 1984; Mitsch *et al.*, 2001; Sabater *et al.*, 2003).

The inclusion of riparian buffer strips into agroecosystems has improved C sequestration, water quality, and soil physical, chemical, and biological properties (Paudel *et al.*, 2011; Udawatta *et al.*, 2009). Studies have shown that riparian buffer strips can reduce N fluxes by up to 90% through a range of processes (Dukes *et al.*, 2002; Kuusemets *et al.*, 2001; Zhao *et al.*, 2009), including plant uptake, denitrification, storage, immobilization and other transformation mechanisms impacting on the chemical inputs from upslope utilized agricultural land (Gundersen *et al.*, 2010; Jaynes and Isenhart, 2014; Schultz *et al.*, 2000).

Agricultural soils are an essential source of N_2O, a potent GHG with a global warming potential 298 times that of CO_2 over a 100-year timescale (IPCC, 2007). The soil and environmental factors driving major N_2O producing processes, i.e., denitrification and nitrification, include the quantity and quality of labile C, hydrological status, N availability, and O_2 concentration (Firestone, 1982; Groffman *et al.*, 1998). Riparian buffer strips are often flooded given their juxtaposition to watercourses, sustain high moisture contents from high water tables, and recycle organic matter elevating soil organic C concentrations (Tufekcioglu *et al.*, 2001), all of which promote microbial denitrification. Agricultural land can be a significant source of NO_3^- in rivers and estuaries (Howarth *et al.*, 2012; Schultz *et al.*, 2000; Zhang *et al.*, 2014), and riparian buffer strip vegetation can help to intercept and process NO_3^--rich surface runoff and subsurface lateral flow from adjacent agricultural land (Groffman *et al.*, 1998; Hefting *et al.*, 2003; Mitsch *et al.*, 2001; Reay *et al.*, 2012), which would otherwise enter freshwaters. Production rates of N_2O have been shown to increase following increases in soil organic C and N since they are an energy source and substrate for microbial N_2O production, respectively (Choi *et al.*, 2006; Garcia and Tiedje, 1982). Denitrification; an anaerobic process whereby soil microbes use NO_3^- under O_2 limitation to produce N_2O and N_2 (Lowrance, 1992), is an effective mechanism for NO_3^- removal in riparian buffer strips, with rates ranging between 2 and 7 g N m^{-2} $year^{-1}$ (Groffman and Hanson, 1997; Kim *et al.*, 2009a; Watts and Seitzinger, 2000). Thus, N transformation within riparian buffer strips with high NO_3^- loads from intensively managed adjacent agricultural land may result in considerable N_2O emissions (Groffman *et al.*, 1998).

Globally, N_2O has been increasing at a rate of 3.8 - 5.1% per annum since the 1990s, and it is the most ozone-depleting substance of the 21st century (Ravishankara *et al.*, 2009; Reay *et al.*, 2012). Currently, N_2O emissions from agroecosystems represent about 60% of all anthropogenic-derived N_2O emissions (Smith *et al.*, 2007). Considering the role of N_2O in ozone depletion (Ravishankara *et al.*, 2009), and the importance of denitrification on N_2O production in riparian buffer strips (Bradley *et al.*, 2011), the increased denitrification rates associated with the insertion of riparian buffer strips may result in unintended trade-offs between emissions to water and air (Groffman *et al.*, 2000; Groffman *et al.*, 1998). Therefore, it is critical to evaluate, compare and understand the extent of N_2O emissions from riparian buffer strips and upslope agricultural land through replicated experimental field measurements.

Accordingly, the study hypothesized that riparian buffer strips are a source of N_2O emissions due to the movement of fertilizer N downslope that accumulates within the riparian buffer area. The objectives of this study were to: (a) investigate soil and environmental factors contributing to N_2O emissions from both riparian buffer strips with different vegetation and upslope permanent pasture; (b) test whether there is a difference in daily N_2O fluxes and cumulative N_2O emissions between riparian buffers strips with different vegetation and upslope permanent pasture, and; (c) identify if a particular riparian buffer strip vegetation provides more significant reductions in N transfers from agricultural land as leached N and N_2O emissions.

4.2 Materials and Methods

Information on the chapter's (i) study site description, (ii) experimental design and treatments, and (iii) field measurements are detailed in Chapter 3 (section 3.2). The methodology described below (Statistical methods) is specific to this chapter, which is not presented under chapter 3.

4.2.1 Statistical analysis

Linear mixed models (LMMs) were used to determine whether the measured soil variables (BD, pH, NH_4^+, TON, and %WFPS) or cumulative N_2O differed with treatment. NH_4^+ and TON were $\log_{10}$ transformed, and cumulative N_2O was square root transformed to satisfy the homogeneity of variance assumption of the analysis. The random structure of each model (accounting for the structure of the experiment) was *block/plot/chamber*. The fixed structure (accounting for treatment effects) was *area/(treatment crop*buffer area),* where *area* is a comparison of the upslope pasture, no-buffer-control and riparian buffer areas of the plots, and *buffer area* is a comparison of the chambers in the upper and lower area of the buffers.

LMMs were also used to assess the relationship between each measured variable and the cumulative N_2O emissions. The data required a square root transformation (with an offset) to meet the analysis's homogeneity of variance assumption. In each of the models, the random structure of the models (accounting for the structure of the experiment) was *block/plot/chamber,* and the fixed structure (accounting for treatments effects) was one of the measured soil variables (BD, pH, NH_4^+, TON or %WFPS).

Pearson’s correlation coefficient (r) was used to indicate the strength of relationships between soil and environmental factors and N_2O emissions. This was tested more formally in the LMMs described above. If LMMs indicated that treatment differences were present, least significant differences (LSD) were calculated to determine which specific pairs of treatments resulted in the significant differences in N_2O emissions. All graphs were generated using SigmaPlot (Systat Software Inc., CA, USA).

4.3 Results

4.3.1. Meteorological data

The total rainfall during the experimental period was 699 mm. The highest daily rainfall event (27.3 mm) was recorded at the end of September 2018. Before this event, the highest daily rainfall events were 13.2, 13.3, and 18.9 mm collected in June, August, and September 2018, respectively. The highest rainfall event was followed by low rainfall events, with the highest (3.5 mm) recorded in November 2018. Daily average air temperature ranged from -3.2 to 21.4°C and soil surface temperatures ranged between 10.1 and 24.0°C. At 10 cm soil depth, temperatures ranged from 2.93 to 19.2°C and, at 30 cm, from 3.84 to 17.7°C (Figure 4.1).

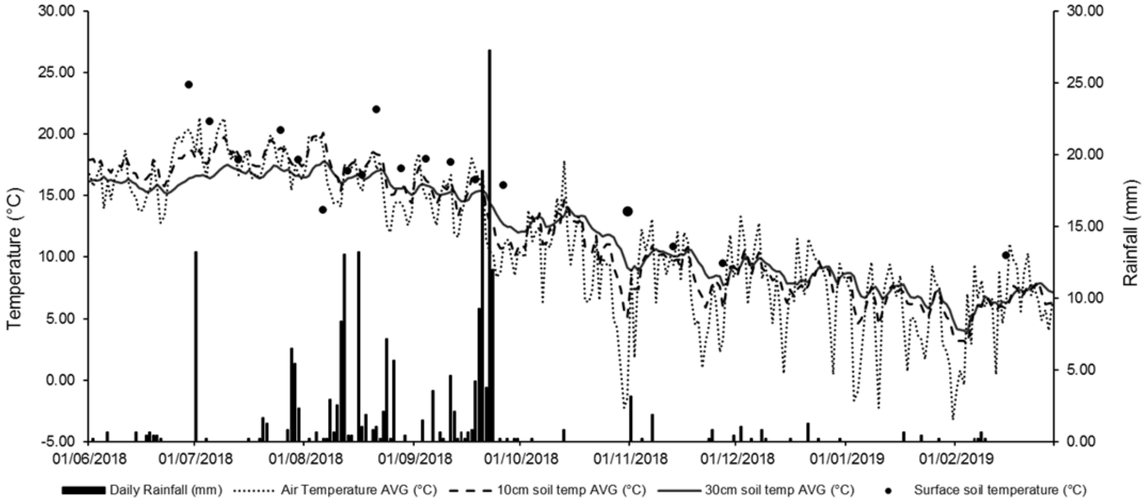

Figure 4. 1: Average daily rainfall, air temperature, soil temperature at 10 cm, 30 cm, and the soil surface during the experimental period. The dots (●) represent an average soil surface temperature (*n*=3) measured during each gas sampling event.

4.3.2 Soil and environmental soil conditions

Soil BD ranged from 1.09 ± 0.05 to 1.21 ± 0.07 g cm^{-3}, with the highest soil BD of 1.21 ± 0.07 g cm^{-3} occurring in the upslope pasture and the no-buffer strip control treatments. This was significantly larger than the willow and woodland riparian buffer treatments, but not the riparian grass buffer strip (*LSD = 0.14*). Soil pH ranged from 5.4 ± 0.09 to 5.7 ± 0.24, and there was no evidence of significant differences (*LSD = 0.38*) between all the treatments. The highest concentration of soil OM occurred in the willow riparian buffer (14.1 ± 0.4%) treatment, which was not significantly higher than the grass (13.1 ± 0.6%) or woodland (13.9 ± 0.4%) riparian buffer treatments but was significantly different to the no-buffer control (10.0 ± 0.7%) treatment and the upslope pasture (9.4 ± 0.3%) (*LSD = 1.92*) (Table 4.1).

Table 4. 1: Mean values (±standard error) of soil characteristics of the upslope pasture and the riparian buffer treatments before the commencement of the current experiment in 2018.

Parameter	**Upslope pasture**	**No-buffer control**	**Grass buffer**	**Willow buffer**	**Woodland buffer**	***LSD***
pH	5.5 ± 0.4	5.5 ± 0.38	5.4 ± 0.41	5.5 ± 0.43	5.4 ± 0.44	0.5
BD (g cm^{-3})	1.2 ± 0.03	1.2 ± 0.07	1.2 ± 0.05	1.2 ± 0.03	1.2 ± 0.07	0.2
Total C (%)	4.3 ± 0.9	4.3 ± 1.1	4.2 ± 1.0	4.5 ± 0.9	4.6 ± 0.6	0.3
Total N (%)	0.46 ± 0.01	0.46 ± 0.01	0.47 ± 0.03	0.48 ± 0.03	0.52 ± 0.05	0.13
C: N	9.2 ± 0.9	9.2 ± 1.0	8.9 ± 0.7	9.4 ± 0.6	8.9 ± 0.7	0.37

4.3.3 Flow and water N

Two storm and flow discharge events (on the 12th of November 2018 and the 11th of February 2019) were observed during the current experimental period (Table 4.2). During the first storm, the willow riparian buffer had the highest total TON load of 18653.7 ± 9404.8 mg (*LSD=192395*), and a higher FWMC of 0.041 ± 0.022 mg N L^{-1} (*LSD=0.059*), whereas the woodland riparian buffer recorded a larger flow (497484 ± 23569 L, *LSD=303482*). All the previous parameters remained insignificant between all the treatments during this storm. During the second storm, TON loads were ~5-times lower than during the first storm, with the largest emitted from the willow riparian buffer (4581 ± 2476.6 mg, *LSD=21284*). Also, the total flow was ~3.5 times lower than recorded during the first storm, with the willow riparian buffer having the highest runoff of 148903 ± 7918 L, *LSD = 137754*). FWMC concentrations ranged from 0.021 ± 0.011 to 0.031 ± 0.015 mg N L^{-1} (*LSD = 0.025*), with the highest (0.031 ± 0.015 mg N L^{-1}) recorded in the willow riparian buffer. Similar to the first storm, all the parameters were insignificant between treatments.

Table 4. 2: Mean (±standard error) TON concentrations, total flow, and flow weighted mean N concentrations during storm events in the no-buffer control and the different downslope riparian buffer treatments.

Storm Date	Parameter	No-buffer control	Grass buffer	Willow buffer	Woodland buffer	*LSD*
12/11/2018	Total TON (mg)	15391.9 ± 5431.1	11076.9 ± 3849.1	18653.7 ± 9404.8	12343.5 ± 9613.1	192395
	Total flow (L)	494825 ± 22186	431947 ± 23071	470371 ± 18893	497484 ± 23569	303482
	FWMC (mg N L^{-1})	0.031 ± 0.012	0.026 ± 0.0096	0.041 ± 0.022	0.024 ± 0.018	0.059
11/02/ 2019	Total TON (mg)	3370.1 ± 584.5	2621.5 ± 991.1	4581 ± 2476.6	3152.4 ± 1576.2	21284
	Total flow (L)	132152 ± 1884.1	113176 ± 14451	147964 ± 5631.3	148903 ± 7918	137754
	FWMC (mg N L^{-1})	0.026 ± 0.0044	0.022 ± 0.0058	0.031 ± 0.015	0.021 ± 0.011	0.0251

4.3.4 Soil mineral N dynamics

Figure 4.2 shows the soil N concentrations determined during sampling days. Figure 4.2 (A) shows that soil TON concentrations during the sampling period were similar between all treatments during the first sampling event prior to the first silage cut and fertilizer application. During the first sampling day after fertilizer application, an increase in soil TON concentration was detected in all the treatments. The most considerable increase of about 10-fold was recorded in the no-buffer control treatment, which showed TON concentrations between 5 and 18 times higher than in the vegetated riparian buffer treatments. Following this, the peak soil TON concentrations decreased to pre-fertilizer application levels for the grass, woodland, and willow riparian buffer treatments. However, they stayed elevated for a more extended period in the no-buffer control treatment and the upslope pasture, which reached similar levels. As shown in Figure 4.2 (B), the soil NH_4^+-N concentrations during the experimental period behaved the same way as soil TON, except that there was no increase in NH_4^+-N in the grass riparian buffer treatment at the sampling time immediately after fertilizer application.

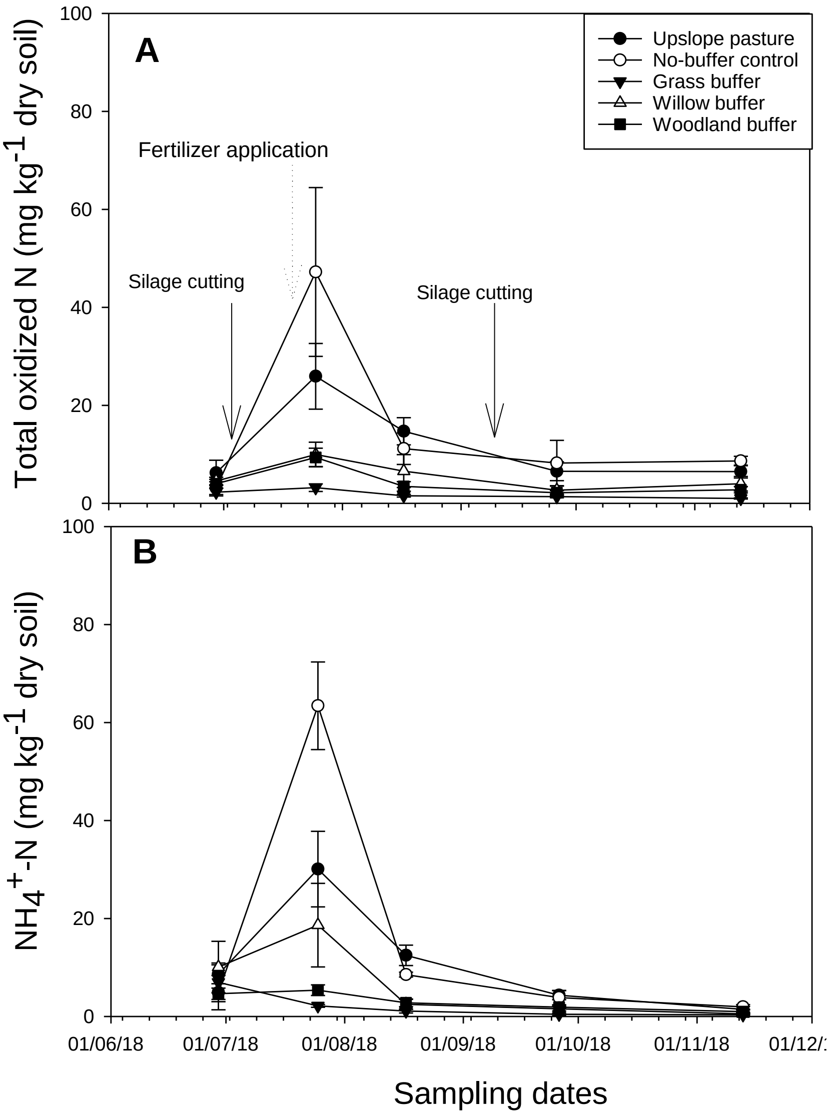

Figure 4. 2: Soil TON (A) and NH_4^+-N (B) dynamics for the upslope pasture and the downslope riparian buffers with different vegetation treatments during the experimental period; data points and error bars represent the treatment means (upslope pasture: *n*=12, no-buffer control: *n*=3, grass, woodland, and willow riparian buffer: *n*=6) and SE during each sampling event.

4.3.5 Water-filled pore spaces

Table 4.3 shows the mean %WFPS for the whole experimental period, and Figure 4.3 (A) shows %WFPS dynamics during the sampling occasions. The mean %WFPS ranged from 56.5 ± 5.1 % to 69.1 ± 5.1%, with the grass riparian buffer treatment having the lowest mean %WFPS. Figure 4.3 (A) shows that %WFPS had a similar temporal trend for all treatments. The most considerable increase in %WFPS was observed after prolonged rainfall events during October 2018.

Table 4. 3: Predicted mean values (± standard error) of soil physical and chemical properties of the upslope pasture and the riparian buffers between June 2018 and February 2019.

Parameter	**Upslope pasture**	**No-buffer control**	**Grass Buffer**	**Willow Buffer**	**Woodland Buffer**	***LSD***
BD (g cm^{-3})	1.21 ± 0.028	1.21 ± 0.05	1.09 ± 0.041	1.20 ± 0.041	1.19 ± 0.041	0.14
pH	5.5 ± 0.16	5.5 ± 0.20	5.4 ± 0.17	5.5 ± 0.17	5.4 ± 0.17	0.38
WFPS (%)	66.1 ± 4.27	61.0 ± 6.33	56.5 ± 5.10	63.0 ± 5.10	69.1 ± 5.10	14.3
Log$_{10}$ NH$_4^+$	0.99 ± 0.10	1.12 ± 0.14	0.18 ± 0.12	0.76 ± 0.12	0.48 ± 0.12	0.32
Log$_{10}$ TON	0.99 ±0.13	1.2 ± 0.16	0.23 ± 0.14	0.68 ± 0.14	0.59 ± 0.14	0.24

4.3.6 Treatment effects on soil explanatory variables

Table 4.4 contains the *p*-values from the tests included in the LMMs for the soil variables. The results indicate that there was no evidence that BD, pH, and %WFPS differed with treatments. There were treatment differences in log$_{10}$ NH$_4^+$, with the average of riparian buffer treatments different to the no-buffer control treatment and upslope pasture; not significantly different to each other (*LSD = 0.27*). All the riparian buffer treatments were different to each other (*LSD = 0.12*). There was no main effect difference between upper and lower chambers, but there was an observed interaction effect. The interaction effect indicated that the grass, willow, and woodland riparian buffer treatments were significantly different in the upper chambers, and only the willow riparian buffer treatment showed a difference between the upper and lower chambers (*LSD = 0.36*) (Table 4.4). Significant differences in log$_{10}$ TON between treatments were also observed. The average of the set of vegetated riparian buffer treatments was different to the no-buffer control treatment and the upslope pasture;

not significantly different to each other (*LSD = 0.21*). The willow and woodland riparian buffers were both significantly different to the grass riparian buffer treatment, but not to each other (*LSD =0.19*) (Table 4.4).

Table 4. 4: *p*-values for tests from linear mixed models (LMMs) on each soil variable.

	BD	**pH**	**$\log_{10}$ NH_4^+**	**$\log_{10}$ TON**	**%WFPS**
Area	0.33	0.78	<0.001	<0.001	0.55
Area * Treatment crop	0.14	0.85	0.001	<0.001	0.11
Area * Buffer area	1	0.96	0.86	0.46	0.91
Area * Treatment crop * Buffer area	1	0.25	0.034	0.69	0.94

4.3.7 N_2O emissions

4.3.7.1 Daily fluxes

Figure 4.3 (A) shows N_2O fluxes measured on the respective sampling days. During most sampling days, the no-buffer control treatment showed higher fluxes than the other treatments, closely followed by the upslope pasture. A slight increase in emissions was detected after fertilizer application for all but the grass riparian buffer treatment. After the first silage cut, N_2O emissions increased for all but the grass buffer treatment. While the upslope pasture and no-buffer control showed a further increase at the second sampling after the silage cut, the vegetated riparian buffer treatments decreased again and remained around the same level as before the silage cut. The grass riparian buffer showed the most minor fluxes, which frequently were found to be negative.

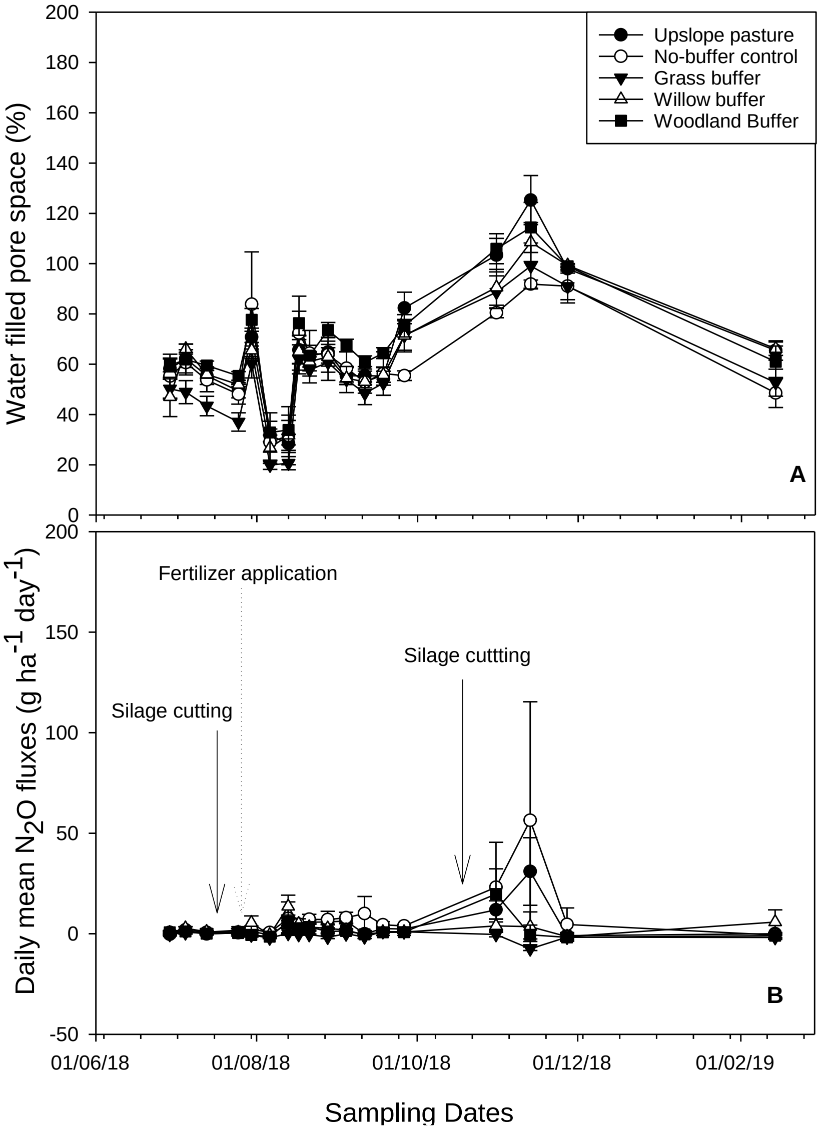

Figure 4. 3: Daily %WFPS dynamics (A) and N_2O fluxes (B) from the upslope pasture and the downslope riparian buffers with different vegetation treatments. Data points and error bars represent the treatment means (upslope pasture: *n*=12, no-buffer control: *n*=3, grass, woodland, and willow riparian buffer: *n*=6) and SE during each sampling day.

4.3.7.2 Total cumulative emissions

Total cumulative emissions followed the descending order: no-buffer control; 1193.2 g N ha^{-1} (95% confidence interval: -129.2-3430) > upslope pasture; 717.7 g N ha^{-1} (95% CI: 10.9-1713) > woodland riparian buffer; 306.3 g N ha^{-1} (95% CI: -392.9-1583)

> willow riparian buffer; 255.1 g N ha^{-1} (95% CI: -413.8-1501) > grass riparian buffer; -310.2 g N ha^{-1} (95% CI:-535.5-492) (Figure 4.4). There was no evidence of differences in N_2O emissions between the upslope pasture, no-buffer control, and the three vegetated riparian buffers (*p* = 0.11). Also, there was no evidence of a difference amongst the three different vegetated riparian buffers (*p* = 0.36) and between the upper and lower parts of the riparian buffer areas (*p* = 0.49). There was also no evidence of a difference of an interaction between the riparian buffer vegetation and the area within the riparian buffer vegetation (lower/upper) (*p* = 0.83).

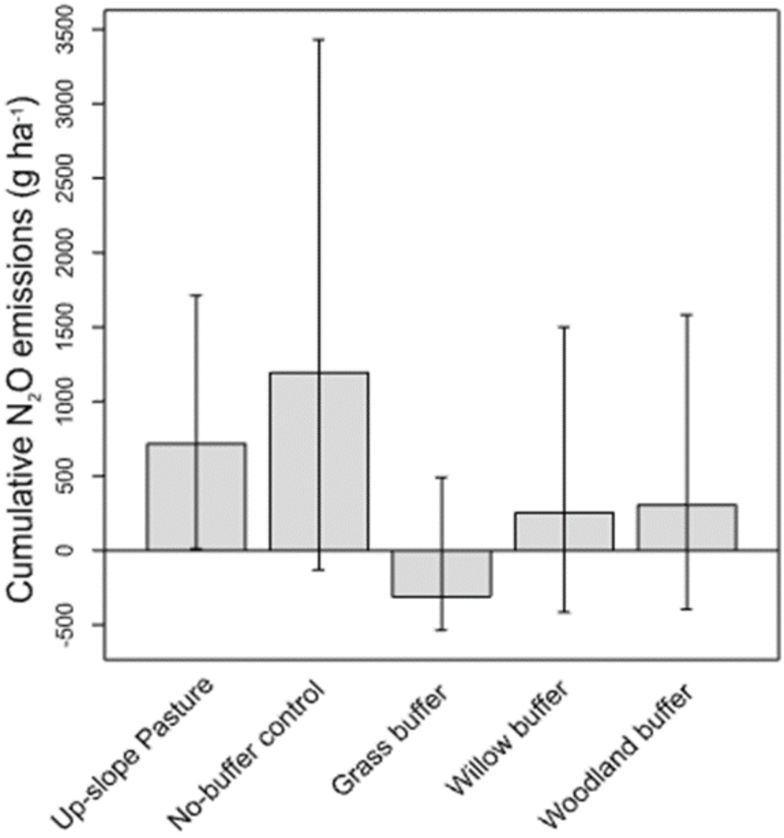

Figure 4. 4: Cumulative N_2O emissions for the whole experimental period from the upslope pasture and downslope riparian buffers with different vegetation treatments. The error bars represent upper 95% limit confidence intervals for the population values of the treatment means

(upslope pasture: *n*=12, no-buffer control: *n*=3, grass, woodland, and willow riparian buffer: *n*=6).

4.3.7.3 Relationships between cumulative N_2O emissions and soil environmental variables

Figure 4.5 and Table 4.5 show that cumulative N_2O emissions were significantly correlated with NH_4^+-N (r = 0.4; *p* = 0.041), soil TON (r= 0.41; *p* = 0.052), pH (r = 0.13; *p* = 0.079), and %WFPS (r = 0.27; *p* = 0.27). Figure 4.6 shows that the cumulative N_2O emissions increased with an increase in NH_4^+-N, soil TON, and %WFPS and decreased with an increase in soil pH.

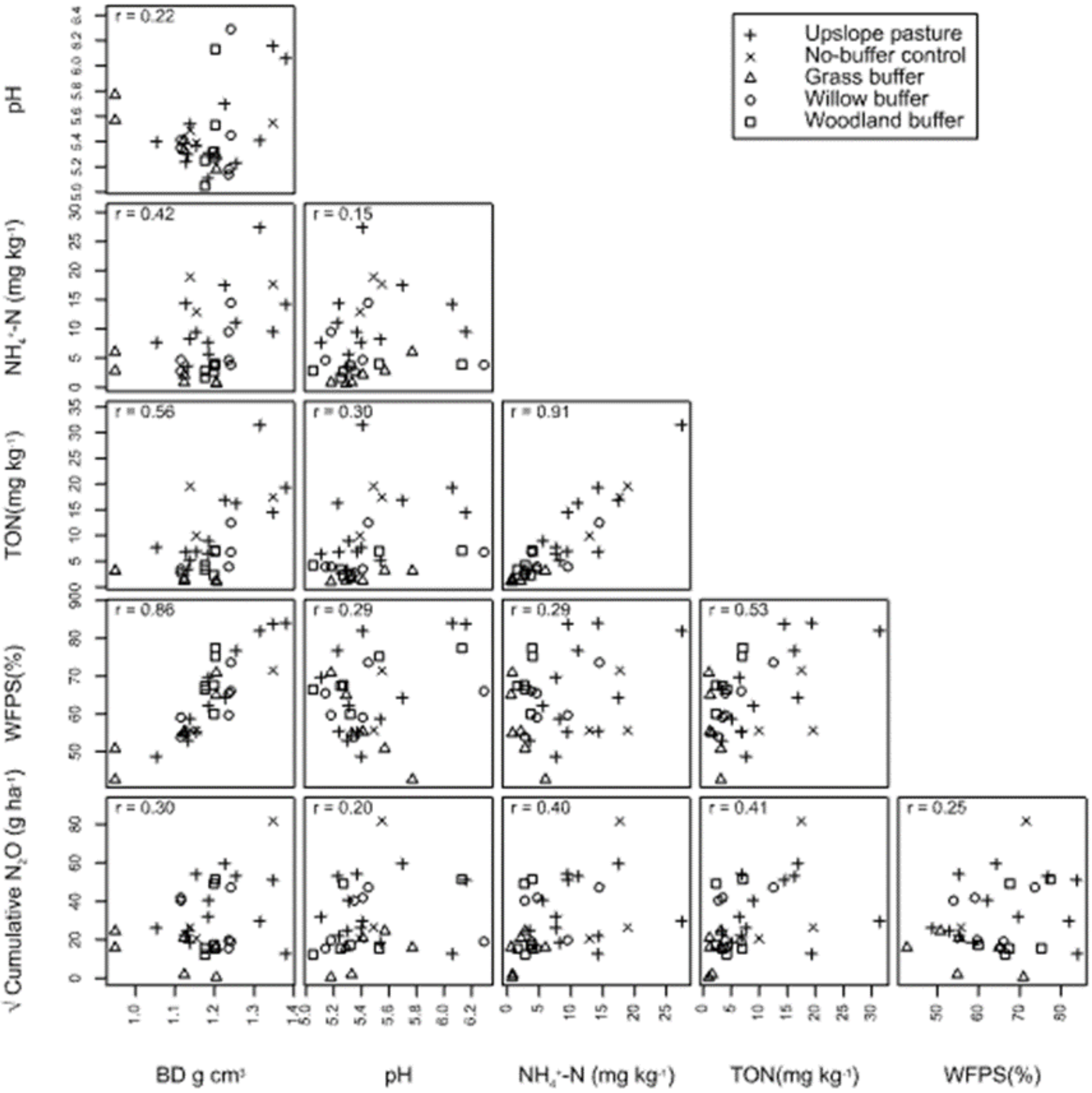

Figure 4. 5: Scatterplots showing the relationships between variables soil BD, pH, TON, and %WFPS for the upslope pasture and the downslope riparian buffers with different vegetation treatments. r = Pearson's correlation coefficient.

4.4 Discussion

4.4.1 N_2O and soil-environmental conditions

The results of the study indicate that the largest N_2O peak observed on the 10th of November 2018 in the no-buffer control treatment and the upslope pasture coincided with the largest %WFPS observed across all the treatments (Figures 4.3 A and B). Soil N_2O emissions further showed to increase with increasing soil %WFPS (Figure 4.6).

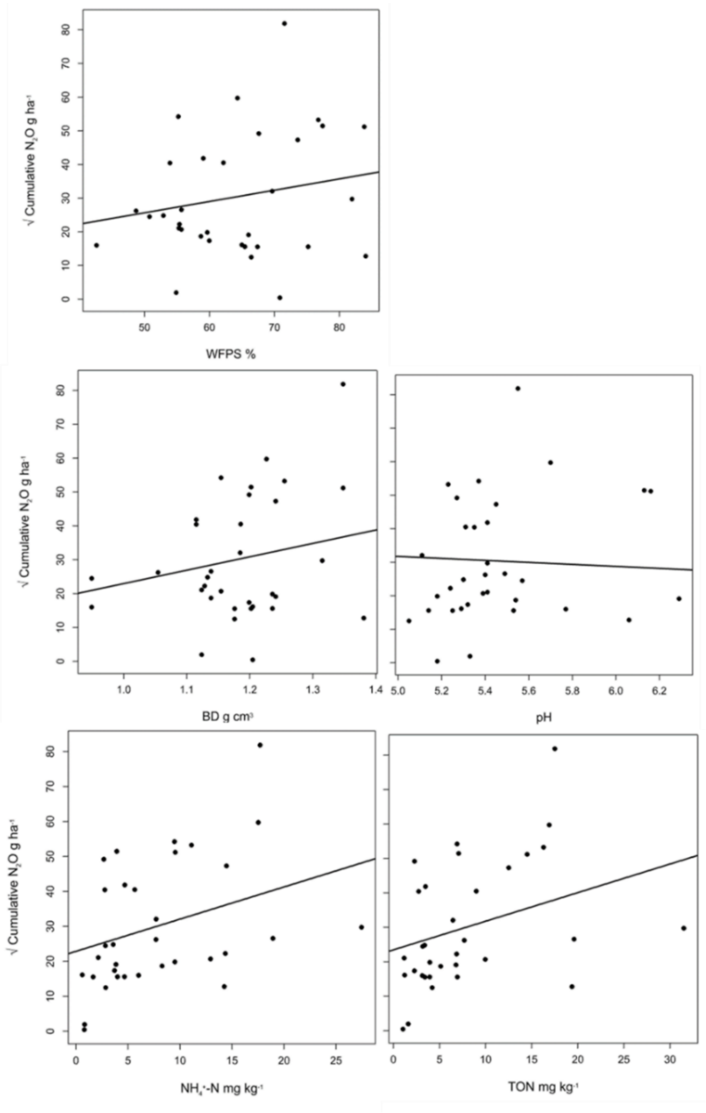

Figure 4. 6: Relationships between cumulative N_2O emissions versus each of the explanatory soil variables.

The findings of the current study are consistent with previous work, particularly Castellano *et al.* (2010) and Keller and Reiners (1994), who reported that N_2O production rates increased with increasing %WFPS when other factors are not finite.

The currents study observed significant correlations between soil NH_4^+-N and N_2O emissions (Figure 4.5 and Table 4.5) and a further increase in N_2O emissions with increasing soil mineral N (NH_4^+-N and TON) (Figure 4.6), similar to reports by other authors, including Perego *et al.* (2016) and Ngoc Tuong Hoang and Maeda (2018). High N_2O production is known to increase when mineral N and %WFPS are not limiting (Clayton *et al.*, 1997; Dobbie and Smith, 2003). This was true for the current study because, despite higher %WFPS in all the treatments coinciding with a larger N_2O peak in the no-buffer control and the upslope pasture, the three vegetated riparian buffer treatments exhibited lower N_2O fluxes during this period (Figures 4.3 A and B). This could have been because this period corresponded with lower mineral N within the three vegetated buffer treatments and higher values in the no-buffer control and the upslope pasture (Figure 4.2). The high mineral N in the no-buffer control treatment and the upslope pasture was as a result of N fertilization and N that most likely moved downslope from the upslope pasture via water transport, while the low mineral N in the three vegetated riparian buffers was due to the fact that the buffer areas were not fertilized directly. This contrasting behaviour of N_2O fluxes between the three vegetated riparian buffer treatments and the no-buffer control and upslope pasture shows that favourable soil conditions may not translate into higher N_2O production when the main substrate (mineral N) of microbial N_2O production is restricted. This result is consistent with other studies reported in international literature (Fisher *et al.*, 2014; Linn and Doran, 1984; Sehy *et al.*, 2003).

Table 4. 5: *p*-values for the slope of the fitted line of the model.

Variable	Intercept	SE intercept	Slope	SE slope	*p*-value
BD	30.19	4.001	39.56	32.640	0.235
pH	30.37	5.231	-2.983	10.8369	0.786
NH_4^+	30.06	3.859	0.9200	0.42779	0.041
TON	30.05	3.701	0.8305	0.40899	0.052
WFPS (%)	30.30	4.129	0.3353	0.29743	0.268

In instances when there is no vegetation to facilitate plant N-uptake, high N_2O production may result (Kim *et al.*, 2013; Snyder *et al.*, 2009). This is due to abundant mineral N being available for dominant microbial N_2O production processes; nitrification and denitrification, particularly when other soil and environmental N_2O production factors are not limiting (Drury *et al.*, 2014; Müller *et al.*, 2004; Sehy *et al.*, 2003). The current study's findings are in line with those of the previous authors since the largest N_2O flux followed immediately after silage cut in the no-buffer control and the upslope pasture (Figure 4.3 B). High cumulative N_2O emissions often coincide with higher N fertilizer application rates (Rochette *et al.*, 2010; Smith *et al.*, 1998). The no-buffer control in the lower part of the plot (area ‘a’ bottom chamber) had higher N_2O emissions than the upslope pasture (area ‘a’ top chamber) because it received N fertilizer and N that most likely moved downslope from the upslope pasture via water transport. The fact that the non-fertilized riparian buffers (grass, willow, and woodland) had much lower N_2O emissions even though they were effectively within the same distance from the upslope pasture shows that higher emissions in the current experiment were found in areas fertilized directly and receiving N via incoming water from the upslope fertilized pasture area.

High soil moisture contents coupled with low mineral N have often been reported to favour N_2O consumption in various agroecosystems (Chapuis-Lardy *et al.*, 2007; Glatzel and Stahr, 2001; LaMontagne *et al.*, 2003). The three vegetated riparian buffers had relatively low mineral N compared to the no-buffer control and the upslope pasture, despite that all the treatments had a higher %WFPS in most of the experimental period (Figures 4.2 A and B and 4.3 A). The negative N_2O emissions in the grass riparian buffer treatment (Figures 4.4) correspond to the lowest mineral N values from all treatments (Figure 4.2). Some riparian buffer vegetation usually retain higher soil moisture, and its deep rooting systems (mainly trees) reduce sub-surface BD and increase soil OM compared to some upslope agricultural lands (Bharati *et al.*, 2002; Marquez *et al.*, 1998). The phenomena of net N_2O consumption (i.e., negative fluxes) is also attributed to a reduced gas diffusivity (primarily associated with high bulk density and waterlogging conditions), leading to N_2O produced in the sub-surface being reduced to N_2 before reaching the soil surface (Arah *et al.*, 1991; Klefoth *et al.*, 2014; Marquez *et al.*, 1998). Thus, in the current study, it could happen that the shallower rooting system of the grass riparian buffer (compared to willow and woodland riparian buffers) could not reduce bulk density in the sub-surface layers but only in the surface layers; thus, N_2O produced in the sub-surface layers in the grass riparian buffer might not have reached the soil surface but was reduced to N_2 through complete denitrification, similar to the findings reported by Arah *et al.* (1991) and Klefoth *et al.* (2014). The phenomena of net N_2O consumption in the grass riparian buffer of the current experiment were, therefore, due to high %WFPS coupling with low mineral N and the impediment of N_2O diffusivity from subsurface layers.

Riparian buffer vegetation with low N-removal efficiencies from run-off water have been reported to result in significantly increased N_2O emissions compared to areas with high N removal efficiencies (Hefting *et al.*, 2006). The findings of the current study were in agreement with such work since high runoff water N and higher N_2O

emissions in the no-buffer control treatment and the lowest run-off N and negative N_2O emissions in the grass buffer treatment were recorded.

4.4.2 N_2O emissions in the upslope pasture and downslope riparian buffers

In order to be considered an air quality threat, riparian buffers must emit significantly greater N_2O than adjacent cropland (Fisher *et al.*, 2014). The results of our study herein suggest that the no-buffer control may be a justifiable concern for air quality compared to the three vegetated buffer treatments. However, there is minor alarm for the woodland and willow riparian buffers (which were at established phase), and there is no concern regarding the grass buffer (fully established); as it was an N_2O sink during the experiment (Figure 4.4). No large N_2O peaks were observed within the three vegetated riparian buffers, which resulted in low N_2O emissions compared to the upslope pasture and the no-buffer control treatment, which had relatively higher N_2O peaks, similar to observations by Kim *et al.* (2009b) and Hefting *et al.* (2003). In the current study herein, greater N_2O emissions were observed from the upslope pasture and no-buffer control compared to the 3-year-old (establishment phase for willow and woodland) vegetated riparian buffers (Figure 4.4). The findings of the current study were in line with findings by Kim *et al.* (2009b), who observed no differences amongst different 15-year old (Schultz *et al.*, 1995) riparian buffer vegetation types but found emissions from these buffers to be significantly lower than from an adjacent maize field they served. Additionally, Groh *et al.* (2015) observed more significant N_2O emissions in an upslope maize field compared to an 18-year old downslope grass riparian buffer that serves it. The results of the current study and international literature suggest that agricultural land may sometimes emit more N_2O than neighbouring vegetated riparian buffers regardless of their age.

Comparing a grass riparian buffer and an adjacent maize field, Hefting *et al.* (2003) reported emissions of 20 and 4 kg N_2O ha^{-1}, respectively, while respective emissions of 3.3 and 2.2 kg N_2O ha^{-1} were reported in a reforested riparian buffer area and an adjacent maize field in another study (Kachenchart *et al.*, 2012); similar to findings of the current study. In the current study, this could been as a result of the N fertilizer applied in the upslope pasture, and this was further attested to by a significant correlation between mineral N and N_2O (Figure 4.5). A study on forest and grass riparian buffers in Indiana reported N_2O emissions of 4.83 and 1.03 kg N_2O ha^{-1}, respectively, compared to values ranging between 6.3 and 7.8 kg N_2O ha^{-1} in the adjacent maize fields (Fisher *et al.*, 2014). The findings of the current study and broader international literature suggest that the intensity of N_2O emissions may vary between upslope utilized land and riparian buffers and may be highly dependent on the buffer vegetation (Fisher *et al.*, 2014; Kim *et al.*, 2009b).

4.4.3 N losses to water

Riparian buffer strips are fundamentally established to protect watercourses from pollutants from agricultural lands (Groffman *et al.*, 1991; Mitsch *et al.*, 2001). The willow riparian buffer (at establishment phase) proved to be of most concern for water quality, compared to all other riparian buffers, since it maintained the highest N-FWMC during both the sampled storm events. Although the willow riparian buffer had a high N-FWMC during both the storms, the N-FWMC of the second storm was ~25% less than that of the first storm. This could have been because most of the fertilizer N applied in the upslope pasture had been washed down with the first storm as there was no subsequent fertilization after the first storm. Therefore, the current study's findings were similar to those reported by Drewry *et al.* (2009) and Davis *et al.* (2019), who observed higher N-FWMC during the first event and almost half in the subsequent event. In a 15-year old switch grass riparian buffer strip, Davis *et al.* (2019) reported FWMC of up to 7.6 mg N L^{-1}, whereas the current study observed a maximum of 0.041 mg N L^{-1}, despite that majority of the riparian buffer treatments being at an establishment phase. It could happen that with age, riparian buffer vegetation may become a secondary N source since some N will be derived from litter mineralization, but this was not formally tested in the current study. The current study further showed that the novel grass riparian buffer strip was the most effective in reducing losses of N to both water and air. This is because it had relatively low N-FWMC and consumed N_2O instead of emitting it like the other riparian buffer treatments.

4.4.4 Implications of the findings

Although the current study was undertaken on a replicated experimental facility, the results have far-reaching implications for both research on non-point source pollution and the development of mitigation measures in agro systems. For instance, DEFRA (2019) and Natural England (2013) reported that some of the most common riparian buffer vegetation in the UK includes a mixture or single stands of grass, trees (i.e., willows), and woodlands. Furthermore, Stutter *et al.* (2019) reported an increasing interest in willows for their biomass energy, their effectiveness as a barrier for soil and nutrient movement from agricultural land to watercourses, their vigorous re-growth following coppicing, and their high adaptability to varying growing conditions. However, the results of the current study point to some concerns for the willow riparian buffer during the establishment phase. This is because in the current experiment, this riparian buffer recorded the highest N-FWMC and emitted relatively copious amounts of N_2O. Thus, the current results signal the need to consider some trade-offs for willow riparian buffers during the establishment phase. Based on the current study results, farmers can be advised to adopt the novel hybrid grass as a riparian buffer treatment to optimize multiple ecosystem co-benefits by mitigating both water and air quality concerns.

4.4.5 Limitations of the findings

Since the experiments of the current study were undertaken using bounded replicate plots, there are inevitably some limitations in scaling up the findings. The results represent the soils, climatic conditions, and management practices associated with the current study's pasture and downslope riparian buffers. Such conditions are representative of 1843 km^2 of agricultural land across England with ruminant grazing farms. Process-based modelling could be used to illustrate the implications of the new experimental evidence on business-as-usual emissions to both water and air in those parts of England. The findings reported herein relate to the establishment phases only of the willow and woodland riparian buffers. Both treatments are likely to be viewed as longer-term management options, especially given the increasing drive in the UK to deliver public goods and services from the management of agricultural land.

4.5 Conclusion

The experimental plot scale results imply that careful selection of riparian buffer vegetation is critical not to risk environmental disbenefits associated with N_2O emissions. The results show that the grass riparian buffer was the best vegetation treatment choice since it was an N_2O sink, and reduced run-off N compared to the other riparian buffer vegetations. Additional studies with different upslope crops and varying soil/rainfall/slope conditions are required to confirm to policy if grass is consistently the best riparian buffer treatment compared with the establishment phases of willow or woodland riparian buffers. Strategic longer-term studies are also required to explore the relative merits of the different vegetation treatments in the mature phases of willow and deciduous woodland. The current results, which cover the establishment phase for both woodland riparian buffer treatments, clearly point to the need to plan for the impacts of different vegetation types in finalizing the selection of mitigation measures for improving sustainability and minimizing unintended trade-offs within pastoral agroecosystems.

4.6 References

Arah, J., Smith K., Crichton I., Li H., 1991. Nitrous oxide production and denitrification in Scottish arable soils. *Journal of Soil Science*, 42:351-367.

Bharati, L., Lee K.-H., Isenhart T., Schultz R., 2002. Soil-water infiltration under crops, pasture, and established riparian buffer in Midwestern USA. *Agroforestry Systems*, 56:249-257.

Bradley, R., Whalen J., Chagnon P.-L., Lanoix M., Alves M., 2011. Nitrous oxide production and potential denitrification in soils from riparian buffer strips: influence of earthworms and plant litter. *Applied Soil Ecology*, 47:6-13.

Castellano, M.J., Schmidt J.P., Kaye J.P., Walker C., Graham C.B., Lin H., Dell C.J., 2010. Hydrological and biogeochemical controls on the timing and magnitude of nitrous oxide flux across an agricultural landscape. *Global Change Biology*, 16:2711-2720.

Chadwick, D., Cardenas L., Misselbrook T., Smith K., Rees R., Watson C., McGeough K., Williams J., Cloy J., Thorman R., 2014. Optimizing chamber methods for measuring nitrous oxide emissions from plot-based agricultural experiments. *European Journal of Soil Science*, 65:295-307.

Chapuis-Lardy, L., Wrage N., Metay A., Chotte J.L., Bernoux M., 2007. Soils, a sink for N_2O? A review. *Global Change Biology*, 13:1-17.

Choi, W.-J., Lee S.-M., Han G.-H., Yoon K.-S., Jung J.-W., Lim S.-S., Kwak J.-H., 2006. Available organic carbon controls nitrification and immobilization of ammonium in an acid loam-textured soil. *Journal of Applied Biological Chemistry*, 49:28-32.

Clayton, H., McTaggart I., Parker J., Swan L., Smith K., 1997. Nitrous oxide emissions from fertilised grassland: A 2-year study of the effects of N fertiliser form and environmental conditions. *Biology & Fertility of Soils*, 25:252-260.

Conen, F., Smith K., 2000. An explanation of linear increases in gas concentration under closed chambers used to measure gas exchange between soil and the atmosphere. *European Journal of Soil Science*, 51:111-117.

Davis, M.P., Groh T.A., Jaynes D.B., Parkin T.B., Isenhart T.M., 2019. Nitrous oxide emissions from saturated riparian buffers: Are we trading a water quality problem for an air quality problem? *Journal of Environmental Quality*, 48:261-269.

DEFRA, 2019. The guide to cross compliance in England 2019, in: FaRA Department for Environment (Ed.), United Kingdom.

De Klein, C., Harvey M., 2012. Nitrous oxide chamber methodology guidelines. Global Research Alliance on Agricultural Greenhouse Gases, Ministry for Primary Industries: Wellington, New Zealand.

Dobbie, K.E., Smith K.A., 2003. Nitrous oxide emission factors for agricultural soils in Great Britain: the impact of soil water-filled pore space and other controlling variables. *Global Change Biology*, 9:204-218.

Drewry, J., Newham L., Croke B., 2009. Suspended sediment, nitrogen and phosphorus concentrations and exports during storm-events to the Tuross estuary, Australia. *Journal of Environmental Management*, 90:879-887.

Drury, C., Reynolds W., Tan C., McLaughlin N., Yang X., Calder W., Oloya T., Yang J., 2014. Impacts of 49-51 years of fertilization and crop rotation on growing season nitrous oxide emissions, nitrogen uptake and corn yields. *Canadian Journal of Soil Science*, 94:421-433.

Dukes, M., Evans R., Gilliam J., Kunickis S., 2002. Effect of riparian buffer width and vegetation type on shallow groundwater quality in the Middle Coastal Plain of North Carolina. *Transactions of the ASAE*, 45:327.

Firestone, M., 1982. Biological denitrification, In: F Stevenson (Ed.), Nitrogen in agricultural soils, American Society of Agronomy, Inc. Crop Science Society of America, Inc. Soil Science Society of America Inc., Madison, Wisconsin, USA. pp. 289-326.

Fisher, K., Jacinthe P., Vidon P., Liu X., Baker M., 2014. Nitrous oxide emission from cropland and adjacent riparian buffers in contrasting hydrogeomorphic settings. *Journal of Environmental Quality*, 43:338-348.

Garcia, J.-L., Tiedje J., 1982. Denitrification in rice soils, In: D YR and H Diem (Eds.), Microbiology of Tropical Soils and Plant Productivity, Springer, London. pp. 187-208.

Glatzel, S., Stahr K., 2001. Methane and nitrous oxide exchange in differently fertilised grassland in southern Germany. *Plant & Soil*, 231:21-35.

Groffman, P.M., Axelrod E.A., Lemunyon J.L., Sullivan W.M., 1991. Denitrification in grass and forest vegetated filter strips. *Journal of Environmental Quality*, 20:671-674.

Groffman, P.M., Gold A.J., Addy K., 2000. Nitrous oxide production in riparian zones and its importance to national emission inventories. *Chemosphere-Global Change Science*, 2:291-299.

Groffman, P.M., Gold A.J., Jacinthe P.-A., 1998. Nitrous oxide production in riparian zones and groundwater. *Nutrient Cycling in Agroecosystems*, 52:179-186.

Groffman, P.M., Hanson G.C., 1997. Wetland denitrification: influence of site quality and relationships with wetland delineation protocols. *Soil Science Society of America Journal*, 61:323-329.

Groh, T.A., Gentry L.E., David M.B., 2015. Nitrogen removal and greenhouse gas emissions from constructed wetlands receiving tile drainage water. *Journal of Environmental Quality*, 44:1001-1010.

Gundersen, P., Laurén A., Finér L., Ring E., Koivusalo H., Sætersdal M., Weslien J.-O., Sigurdsson B.D., Högbom L., Laine J., 2010. Environmental services provided from riparian forests in the Nordic countries. *Ambio*, 39:555-566.

Hefting, M.M., Bobbink R., de Caluwe H., 2003. Nitrous oxide emission and denitrification in chronically nitrate-loaded riparian buffer zones. *Journal of Environmental Quality*, 32:1194-1203.

Hefting, M.M., Bobbink R., Janssens M.P., 2006. Spatial variation in denitrification and N_2O emission in relation to nitrate removal efficiency in a N-stressed riparian buffer zone. *Ecosystems*, 9:550-563.

Howarth, R., Swaney D., Billen G., Garnier J., Hong B., Humborg C., Johnes P., Mörth C.-M., Marino R., 2012. Nitrogen fluxes from the landscape are controlled by net anthropogenic nitrogen inputs and by climate. *Frontiers in Ecology & the Environment*, 10:37-43.

Hubbard, R.K., Sheridan J.M., Lowrance R., Bosch D.D., Vellidis G., 2004. Fate of nitrogen from agriculture in the southeastern Coastal Plain. *Journal of Soil & Water Conservation*, 59:72-86.

IPCC, 2007. Changes in atmospheric constituents and in radiative forcing. Chapter 2, Climate Change 2007. The Physical Science Basis.

Jaynes, D.B., Isenhart T.M., 2014. Reconnecting tile drainage to riparian buffer hydrology for enhanced nitrate removal. *Journal of Environmental Quality*, 43:631-638.

Jumppanen, T., Jokinen M., Airo J., Klemm M., Hoger D., Suoniemi-Kähärä A., 2014. Automated Total Oxidized Nitrogen Method Using Vanadium as Reductant with Correlation to Cadmium and Hydrazine Reductant Methods in Sea, Natural, and Waste Waters, Thermo Scientific, Massachusetts, USA.

Kachenchart, B., Jones D.L., Gajaseni N., Edwards-Jones G., Limsakul A., 2012. Seasonal nitrous oxide emissions from different land uses and their controlling factors in a tropical riparian ecosystem. *Agriculture, Ecosystems, & Environment*, 158:15-30.

Keller, M., Reiners W.A., 1994. Soil-atmosphere exchange of nitrous oxide, nitric oxide, and methane under secondary succession of pasture to forest in the Atlantic lowlands of Costa Rica. *Global Biogeochemical Cycles*, 8:399-409.

Kim, D.-G., Hernandez-Ramirez G., Giltrap D., 2013. Linear and nonlinear dependency of direct nitrous oxide emissions on fertilizer nitrogen input: A meta-analysis. *Agriculture, Ecosystems, & Environment*, 168:53-65.

Kim, D.-G., Isenhart T., Parkin T., Schultz R., Loynachan T., 2009a. Nitrate and dissolved nitrous oxide in groundwater within cropped fields and riparian buffers. *Biogeosciences Discussions*, 6:651-685.

Kim, D., Isenhart T.M., Parkin T.B., Schultz R.C., Loynachan T.E., Raich J.W., 2009b. Nitrous oxide emissions from riparian forest buffers, warm-season and cool-season grass filters, and crop fields. *Biogeosciences Discussions*, 6:607.

Klefoth, R.R., Clough T.J., Oenema O., Van Groenigen J.-W., 2014. Soil bulk density and moisture content influence relative gas diffusivity and the reduction of nitrogen-15 nitrous oxide. *Vadose Zone Journal*, 13:vzj2014. 07.0089.

Kuusemets, V., Mander Ü., Lohmus K., Ivask M., 2001. Nitrogen and phosphorus variation in shallow groundwater and assimilation in plants in complex riparian buffer zones. *Water Science & Technology*, 44:615-622.

LaMontagne, M.G., Duran R., Valiela I., 2003. Nitrous oxide sources and sinks in coastal aquifers and coupled estuarine receiving waters. *Science of the Total Environment*, 309:139-149.

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 1, In: P Matson and R Harriss (Eds.), Biogenic Trace Gases: Measuring Emissions from Soil and Water, Blackwell Publishing, Massachusetts, USA. pp. 1267-1272.

Livingston, G., Hutchinson G., 1995. Enclosure-based measurement of trace gas exchange: applications and sources of error, In: P Matson and RC Harris (Eds.), Biogenic Trace Gases: Measuring Emissions from Soil and Water, Blackwell Publishing, Massachusetts, USA. pp. 14-51.

Lowrance, R., 1992. Groundwater nitrate and denitrification in a coastal plain riparian forest. *Journal of Environmental Quality*, 21:401-405.

Lowrance, R., Dabney S., Schultz R., 2002. Improving water and soil quality with conservation buffers. *Journal of Soil & Water Conservation*, 57:36A-43A.

Lowrance, R., Todd R., Fail Jr J., Hendrickson Jr O., Leonard R., Asmussen L. 1984. Riparian forests as nutrient filters in agricultural watersheds. *BioScience*, 34:374-377.

Macleod, C.J.A., Humphreys M.W., Whalley W.R., Turner L., Binley A., Watts C.W., Skøt L., Joynes A., Hawkins S., King I.P., O'Donovan S., Haygarth P.M. 2013. A novel grass hybrid to reduce flood generation in temperate regions. *Scientific Reports*, 3:1683.

Marquez, C.O., Cambardella C.A., Isenhart T.M., Schultz R.C., 1998. Assessing soil quality in a riparian buffer by testing organic matter fractions in central Iowa, USA. *Agroforestry Systems*, 44:133-140.

Mitsch, W.J., Day J.W., Gilliam J.W., Groffman P.M., Hey D.L., Randall G.W., Wang N., 2001. Reducing Nitrogen Loading to the Gulf of Mexico from the Mississippi River Basin: Strategies to Counter a Persistent Ecological Problem: Ecotechnology-the use of natural ecosystems to solve environmental problems-should be a part of efforts to shrink the zone of hypoxia in the Gulf of Mexico. *AIBS Bulletin*, 51:373-388.

Mosier, A., Duxbury J., Freney J., Heinemeyer O., Minami K., 1996. Nitrous oxide emissions from agricultural fields: assessment, measurement and mitigation. *Plant & Soil*, 181:95-108.

Müller, C., Stevens R., Laughlin R., Jäger H.-J., 2004. Microbial processes and the site of N_2O production in a temperate grassland soil. *Soil Biology & Biochemistry*, 36:453-461.

Natural England, N., 2013. Entry Level Stewardship–Environmental Stewardship Handbook, DEFRA, UK.

Ngoc Tuong Hoang, V., Maeda M., 2018. Interactive effects of ammonium application rates and temperature on nitrous oxide emission from tropical agricultural soil. *Soil Science & Plant Nutrition*, 64:767-773.

Paudel, B.R., Udawatta R.P., Anderson S.H., 2011. Agroforestry and grass buffer effects on soil quality parameters for grazed pasture and row-crop systems. *Applied Soil Ecology*, 48:125-132.

Perego, A., Wu L., Gerosa G., Finco A., Chiazzese M., Amaducci S., 2016. Field evaluation combined with modelling analysis to study fertilizer and tillage as factors affecting N_2O emissions: A case study in the Po valley (Northern Italy). *Agriculture, Ecosystems, & Environment*, 225:72-85.

Ravishankara, A., Daniel J.S., Portmann R.W., 2009. Nitrous oxide (N_2O): the dominant ozone-depleting substance emitted in the 21st century. *Science*, 326:123-125.

Reay, D.S., Davidson E.A., Smith K.A., Smith P., Melillo J.M., Dentener F., Crutzen P.J., 2012. Global agriculture and nitrous oxide emissions. *Nature Climate Change*, 2:410.

Rochette, P., 2011. Towards a standard non-steady-state chamber methodology for measuring soil N_2O emissions. *Animal Feed Science & Technology*, 166:141-146.

Rochette, P., Tremblay N., Fallon E., Angers D., Chantigny M., MacDonald J., Bertrand N., Parent L.É., 2010. N_2O emissions from an irrigated and non-irrigated organic soil in eastern Canada as influenced by N fertilizer addition. *European Journal of Soil Science*, 61:186-196.

Sabater, S., Butturini A., Clement J.-C., Burt T., Dowrick D., Hefting M., Matre V., Pinay G., Postolache C., Rzepecki M., 2003. Nitrogen removal by riparian buffers along a European climatic gradient: patterns and factors of variation. *Ecosystems*, 6:0020-0030.

Schultz, R., Colletti J., Isenhart T., Marquez C., Simpkins W., Ball C., Schultz O., 2000. Riparian forest buffer practices, In: H Garrett, et al. (Eds.), North American Agroforestry: An Integrated Science and Practice American Society of Agronomy, Madison, Wisconsin. pp. 189-281.

Schultz, R.C., Collettil J., Isenhart T., Simpkins W., Mize C., Thompson M., 1995. Design and placement of a multi-species riparian buffer strip system. *Agroforestry Systems*, 29:201-226.

Sehy, U., Ruser R., Munch J.C., 2003. Nitrous oxide fluxes from maize fields: relationship to yield, site-specific fertilization, and soil conditions. *Agriculture, Ecosystems, & Environment*, 99:97-111.

Smith, K.A., McTaggart I.P., Dobbie K.E., Conen F., 1998. Emissions of N_2O from Scottish agricultural soils, as a function of fertilizer N. *Nutrient Cycling in Agroecosystems*, 52:123-130.

Smith, P., Martino D., Cai Z., Gwary D., Janzen H., Kumar P., McCarl B., Ogle S., O'Mara F., Rice C., 2007. Greenhouse gas mitigation in agriculture. *Philosophical Transactions of the Royal Society B: Biological Sciences*, 363:789-813.

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*, 133:247-266.

Stutter, M., Kronvang B., Ó hUallacháin D., Rozemeijer J., 2019. Current insights into the effectiveness of riparian management, attainment of multiple benefits, and potential technical enhancements. *Journal of Environmental Quality*, 48:236-247.

Tufekcioglu, A., Raich J.W., Isenhart T.M., Schultz R.C., 2001. Soil respiration within riparian buffers and adjacent crop fields. *Plant & Soil*, 229:117-124.

Udawatta, R.P., Kremer R.J., Garrett H.E., Anderson S.H., 2009. Soil enzyme activities and physical properties in a watershed managed under agroforestry and row-crop systems. *Agriculture, Ecosystems, & Environment*, 131:98-104.

Watts, S.H., Seitzinger S.P., 2000. Denitrification rates in organic and mineral soils from riparian sites: a comparison of N_2 flux and acetylene inhibition methods. *Soil Biology & Biochemistry*, 32:1383-1392.

Zhang, Y., Collins A., Murdoch N., Lee D., Naden P., 2014. Cross sector contributions to river pollution in England and Wales: Updating waterbody scale information to support policy delivery for the Water Framework Directive. *Environmental Science & Policy*, 42:16-32.

Zhao, T., Xu H., He Y., Tai C., Meng H., Zeng F., Xing M., 2009. Agricultural non-point nitrogen pollution control function of different vegetation types in riparian wetlands: A case study in the Yellow River wetland in China. *Journal of Environmental Sciences*, 21:933-939.

CHAPTER 5.0

SOIL CH_4 FLUXES IN A CROPLAND WITH AN UPSLOPE PERMANENT PASTURE AND RIPARIAN BUFFER STRIPS WITH VARYING VEGETATION

This chapter is *published* in the journal “**Journal of Plant Nutrition and Soil Science**” as:

Dlamini JC, Cardenas LM, Tesfamariam EH, Dunn R, Hawkins JMB, Blackwell MSA, Evans J, Collins AL. **2022**. Soil methane (CH_4) fluxes in cropland with permanent pasture and riparian buffers strips with different vegetation. *Journal of Plant Nutrition and Soil Science*, 185 (1): 132 -144. DOI: https://doi.org/10.1002/jpln.202000473

Corresponding author: JCD

Author contributions:

JCD, JE, EHT, LMC, RD, MSAB, ALC: Conceptualization, Methodology, Software. **JCD:** Data curation, Writing- Original draft preparation. **JD, JE:** Visualization, Investigation. **EHT, LMC:** Supervision. **JCD, JE:** Software, Validation. **EHT, LMC, RD, MSAB, ALC:** Writing- Reviewing and Editing.

Abstract

Methane has a GWP 28-times that of CO_2 over a 100-year horizon. Riparian buffers strips are widely implemented for their water quality protection functions along agricultural land, but conditions prevailing within them may increase the production of radiative GHGs, including CH_4. However, a few information is available regarding the dynamics of unintended emissions of soil CH_4 in these commonplace features of agroecosystems and how the dynamics compare to those for agricultural land. To understand the dynamics of soil CH_4 fluxes from permanent pasture and contiguous riparian buffer strips with different (grass, willow, and woodland) vegetation as well controls with no buffer vegetation, an experiment was carried out using the static chamber technique on a replicated plot-scale facility. Gas fluxes were measured periodically with soil and environmental variables between June 2018 and February 2019 at North Wyke, United Kingdom. Soils under all treatments were sinks of CH_4 with the willow riparian buffer (-2555 ± 318.7 g CH_4 ha^{-1}) having the lowest soil CH_4 flux followed by the grass riparian buffer (-2532 ± 318.7 g CH_4 ha^{-1}), woodland riparian buffer (-2318.0 ± 246.4 g CH_4 ha^{-1}), no-buffer control (-1938.0 ± 374.4 g CH_4 ha^{-1}), and lastly the upslope pasture (-1328.0 ± 89.0 g CH_4 ha^{-1}) which had a higher flux. The three vegetated riparian buffers were more substantial soil CH_4 sinks, suggesting that they may be useful in reducing soil CH_4 fluxes into the atmosphere in agroecosystems.

5.1 Introduction

Since the start of the Industrial Revolution, human activities have resulted in an increase in atmospheric CH_4 concentrations compared to pre-industrial values (700ppb in 1750 to 1782ppb in 2006) (Borrel *et al.*, 2011), with a majority of CH_4 fluxes to the atmosphere originating in soils (Ghosh *et al.*, 2014). Generally, CH_4 is emitted in smaller quantities than CO_2, but, over a 100-year period, 1-kg of CH_4 has a GWP 28-times than that of CO_2 (IPCC, 2014).

Soils have often been documented as both sources and sinks of CH_4 (Cameron *et al.*, 2021; Ghosh *et al.*, 2014). In anaerobic soil conditions, CH_4 is formed through the breakdown of organic compounds at a very low redox potential (Smith *et al.*, 2018). Therefore, large CH_4 fluxes are typical in environments where anoxic fermentation is favoured (Conrad, 2020; Philippot *et al.*, 2009). On the other hand, well-drained, aerobic soils have been identified as significant atmospheric CH_4 sinks due to CH_4 oxidation by methanotrophic bacteria into methanol (CH_3OH) for energy as well as into CO_2 in the presence of molecular O_2 (Papen *et al.*, 2001; Sadasivam and Reddy, 2014). This suggests that a net CH_4 flux from soils is a result of the balance between methanotrophy (microbial consumption) and methanogenesis (microbial production under anaerobic conditions) (Conrad, 2009; Dutaur and Verchot, 2007). In soils where oxidation exceeds production, methanotrophy tends to be a dominant process resulting in soil CH_4 consumption (Reddy *et al.*, 2014). Methane consumption may be reduced by cultivation and NH_4^+-N fertilizer application in cultivated soils, while permanent forest and grassland soils are well documented as active CH_4 sinks (Ball *et al.*, 2002; Merino *et al.*, 2004; Tate *et al.*, 2007). Methane-oxidizing bacteria (MOB) are generally inhibited by NH_4^+-N fertilizer leading to reduced CH_4 oxidation and resultant larger CH_4 fluxes from fertilized and cultivated soils (Alam and Jia, 2012; Finn *et al.*, 2020). In contrast, soils under permanent vegetation improve aeration which increases soil CH_4 oxidation and subsequently lowers soil CH_4 fluxes (Butterbach-Bahl and Papen, 2002; Veloso *et al.*, 2019).

Riparian buffer strips are increasingly being used to protect the water quality of surface waters by attenuating the transfer of pollutants from agricultural land into them (Jacinthe, 2015). In the past two decades, riparian buffer strips' water quality protection functions have been well documented (Lowrance *et al.*, 2002; Polyakov *et al.*, 2005; Vidon and Hill, 2006). Some work on riparian buffer strips has studied GHGs, including N_2O emissions (Fisher *et al.*, 2014; Iqbal *et al.*, 2015) in such agro systems. Little, however, is reported about other radiative gases, including CH_4, and how fluxes in riparian buffers compare with fluxes from adjacent agricultural land they serve (Kim *et al.*, 2010). As a result of the location of riparian buffer strips in the landscape, they are often seasonally inundated by floodwaters and often have high water tables, which upon contact with upper soil layers, increases some biological activities, including methanogenesis (Jacinthe *et al.*, 2015). The anoxic conditions created by periodic flooding as well as the accumulation of soil C and other organic compounds, increased anaerobic conditions, and restricted O_2 diffusivity, can be critical drivers of CH_4 fluxes in riparian buffers (Ballantyne *et al.*, 2014; Blazejewski *et al.*, 2009). These processes with the potential to increase CH_4 may offset the environmental benefits to water quality provided by riparian buffer strips. On the contrary, in the current study, CH_4 measurements were done only for 8-9 months, and the topsoil were mostly aerated; thus, their effect of soil CH_4 fluxes could be overestimated. This could been because, in aerobic topsoil conditions similar to the current study, soil CH_4 produced in the deeper anoxic soil profiles may be oxidized to CO_2 before reaching the soil surface (Keppler *et al.*, 2009; Nazaries *et al.*, 2013).

Against this context, soil CH_4 fluxes were investigated from permanent pasture and compared to those from riparian buffer strips with different vegetation in a replicated large plot experiment established in 2016 for water quality purposes in the UK. The objective of this study was to compare CH_4 fluxes in a permanent upslope pasture and downslope riparian buffer strips with different vegetation. It was hypothesized that different soil properties developed under the forested riparian buffer strips (woodland and willow) due to their deep root systems would result in lower CH_4 fluxes followed by the grass riparian buffer strips. In comparison, the permanent upslope pasture and no-buffer control subject to regular NH_4^+-N fertilizer applications will result in higher CH_4 fluxes from the soil to the atmosphere.

5.2 Materials and Methods

Information on the chapter's (i) study site description, (ii) experimental design and treatments, and (iii) field measurements are detailed in Chapter 3 (section 3.2). The methodology described below (Statistical methods) is specific to this chapter, which is not presented under chapter 3.

5.2.1 Statistical analysis

The data were analysed using LMMs in Genstat 20 (VSN International, Hemel Hempstead, UK). Linear mixed models were used to determine whether cumulative soil CH_4 fluxes or any of the measured soil variables (BD, pH, NH_4^+, TON, %WFPS, and OM) differed with treatment. Soil NH_4^+ and TON were $\log_{10}$ transformed to satisfy the homogeneity of variance assumption of the analysis. The random structure of each model (accounting for the structure of the experiment) was *block/plot/chamber*. The fixed structure (accounting for treatment effects) was *area/(treatment crop*buffer area).* The structure gives the following four tests: (i) *area*-tests for any difference between main crop vs. control area vs. buffer, (ii) *area*treatment*crop* - tests for differences between grass, willow and woodland riparian buffers, (iii) *area*buffer area* - tests for the differences between upper and lower chambers within the riparian buffers with differing vegetation, and (iv) *area*treatment crop*buffer area* - tests for interaction between riparian buffer type and distance, i.e., whether the difference between the upper and lower area of the riparian buffers differed depending on the riparian buffer vegetation (or vice versa). Linear mixed models were also used to assess the relationships between cumulative soil CH_4 fluxes and each measured variable.

Pearson's correlation coefficient (r) was used to indicate the strength of relationships between soil and environmental factors and cumulative soil CH_4 fluxes. This was tested more formally in the linear mixed models described above. If the LMMs indicated that treatment differences were present, LSDs were calculated to determine which specific pairs of treatments resulted in the significant differences in cumulative soil CH_4 fluxes. All graphs were generated using SigmaPlot V14.5 (Systat Software Inc., CA, USA).

5.3 Results

5.3.1 Meteorological and soil characteristics

The minimum temperature ranged from 2.2°C (January 2019) to 14.1°C (July 2018), while the maximum temperature ranged from 7.2°C (January 2019) to 23.3°C (July 2018). The mean temperature ranged from 4.6°C (January 2019) to 18.7°C (July 2018) °C. On the other hand, soil surface temperature ranged from 10.1 (January 2019) to 19.3°C (July 2018) (Figure 5.1 A). Monthly rainfall ranged from 2 to 168 mm, and the total rainfall during the experimental period was 699 mm. The highest rainfall of 168 mm was received during November 2018, whilst the lowest of 2 mm was received in June 2018 (Figure 5.1 B).

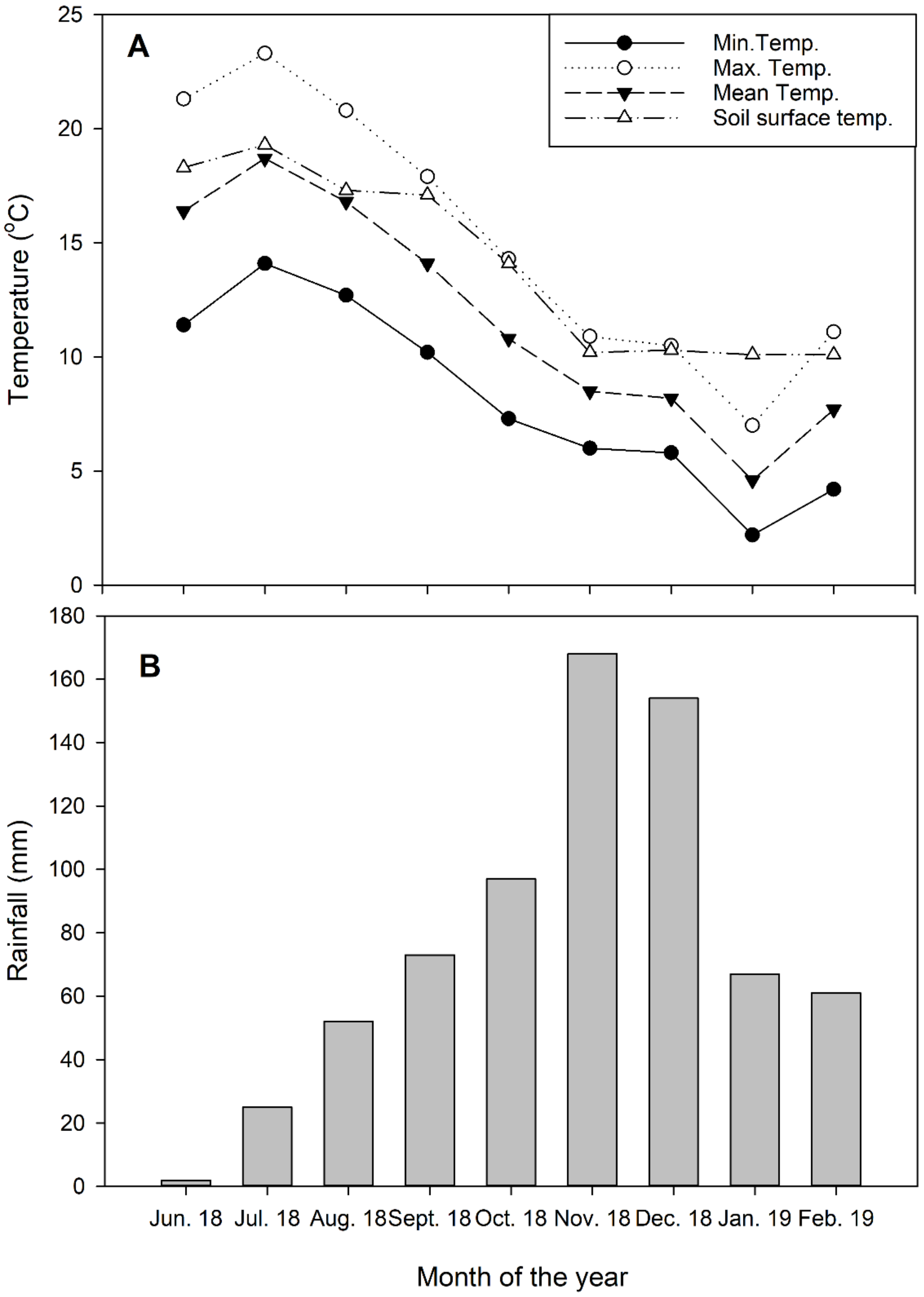

Figure 5. 1: Monthly (A) minimum, maximum and soil surface temperatures, and (B) rainfall in the site during the experimental period.

5.3.2 Treatment effects on explanatory variables

Table 5.1 shows that there was evidence of treatment differences in $\log_{10}NH_4^+$-N, with the no-buffer control having significantly larger $\log_{10}NH_4^+$-N concentrations compared to the three differently vegetated riparian buffer strips (significantly different from each other), which was however not significantly different to the upslope pasture. There was no main effect significant difference between the upper and lower chambers within each of the different vegetated riparian buffer strips, but there was an interaction effect. This indicates that the riparian buffer vegetation treatments were only different in the upper chambers. The willow riparian buffer was the only treatment with significant differences between the upper and lower chambers. Similar to $\log_{10}NH_4^+$-N, there was evidence of treatment differences in $\log_{10}$TON concentration, with the no-buffer control treatment having the highest $\log_{10}$TON concentration compared to the differently vegetated riparian buffer strips, which was however not significantly different to the upslope pasture.

Table 5. 1: *p*-values for tests from LMMs on each soil variable.

	BD	**pH**	**$\log_{10}$ NH$_4$**	**$\log_{10}$ TON**	**%WFPS**	**OM**
Area	0.33	0.78	<0.001	<0.001	0.55	<0.001
Area * Treatment	0.14	0.85	0.001	<0.001	0.11	0.36
Area * Buffer area	1	0.96	0.863	0.46	0.91	0.61
Area * Treatment * Buffer area	1	0.25	0.034	0.69	0.94	0.82

5.3.3 Soil CH_4 fluxes

5.3.3.1 Daily soil CH_4 fluxes

Daily CH_4 fluxes from all treatments during the study period were mostly negative, reflecting soil CH_4 consumption/uptake, except on three occasions in the upslope pasture and one occasion in the no-buffer control treatment (Figure 5.2). The largest daily soil CH_4 flux was 7.0 ± 1.4 g CH_4 ha^{-1} day^{-1} in the upslope pasture at the end of September 2018 which was followed by a flux decline in all treatments. The lowest daily soil CH_4 flux was -22.9 ± 0.9 g CH_4 ha^{-1} day^{-1} in the no-buffer control treatment in early October 2018. The average daily soil CH_4 fluxes for all the treatments ranged from -5.1 ± 0.3 to -11.5 ± 0.9 g CH_4 ha^{-1} day^{-1} with the upslope pasture exhibiting a large mean daily soil CH_4 flux of -5.1 ± 0.3 g CH_4 ha^{-1} day^{-1}.

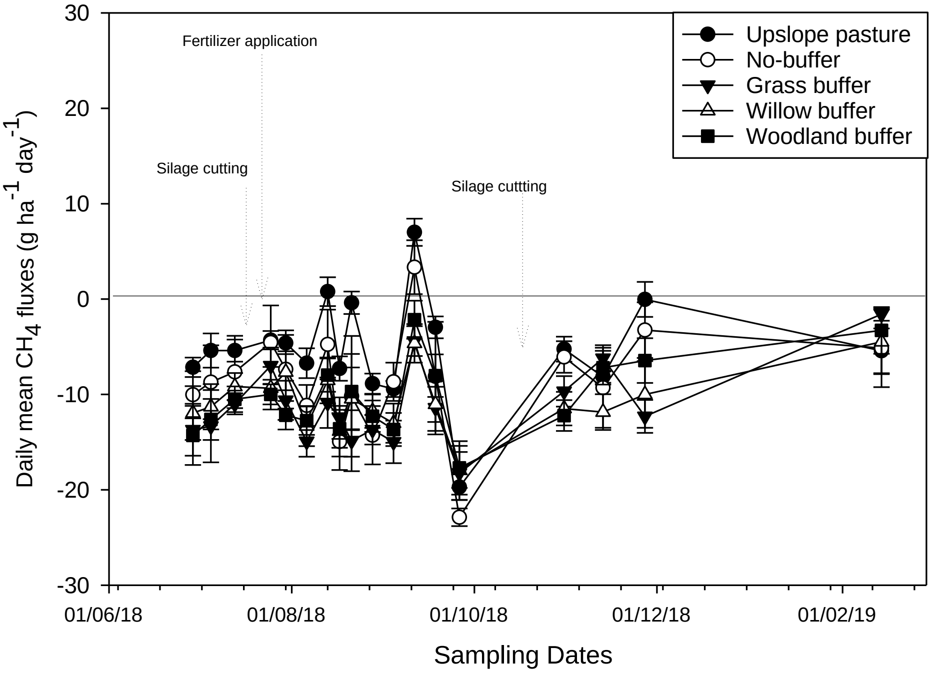

Figure 5. 2: CH_4 fluxes from the upslope pasture and the downslope riparian buffers with different vegetation treatments. Data points and error bars represent the treatment means (upslope pasture: *n*=12, no-buffer control: *n*=3, grass, wood, and willow riparian buffer: *n*=6) and SE during each sampling day. The line at zero flux is included to indicate mostly negative fluxes.

5.3.3.2 Cumulative soil CH_4 fluxes

Cumulative soil CH_4 fluxes followed the ascending order: willow riparian buffer strip (-2555 ± 318.7 g ha^{-1}) < grass riparian buffer (-2532 ± 318.7 g ha^{-1}) < woodland riparian buffer (-2318.0 ± 318.7 g ha^{-1}) < no-buffer control (-1938.0 ± 279.7 g ha^{-1}) < upslope pasture (-1328.0 ± 279.7 g ha^{-1}) (Figure 5.3). The upslope pasture buffer had a significantly (*p = 0.0013*) large cumulative soil CH_4 flux compared to the remainder of the treatments. But there were no differences in cumulative soil CH_4 fluxes between the upper and lower buffer strip areas (*p = 0.71*). Also, there was no evidence of interaction between the upslope pasture and the upper and lower riparian buffer areas.

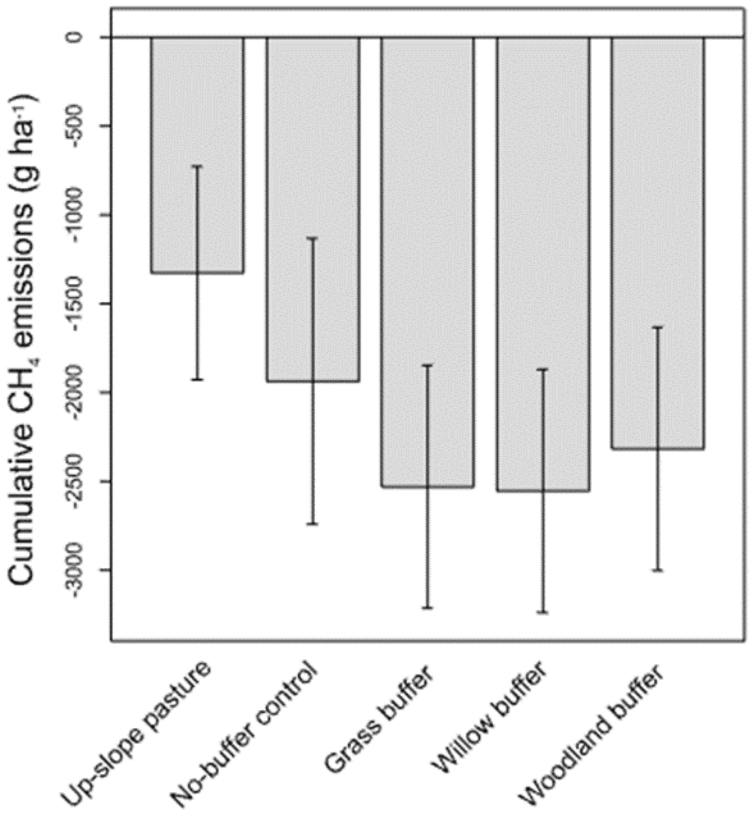

Figure 5. 3: Cumulative CH_4 fluxes for the whole experimental period from the upslope pasture and downslope riparian buffers with different vegetation treatments. Error bars represent 95% confidence intervals

(upslope pasture: *n*=12, no-buffer control: *n*=3, grass, wood, and willow riparian buffers: *n*=6).

5.3.3.3 Relationships between cumulative soil CH_4 fluxes and measured soil variables including treatment effects

There were significant relationships between cumulative soil CH_4 fluxes and NH_4^+ (r= 0.45; *p* = 0.0023), TON (r = 0.51; *p* = 0.001), and OM (r =0.64; *p* = 0.001). (Figure 4.4 and Table 4.2). Cumulative soil CH_4 fluxes increased with an increase in soil BD, pH, NH_4^+, TON, and %WFPS and decreased with an increase in OM (Figure 4.5).

Table 5. 2: *p*-values for the slope of the fitted line of the models.

Variable	Intercept	SE intercept	Slope	SE slope	*p*-value
BD	-2676	1673	568.5	1398.04	0.69
pH	-4010	2725	367.5	497.4	0.47
$\log_{10}$ NH_4^+	-2677	277.6	919.7	277.8	0.002
$\log_{10}$ TON	-2859	280.9	1151	301.9	<0.001
%WFPS	-2245	908.8	3.8	13.7	0.79
OM	437.6	499.2	207.9	37.9	<0.001

5.4 Discussion

5.4.1 Soil CH_4 fluxes and measured soil variables

Results from this study show that daily incidences of soil CH_4 fluxes (Figure 5.2) were similar to other authors, particularly Dutaur and Verchot (2007) and Reay *et al.* (2007), who reported that soils could be both a sources and a sinks for soil CH_4 fluxes. Furthermore, the results show daily soil CH_4 fluxes after N fertilizer application, which also coincided with an increase in soil %WFPS (Figure 5.5 A and 5.2). These results are in agreement with the findings reported by Tate *et al.* (2007), Wang *et al.* (2014), and Xingren *et al.* (2017) who observed that NH_4^+-N fertilizer inhibits CH_4 oxidation to

CO_2, thus reducing the soil CH_4 sink capability, explaining the observed large daily soil CH_4 fluxes after fertilizer application, particularly in the upslope pasture and no-buffer control. In the current experiment, it is likely that the inhibitory role of NH_4^+-N on CH_4 oxidation to CO_2 in the N-fertilized no buffer control and upslope pasture resulted in the exponential increase in cumulative soil CH_4 fluxes associated with significant correlations with soil mineral N (Figure 5.4) as well as increases in with increasing soil mineral N (Figure 5.5).

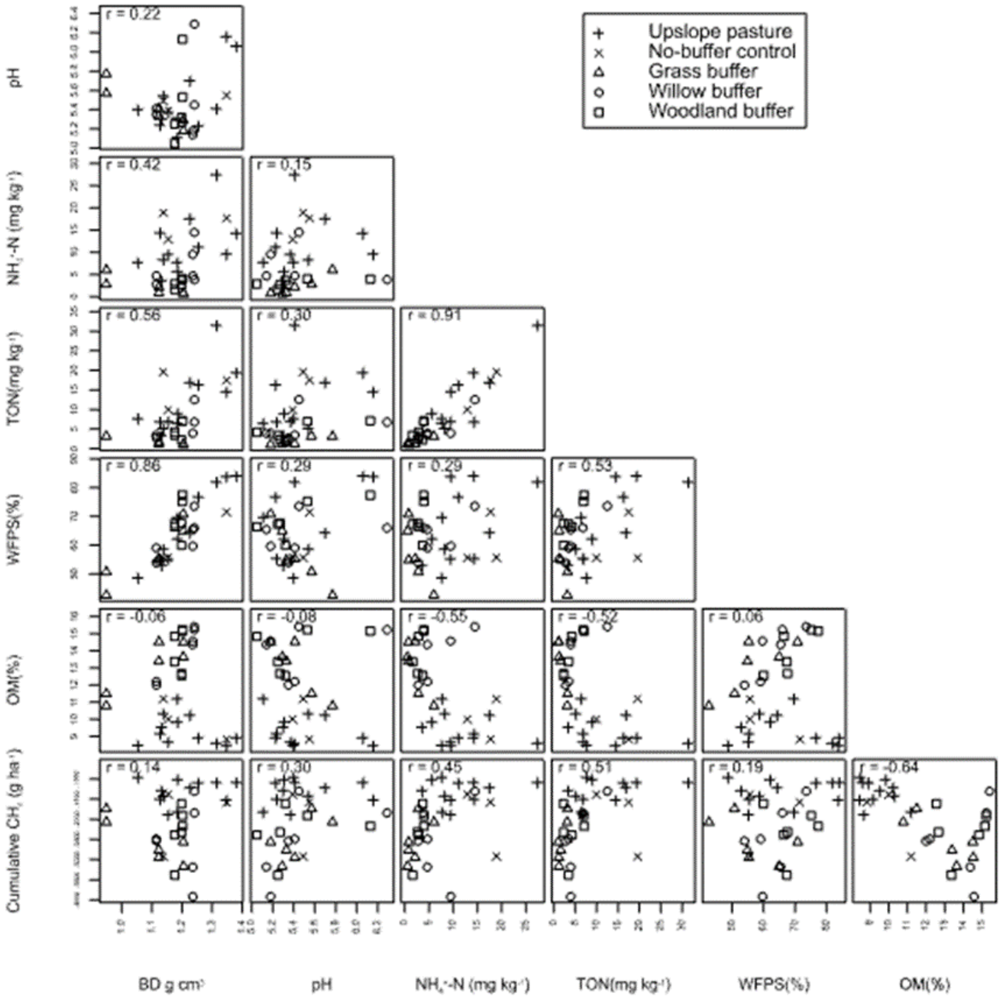

Figure 5. 4: Scatterplot showing the relationships between the variables soil pH, NH_4^+-N, TON, %WFPS, OM, BD and cumulative CH_4 fluxes for the upslope

pasture and the downslope riparian buffers with different vegetation treatments. r = Pearson's correlation coefficient.

The inhibitory effect of NH_4^+-N fertilizer addition on CH_4 oxidation could be attributed to the fact that CH_4 monooxygenase of methanotrophs can oxidize a variety of substrates besides soil CH_4 (Bian *et al.*, 2019; Wang *et al.*, 2014). Thus, the majority higher soil CH_4 fluxes in the upslope pasture compared to the downslope riparian buffer during the experimental period (Figure 5.2 B) could have been a result of the N fertilizer directly applied in the upslope pasture and the no-buffer control areas. On the contrary, the riparian buffers only received secondary N leached downslope from the upslope pasture in conjunction with runoff, which might not have necessarily been in the form of NH_4^+-N, which is known to inhibit CH_4 oxidation. It could happen that the applied fertilizer N in upslope pasture and no-buffer control might have reduced the capacity of the treatments to consume CH_4, but this was not confirmed in the current study.

Soil moisture content is well documented as a regulator of soil CH_4 fluxes (Le Mer and Roger, 2001; Natali *et al.*, 2015; Veloso *et al.*, 2019; Wang *et al.*, 2017) since increased soil moisture impedes O_2 diffusivity, which reduces methanotrophic oxidation activities, thus allowing soil CH_4 fluxes (Konda *et al.*, 2010; Smith *et al.*, 2018; Wachiye *et al.*, 2020). Similar to the previous studies, the current study observed that soil CH_4 fluxes increased with increasing soil %WFPS (Figure 5.5). Higher soil %WFPS is attributed to soil structural alterations including reduced macro-porosity, increasing anaerobicity and reduced soil CH_4 fluxes (Butterbach-Bahl and Papen, 2002; Veloso *et al.*, 2019). The observed increases in cumulative soil CH_4 fluxes with increasing soil BD in the current study (Figure 5.5) are consistent with the results of the previous work cited above.

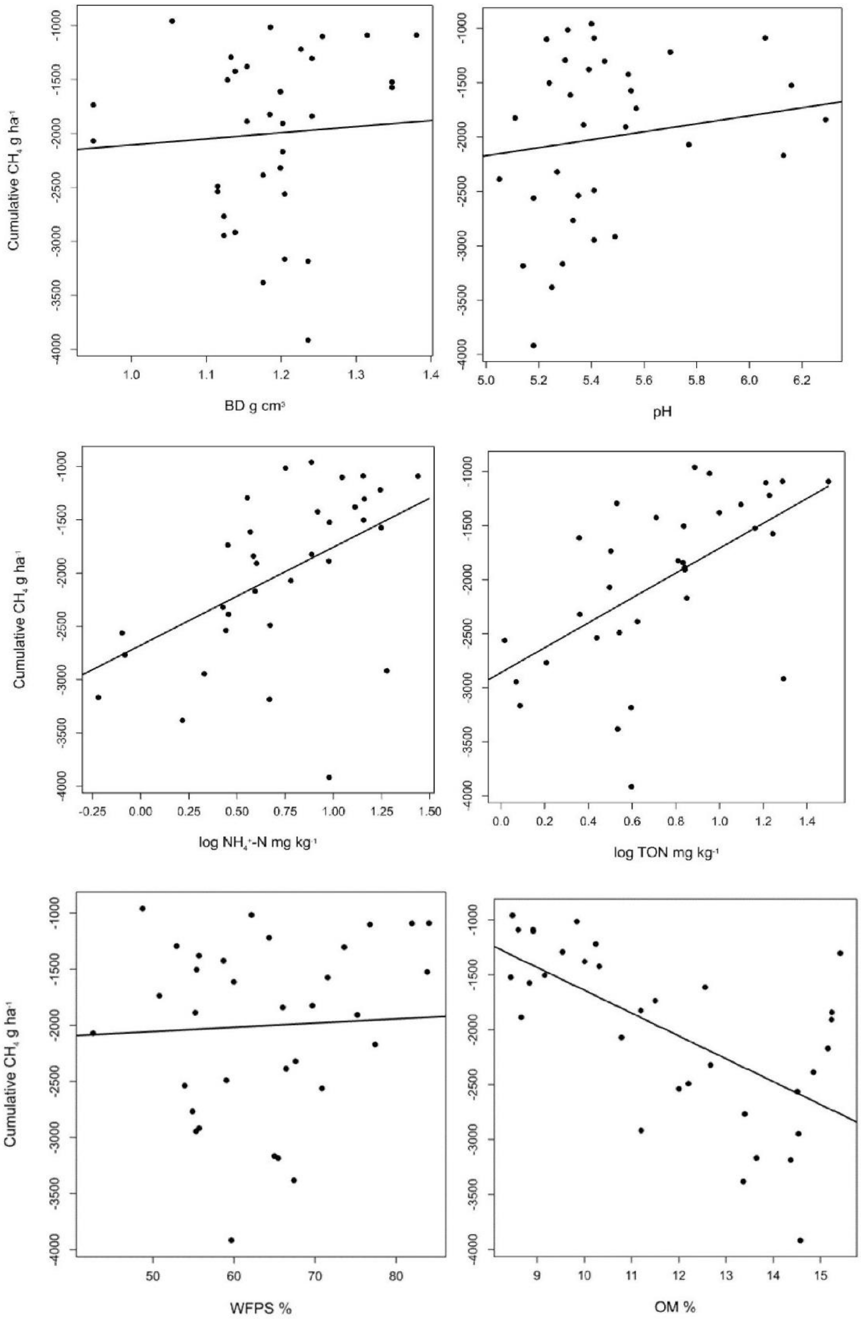

Figure 5. 5: Relationships between cumulative CH$_4$ fluxes and each of the explanatory soil variables.

Soil OM derived from plant litter is converted into soil organic C (an electron donor), which microbes further convert into CH_4 (Megonigal and Guenther, 2008); thus it is expected that vegetation that produces a lot of OM (i.e. leaves) that enters the soil will have a higher CH_4 fluxes. On the contrary, in the current experiment, the willow riparian buffer, which had the highest mean OM concentration, had the lowest cumulative soil CH_4 fluxes instead (Table 5.1 and Figure 5.3). There was also a significant negative correlation between soil OM and cumulative soil CH_4 fluxes (Figure 5.4), as well as a decrease in cumulative soil CH_4 fluxes with an increase in soil OM (Figure 5.5). It is possible that the OM derived of the litter of the willow riparian buffer vegetation was of high quantity but low quality with regard to labile C content; similar to other authors, particularly Dlamini *et al.* (2020) and Surey *et al.* (2020). The aforementioned authors observed that organic material containing highly labile C compounds is readily available for soil microbial degradation.

5.4.2 Soil CH_4 fluxes in upslope pasture and downslope riparian buffer strips

The cumulative soil CH_4 fluxes in all treatments indicate that the soils under the riparian buffers with different vegetation as well as in the upslope pasture and no-buffer control functioned as a sink for soil CH_4 fluxes. Similar findings were reported by McLain and Martens (2006), Kim *et al.* (2010) and Jacinthe (2015). The upslope pasture buffer had the largest quantities of cumulative soil CH_4 fluxes compared to the other treatments, and willow riparian buffer had the least fluxes. Despite this, the upslope pasture had lower cumulative soil CH_4 fluxes (-1.3 kg CH_4 ha^{-1}) compared to the values reported for maize (*Zea mays* L.) (-0.8 kg CH_4 ha^{-1}) by Kim *et al.* (2010) in a loamy soils in Iowa. Such comparisons highlight that repeated cultivation associated with annual crops (i.e., maize) as opposed to the less frequent cultivation associated with permanent pasture production (i.e., the upslope pasture in the current study) can further reduce the capability of soil under maize production to reduce soil CH_4 fluxes (Ball *et al.*, 2002; Tate *et al.*, 2007).

Despite the vegetation in the riparian buffer strips being only 3-years old, they had lower soil CH_4 flux (all below -2 kg CH_4 ha^{-1}) than both forested and grass riparian buffer strips (between 7 and 17 years old, respectively) in the Bear Creek Watershed of Iowa (fluxes between -0.84 and 0.04 g CH_4 ha^{-1}) reported by Kim *et al.* (2010). The soil CH_4 flux values observed in the vegetated riparian buffers of the current study were similar to those reported in other studies; e.g. Robertson *et al.* (2000) and Hernandez-Ramirez *et al.* (2009), who reported low soil CH_4 fluxes when soil tillage was limited. The phenomena of low soil CH_4 fluxes in such systems is attributed to the negative effects of tillage on methanotrophic activity (Hütsch, 2001) as well as the more stable and porous soil structure typically associated with reduced tillage, which facilitates soil CH_4 fluxes diffusion into oxidizing zones (Nan *et al.*, 2020).

The significant soil CH_4 fluxes in the upslope pasture and lower fluxes from the vegetated riparian buffers agree with results reported by Merino *et al.* (2004) and Tate *et al.* (2007) among others, who reported that forest riparian soils are the most active sinks of soil CH_4 fluxes followed by grasslands and cultivated soils. The inhibitory effect of NH_4^+-N fertilizer addition to soils on CH_4 oxidation has been reported in soils under different agricultural uses (Wang *et al.*, 2014; Xingren *et al.*, 2017). Thus, the significant soil CH_4 fluxes in the upslope pasture of the current study could have been a result of the applied NH_4^+-N fertilizer having increased the soil CH_4 fluxes, which is also in agreement with previous studies (Butterbach-Bahl and Papen, 2002; Le Mer and Roger, 2001).

In some instances, instead of being CH_4 sinks, vegetated riparian buffers may produce more CH_4 than the upslope agricultural land they serve. For example, in two separate locations in Indiana, Jacinthe *et al.* (2015) observed higher soil CH_4 fluxes in both forest (0.92 kg CH_4 ha^{-1}) and grass (1.08 kg CH_4 ha^{-1}) riparian buffers compared to their respective upslope maize fields (0.05 and 0.04 kg CH_4 ha^{-1}, respectively). The results of the current study suggest that perennial crops, (i.e., the upslope pasture and no buffer control in the current experiment), may sometimes be sinks for soil CH_4, but the grass, willow and woodland riparian buffer were larger sinks in the current study. However, some literature suggests that annual crops (i.e., maize) and the riparian buffer strips that serve them may sometimes be sources of CH_4, illustrating that careful assessment of the potential trade-offs for atmospheric emissions is required when riparian buffers are used to target water quality issues, since co-benefits for both water quality and gaseous emissions may not exist in all settings and at all times.

The current study further suggests that as well as providing beneficial water-quality functions, grass, woodland, and willow riparian buffers serving a permanent pasture may be significant sinks for CH_4. The fact these riparian buffers consume CH_4 in the current experiment suggests that these may simultaneously reduce water quality threats while not posing atmospheric pollution concerns through increased soil CH_4 fluxes, primarily when they serve permanent un-grazed pastures. Despite the current study being carried out on plots situated on a single soil type, climatic zone and agricultural system, the results reported supplies a basis for exploring the application of different riparian buffer strips in areas with different soils and environmental settings.

5.5 Conclusion

The hypothesis that the upslope pasture will have larger daily soil CH_4 fluxes and as a result higher cumulative soil CH_4 fluxes than forested (i.e., willow and woodland) riparian buffers can be accepted because the results of the current study show higher cumulative soil CH_4 fluxes in the upslope pasture and lower fluxes in forested riparian buffers. Despite that our database has limitations, these results suggest that all the vegetation types for riparian buffers tested in this study may be useful for soil CH_4 flux mitigation in similar agroecosystems. More generally, the results of the current study will be useful for policymakers as well as scientists requiring calibrating mechanistic models that explore mitigation measures for soil CH_4 fluxes in agroecosystems through the use of different riparian buffers.

5.6 References

Alam, M.S., Jia Z., 2012. Inhibition of methane oxidation by nitrogenous fertilizers in a paddy soil. *Frontiers in Microbiology*, 3:246.

Ball, B., McTaggart I.P., Watson C., 2002. Influence of organic ley-arable management and afforestation in sandy loam to clay loam soils on fluxes of N_2O and CH_4 in Scotland. *Agriculture, Ecosystems, & Environment*, 90:305-317.

Ballantyne, D.M., Hribljan J.A., Pypker T.G., Chimner R.A., 2014. Long-term water table manipulations alter peatland gaseous carbon fluxes in Northern Michigan. *Wetlands Ecology & Management*, 22:35-47.

Bian, R., Shi W., Duan Y., Chai X., 2019. Effect of soil types and ammonia concentrations on the contribution of ammonia-oxidizing bacteria to CH_4 oxidation. *Waste Management & Research*, 37:698-705.

Blazejewski, G.A., Stolt M.H., Gold A.J., Gurwick N., Groffman P.M., 2009. Spatial distribution of carbon in the subsurface of riparian zones. *Soil Science Society of America Journal*, 73:1733-1740.

Borrel, G., Jézéquel D., Biderre-Petit C., Morel-Desrosiers N., Morel J.-P., Peyret P., Fonty G., Lehours A.-C., 2011. Production and consumption of methane in freshwater lake ecosystems. *Research in Microbiology*, 162:832-847.

Butterbach-Bahl, K., Papen H., 2002. Four years continuous record of CH_4-exchange between the atmosphere and untreated and limed soil of a N-saturated spruce and beech forest ecosystem in Germany. *Plant & Soil*, 240:77-90.

Cameron, C., Hutley L.B., Munksgaard N.C., Phan S., Aung T., Thinn T., Aye W.M., Lovelock C.E., 2021. Impact of an extreme monsoon on CO_2 and CH_4 fluxes from mangrove soils of the Ayeyarwady Delta, Myanmar. *Science of the Total Environment*, 760:143422.

Conrad, R., 2009. The global methane cycle: recent advances in understanding the microbial processes involved. *Environmental Microbiology Reports*, 1:285-292.

Conrad, R., 2020. Importance of hydrogenotrophic, aceticlastic and methylotrophic methanogenesis for methane production in terrestrial, aquatic and other anoxic environments: a mini review. *Pedosphere*, 30:25-39.

Dlamini, J., Chadwick D., Hawkins J., Martinez J., Scholefield D., Ma Y., Cárdenas L., 2020. Evaluating the potential of different carbon sources to promote denitrification. *Journal of Agricultural Sciences*, 158:194-205.

Dutaur, L., Verchot L.V., 2007. A global inventory of the soil CH_4 sink. *Global Biogeochemical Cycles*, 21.

Finn, D.R., Ziv-El M., van Haren J., Park J.G., del Aguila-Pasquel J., Urquiza–Muñoz J.D., Cadillo-Quiroz H., 2020. Methanogens and methanotrophs show nutrient-dependent community assemblage patterns across tropical peatlands of the Pastaza-Maranon Basin, Peruvian Amazonia. *Frontiers in Microbiology*, 11:746.

Fisher, K., Jacinthe P., Vidon P., Liu X., Baker M., 2014. Nitrous oxide emission from cropland and adjacent riparian buffers in contrasting hydrogeomorphic settings. *Journal of Environmental Quality*, 43:338-348.

Ghosh, A., Patra P., Ishijima K., Umezawa T., Ito A., Etheridge D., Sugawara S., Kawamura K., Miller J., Dlugokencky E., 2014. Variations in global methane sources and sinks during 1910–2010. *Atmospheric Chemistry & Physics Discussions*, 14:27619-27661.

Hernandez-Ramirez, G., Brouder S.M., Smith D.R., Van Scoyoc G.E., 2009. Greenhouse gas fluxes in an eastern corn belt soil: weather, nitrogen source, and rotation. *Journal of Environmental Quality*, 38:841-854.

Hütsch, B.W., 2001. Methane oxidation in non-flooded soils as affected by crop production. *European Journal of Agronomy*, 14:237-260.

IPCC, 2014. Climate change 2014: synthesis report. Contribution of Working Groups I, II and III to the fifth assessment report of the Intergovernmental Panel on Climate Change IPCC.

Iqbal, J., Parkin T.B., Helmers M.J., Zhou X., Castellano M.J., 2015. Denitrification and nitrous oxide emissions in annual croplands, perennial grass buffers, and restored perennial grasslands. *Soil Science Society of America Journal*, 79:239-250.

Jacinthe, P.-A., Vidon P., Fisher K., Liu X., Baker M., 2015. Soil methane and carbon dioxide fluxes from cropland and riparian buffers in different hydrogeomorphic settings. *Journal of Environmental Quality*, 44:1080-1090.

Jacinthe, P., 2015. Carbon dioxide and methane fluxes in variably-flooded riparian forests. *Geoderma*, 241:41-50.

Keppler, F., Boros M., Frankenberg C., Lelieveld J., McLeod A., Pirttilä A.M., Röckmann T., Schnitzler J.-P., 2009. Methane formation in aerobic environments. *Environmental Chemistry*, 6:459-465.

Kim, D.-G., Isenhart T.M., Parkin T.B., Schultz R.C., Loynachan T.E., 2010. Methane flux in cropland and adjacent riparian buffers with different vegetation covers. *Journal of Environmental Quality*, 39:97-105. DOI: 10.2134/jeq2008.0408.

Konda, R., Ohta S., Ishizuka S., Heriyanto J., Wicaksono A., 2010. Seasonal changes in the spatial structures of N_2O, CO_2, and CH_4 fluxes from *Acacia mangium* plantation soils in Indonesia. *Soil Biology & Biochemistry*, 42:1512-1522.

Le Mer, J., Roger P., 2001. Production, oxidation, emission and consumption of methane by soils: a review. *European Journal of Soil Biology*, 37:25-50.

Lowrance, R., Dabney S., Schultz R., 2002. Improving water and soil quality with conservation buffers. *Journal of Soil & Water Conservation*, 57:36A-43A.

McLain, J.E., Martens D.A., 2006. Moisture controls on trace gas fluxes in semiarid riparian soils. *Soil Science Society of America Journal*, 70:367-377.

Megonigal, J.P., Guenther A.B., 2008. Methane emissions from upland forest soils and vegetation. *Tree Physiology*, 28:491-498.

Merino, A.n., Pérez-Batallón P., Macías F., 2004. Responses of soil organic matter and greenhouse gas fluxes to soil management and land use changes in a humid temperate region of southern Europe. *Soil Biology & Biochemistry*, 36:917-925.

Nan, W., Li S., Dong Z., Yao P., 2020. CH_4 fluxes and diffusion within soil profiles subjected to different fertilizer regimes on China's Loess Plateau. *Agriculture Ecosystems & Environment*, 287:106679.

Natali, S.M., Schuur E.A., Mauritz M., Schade J.D., Celis G., Crummer K.G., Johnston C., Krapek J., Pegoraro E., Salmon V.G., 2015. Permafrost thaw and soil moisture driving CO_2 and CH_4 release from upland tundra. *Journal of Geophysical Research: Biogeosciences*, 120:525-537.

Nazaries, L., Murrell J.C., Millard P., Baggs L., Singh B.K., 2013. Methane, microbes and models: fundamental understanding of the soil methane cycle for future predictions. *Environmental Microbiology*, 15:2395-2417.

Papen, H., Daum M., Steinkamp R., Butterbach-Bahl K., 2001. N_2O and CH_4 fluxes from soils of a N-limited and N-fertilized spruce forest ecosystem of the temperate zone. *Journal of Applied Botany*, 75:159-163.

Philippot, L., Hallin S., Börjesson G., Baggs E., 2009. Biochemical cycling in the rhizosphere having an impact on global change. *Plant & Soil*, 321:61-81.

Polyakov, V., Fares A., Ryder M.H., 2005. Precision riparian buffers for the control of nonpoint source pollutant loading into surface water: A review. *Environmental Reviews*, 13:129-144.

Reay, D.S., Smith K., Hewitt C., 2007. Methane: importance, sources and sinks, In: DS Reay (Ed.), Greenhouse gas sinks, CAB International, Wallingford, Oxfordshire, UK. pp. 143-151.

Reddy, K.R., Yargicoglu E.N., Yue D., Yaghoubi P., 2014. Enhanced microbial methane oxidation in landfill cover soil amended with biochar. *Journal of Geotechnical & Geoenvironmental Engineering*, 140:04014047.

Robertson, G.P., Paul E.A., Harwood R.R., 2000. Greenhouse gases in intensive agriculture: contributions of individual gases to the radiative forcing of the atmosphere. *Science*, 289:1922-1925.

Sadasivam, B.Y., Reddy K.R., 2014. Landfill methane oxidation in soil and bio-based cover systems: a review. *Reviews in Environmental Science & Bio/Technology*, 13:79-107.

Smith, K., Ball T., Conen F., Dobbie K., Massheder J., Rey A., 2018. Exchange of greenhouse gases between soil and atmosphere: interactions of soil physical factors and biological processes. *European Journal of Soil Science*, 69:10-20.

Surey, R., Lippold E., Heilek S., Sauheitl L., Henjes S., Horn M.A., Mueller C.W., Merbach I., Kaiser K., Böttcher J., 2020. Differences in labile soil organic matter explain potential denitrification and denitrifying communities in a long-term fertilization experiment. *Applied Soil Ecology*, 153:103630.

Tate, K.R., Ross D., Saggar S., Hedley C., Dando J., Singh B.K., Lambie S.M., 2007. Methane uptake in soils from Pinus radiata plantations, a reverting shrubland and adjacent pastures: effects of land-use change, and soil texture, water and mineral nitrogen. *Soil Biology & Biochemistry*, 39:1437-1449.

Veloso, M.G., Dieckow J., Zanatta J.A., Pergher M., Bayer C., Higa R.C., 2019. Long-term loblolly pine land use reduces methane and net greenhouse gas emissions in a subtropical Cambisol, despite increasing nitrous oxide. *Annals of Forest Science*, 76:86.

Vidon, P.G., Hill A.R., 2006. A landscape-based approach to estimate riparian hydrological and nitrate removal functions 1. *Journal of the American Water Resources Association,* 42:1099-1112.

Wachiye, S., Merbold L., Vesala T., Rinne J., Rasanen M., Leitner S., Pellikka P., 2020. Soil greenhouse gas emissions under different land-use types in savanna ecosystems of Kenya. *Biogeosciences*, 17:2149-2167.

Wang, Y., Cheng S., Fang H., Yu G., Xu M., Dang X., Li L., Wang L., 2014. Simulated nitrogen deposition reduces CH_4 uptake and increases N_2O emission from a subtropical plantation forest soil in southern China. *PloS One*, 9:e93571.

Wang, Z.P., Han S.J., Li H.L., Deng F.D., Zheng Y.H., Liu H.F., Han X.G., 2017. Methane production explained largely by water content in the heartwood of living trees in upland forests. *Journal of Geophysical Research: Biogeosciences*, 122:2479-2489.

Xingren, L., Zhang Q., Shenggong L., Zhang L., Jianqiang R., 2017. Simulated NH_4^+-N deposition inhibits CH_4 uptake and promotes N_2O emission in the meadow steppe of Inner Mongolia, China. *Pedosphere*, 27:306-317.

CHAPTER 6.0

SOIL CO_2 FLUXES IN A CROPLAND WITH AN UPSLOPE PERMANENT PASTURE AND DOWNSLOPE RIPARIAN BUFFERS WITH VARYING VEGETATION

This chapter is *accepted* for publication in the journal “**Journal of Plant Nutrition and Soil Science**” as:

Dlamini JC, Tesfamariam EH, Dunn RM, Evans J, Hawkins JMB, Blackwell MSA, Collins AL, Cardenas LM. Soil carbon dioxide (CO_2) fluxes in permanent upslope pasture and downslope riparian buffers with varying vegetation. *Journal of Plant Nutrition and Soil Science*, 2022.

Corresponding author: JCD

Author contributions:

JCD, JE, EHT, LMC, RD, MSAB, ALC: Conceptualization, Methodology, Software. **JCD:** Data curation, Writing- Original draft preparation. **JCD, JE:** Visualization, Investigation. **EHT, LMC:** Supervision. **JCD, JE:** Software, Validation. **EHT, LMC, RD, MSAB, ALC:** Writing- Reviewing and Editing.

Abstract

Riparian buffers are primarily implemented for their water quality functions in agroecosystems. Their location in the agricultural landscape allows them to intercept and process pollutants from immediately adjacent agricultural land. Vegetated riparian buffers recycle soil OM which elevates soil C, which upon mineralization in the soil release CO_2. The elevated soil C and seasonally anoxic environments associated with riparian buffers promote processes including denitrification and fermentation which further increases soil CO_2 production. Against this context, a replicated plot-scale experiment was established at North Wyke, UK to measure the extent of soil CO_2 emissions in a permanent pasture served by a grass, willow, and woodland riparian buffers as well as a no buffer control. Soil CO_2 was measured using the static chamber technique in conjunction with soil and environmental variables between June 2018 and February 2019. Cumulative soil CO_2 fluxes were in the descending order: woodland riparian buffer; 11927.8 ± 1987.9 kg ha^{-1} > no buffer control; 11101.3 ± 3700.4 kg ha^{-1} > grass riparian buffer; 10826.4 ± 2551.8 kg ha^{-1} > upslope pasture; 10554.6 ± 879.5 kg ha^{-1} > willow riparian buffer; 9294.9 ± 1549.2 5 kg ha^{-1}. There was, however, no evidence of significant differences amongst all treatments of the current study. Despite lack of statistical differences, the results of the study show that the woodland riparian buffer may emit the larger soil CO_2 compared to the remainder of the other riparian buffers as well as the upslope pasture it serves. The findings may be useful in developing soil CO_2 mitigation strategies through careful selection of riparian buffer vegetation and in calibrating mechanistic models for simulating CO_2 emissions from similar agro systems.

6.1 Introduction

Riparian buffer strips are best management practices for protecting freshwater ecosystems from various pollutants, including N, P, pesticides and herbicides, emanating from agricultural lands (Jacinthe *et al.*, 2015; Tonderski, 1996; Valkama *et al.*, 2019). On top of providing various environmental and ecosystem services, the juxtaposition of riparian buffer strips in an agricultural landscape allow them to abate and process pollutants through a number of processes including mineralization and denitrification amongst others (Jaynes and Isenhart, 2014; Naiman and Decamps, 1997).

Against the context of soil and water conservation benefits, through their vegetation, vegetated riparian buffer strips recycle OM; elevating soil C (Blazejewski *et al.*, 2009) which accelerates soil CO_2 production through C-mineralization and microbial respiration in soils (Tufekcioglu *et al.*, 2001). For instance Franzluebbers *et al.* (2000), Harrison-Kirk *et al.* (2013), and Lundquist *et al.* (1999) reported that an increase in soil SOC increases C mineralization and the resulting increased CO_2 production and subsequent emissions from soils. This implies that although a remarkable amount of atmospheric C in riparian buffer vegetation is sequestered in the vegetative component via photosynthesis, the soil component can be a significant source of CO_2 through increased microbial respiration (Capon *et al.*, 2013). A few authors have raised concerns surrounding CO_2 emissions from vegetated riparian zones, which could invalidate their C sequestration potential (Vidon *et al.*, 2016) as well as their soil and water conservation roles (Mitsch *et al.*, 2001; Sabater *et al.*, 2003). Atmospheric CO_2, some of which is sourced from soils through respiration and other processes, is one of the major greenhouse gases and has a major impact on the global warming (Ray *et al.*, 2020).

Despite the role of CO_2 in the greenhouse gas effect and the potential role of riparian buffers in CO_2 emissions, the understanding of the functional traits driving soil respiration derived CO_2 emissions in riparian buffer zones (De Carlo *et al.*, 2019; Soosaar *et al.*, 2011) in comparison with emissions and drivers in adjacent agricultural land remains elusive and poorly quantified (Jacinthe *et al.*, 2015). The study aimed to (i) identify soil and environmental drivers of soil respiration derived CO_2 from an upslope permanent pasture and downslope riparian buffers with varying vegetation, and (ii) quantify soil respiration derived CO_2 emissions in an upslope permanent pasture and downslope riparian buffers with varying vegetation.

6.2 Materials and Methods

Information on the chapter's (i) study site description, (ii) experimental design and treatments, and (iii) field measurements are detailed in Chapter 3 (section 3.2). The methodology described below (Statistical methods) is specific to this chapter, which is not presented under chapter 3.

6.2.1 Statistical analysis

The data were analysed using LMMs in Genstat 20 (VSN International, Hemel Hempstead, UK). Linear mixed models were used to determine whether cumulative soil CO_2 fluxes or any of the measured soil variables (BD, pH, NH_4^+, TON, %WFPS, and OM) differed with treatment. The random structure of each model (accounting for the structure of the experiment) was *block/plot*. The fixed structure (accounting for treatment effects) was *area / (treatment crop*buffer area).* The structure gives the following four tests: (i) *treatment area*-tests for any difference between main crop vs. control area vs. buffer, (ii) *Treatment area*treatment crop* -tests for differences between grass, willow and woodland riparian buffers, (iii) *Treatment area*buffer area*

-tests for the difference between upper and lower chambers within the riparian buffers with differing vegetation, and (iv) *Treatment area*treatment crop*buffer area* -tests for interaction between riparian buffer type and distance, i.e., whether the difference between the upper and lower area of the buffers differed depending on the riparian buffer vegetation (or vice versa). Linear mixed models were also used to assess the relationship between cumulative soil CO_2 fluxes and each measured soil variables.

Pearson's correlation coefficient (r) was used to indicate the strength of relationships between soil and environmental factors and cumulative soil CO_2 fluxes. This was tested more formally in the linear mixed models described above. If the LMMs indicated that treatment differences were present, LSDs were calculated to determine which specific pairs of treatments resulted in the significant differences in cumulative soil CO_2 fluxes. All graphs were generated using SigmaPlot (Systat Software Inc., CA, USA).

6.3 Results

6.3.1 Variability of soil CO_2 fluxes

At the commencement of experiment, CO_2 fluxes were <160 kg ha^{-1} day^{-1} in all the treatments, with the largest of 153.4 ± 7.4 kg ha^{-1} day^{-1} recorded in the grass riparian buffer. At the second sampling event, CO_2 fluxes peaked up 212.7 ± 30.3 kg ha^{-1} day^{-1} in the no buffer control, which however spiralled downwards to 69.1 ± 30.7 kg ha^{-1} day^{-1} in the same treatment at the second sampling event but remained larger in the rest of the treatments. A second peak was observed at the end of the August 2018, with the largest flux of 228.1 ± 93.1 kg ha^{-1} day^{-1}. Afterwards, CO_2 fluxes in all treatments had a downward spiral until the end of the experiment (Figure 6.1).

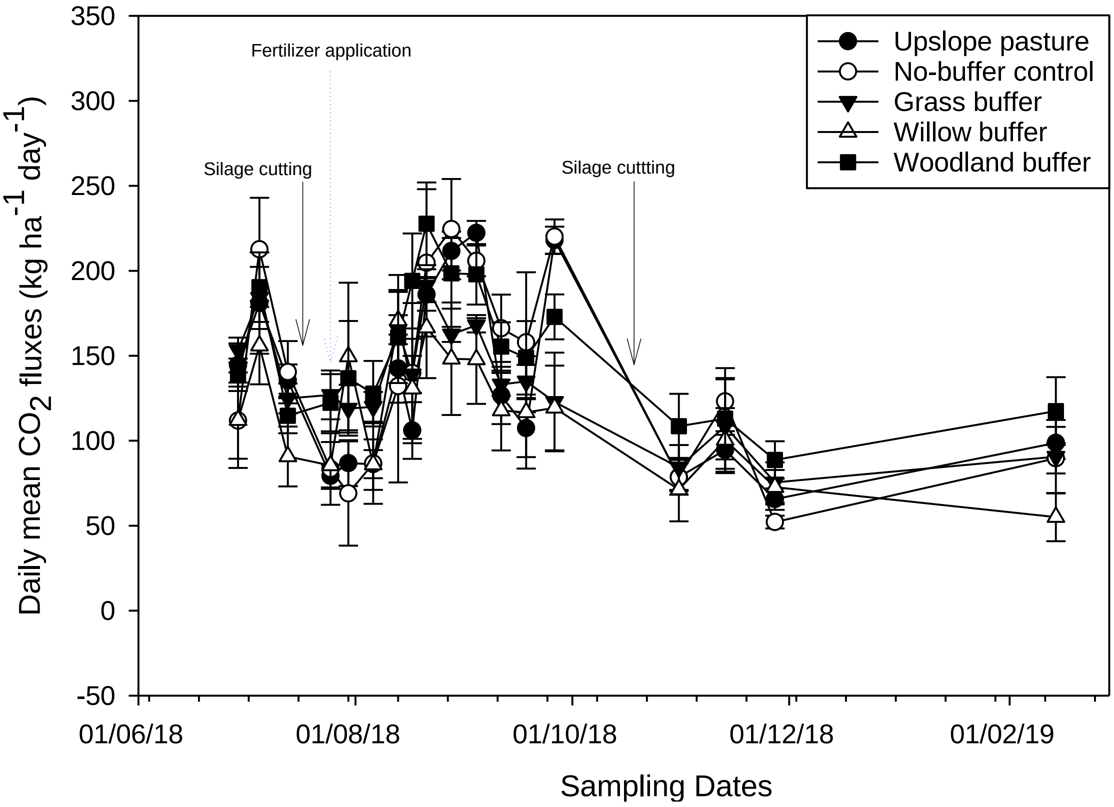

Figure 6. 1: Daily CO_2 fluxes in the upslope pasture and downslope riparian buffers. Data points and error bars represent the treatment means (upslope pasture: *n* = 12, no-buffer control: *n* = 3, grass, woodland and willow riparian buffers: *n* = 6) and SE during each sampling day.

6.3.2 Variability of cumulative soil CO_2 emissions

There was no evidence of treatment differences in cumulative soil CO_2 emissions in the current study (Figure 6.2). Despite the lack of significant differences in treatments, CO_2 fluxes followed the descending order of woodland riparian buffer; 11899 ± 1197 kg ha^{-1} > no buffer control; 11101.3 ± 1435 kg ha^{-1} > grass riparian buffer; 10954 ± 1197 kg ha^{-1} > upslope pasture; 10554.6 ± 989 kg ha^{-1} > willow riparian buffer; 9196 ± 1197 kg ha^{-1}.

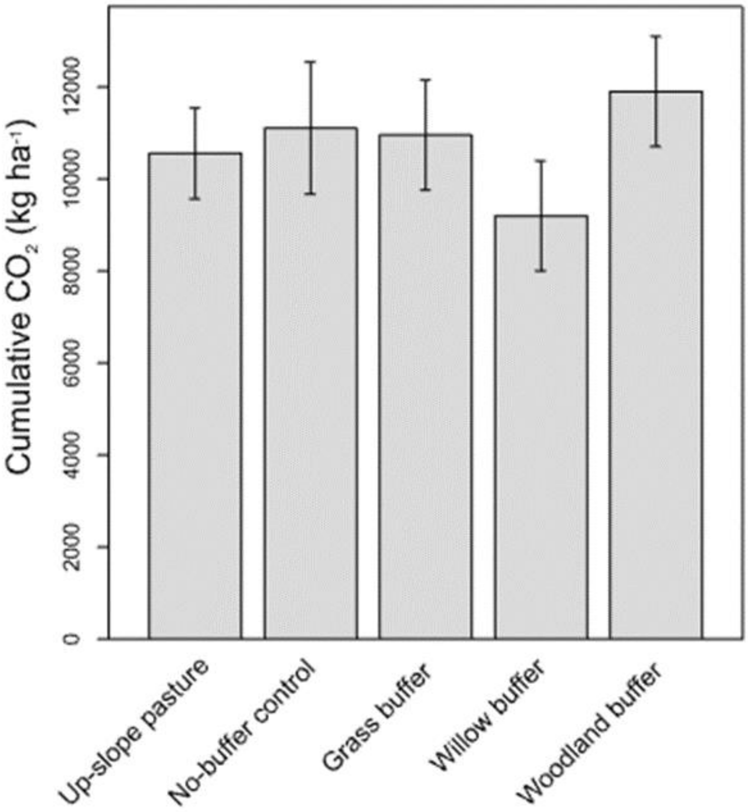

Figure 6. 2: Cumulative CO_2 emissions for the whole experimental period from the upslope permanent pasture and different downslope buffer vegetation. Error bars represent 95% confidence intervals (upslope pasture: *n* = 12, no-buffer control: *n* = 3, grass, woodland and willow riparian buffers: *n* = 6).

6.3.3 Relationships of cumulative CO_2 and explanatory variables

There was no evidence of any significant linear relationships between cumulative soil CO_2 emissions and any of the measured soil and environmental variables (Table 6.1 and Figure 6.3). Although not significant, an increase was observed in cumulative soil CO_2 emissions with every increase in soil pH, %WFPS, and OM, and a decrease with every increase on soil BD, NH_4^+-N, and TON (Figure 6.4).

Table 6. 1: *p*-values for the slope of the fitted line of the model for CO_2 and measured soil variables.

Variable	Intercept	Standard error intercept	Slope	Standard error slope	*p*-value
BD	14779	5052	-3463	4190.7	0.42
pH	8399	8325	417.1	1515.9	0.79
NH_4^+-N	10939	1047	-33.0	60.2	0.59
TON	10887	1064	-26.2	58.3	0.66
%WFPS	9993	2756	10.7	41.1	0.81
OM	10262	2023	35.4	155.0	0.82

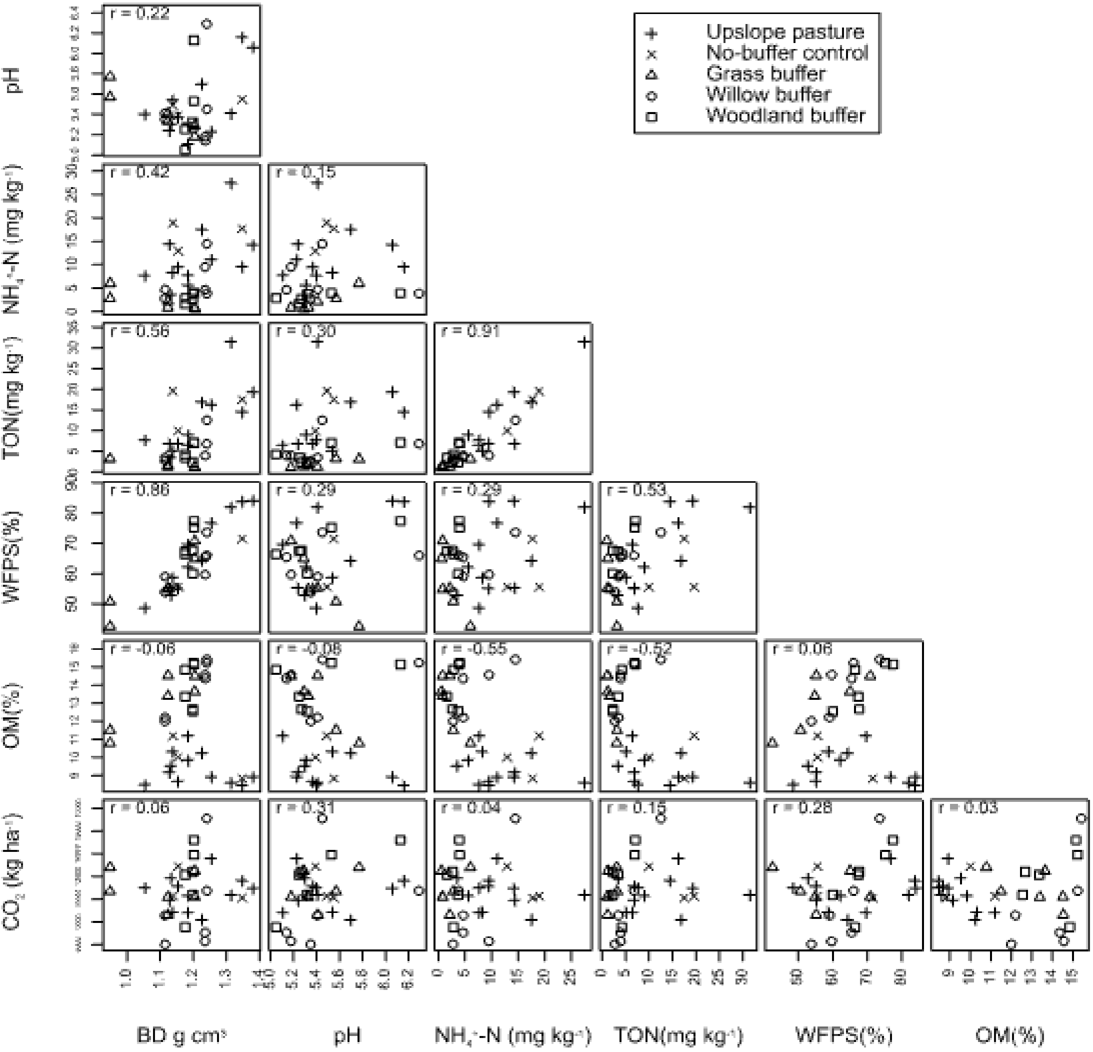

Figure 6. 3: Scatterplot showing the relationships between the variables soil pH, NH_4^+-N, TON, %WFPS, OM, BD and cumulative CO_2 emissions for the upslope permanent pasture and the downslope riparian buffers with different vegetation treatments. r = Pearson's correlation coefficient.

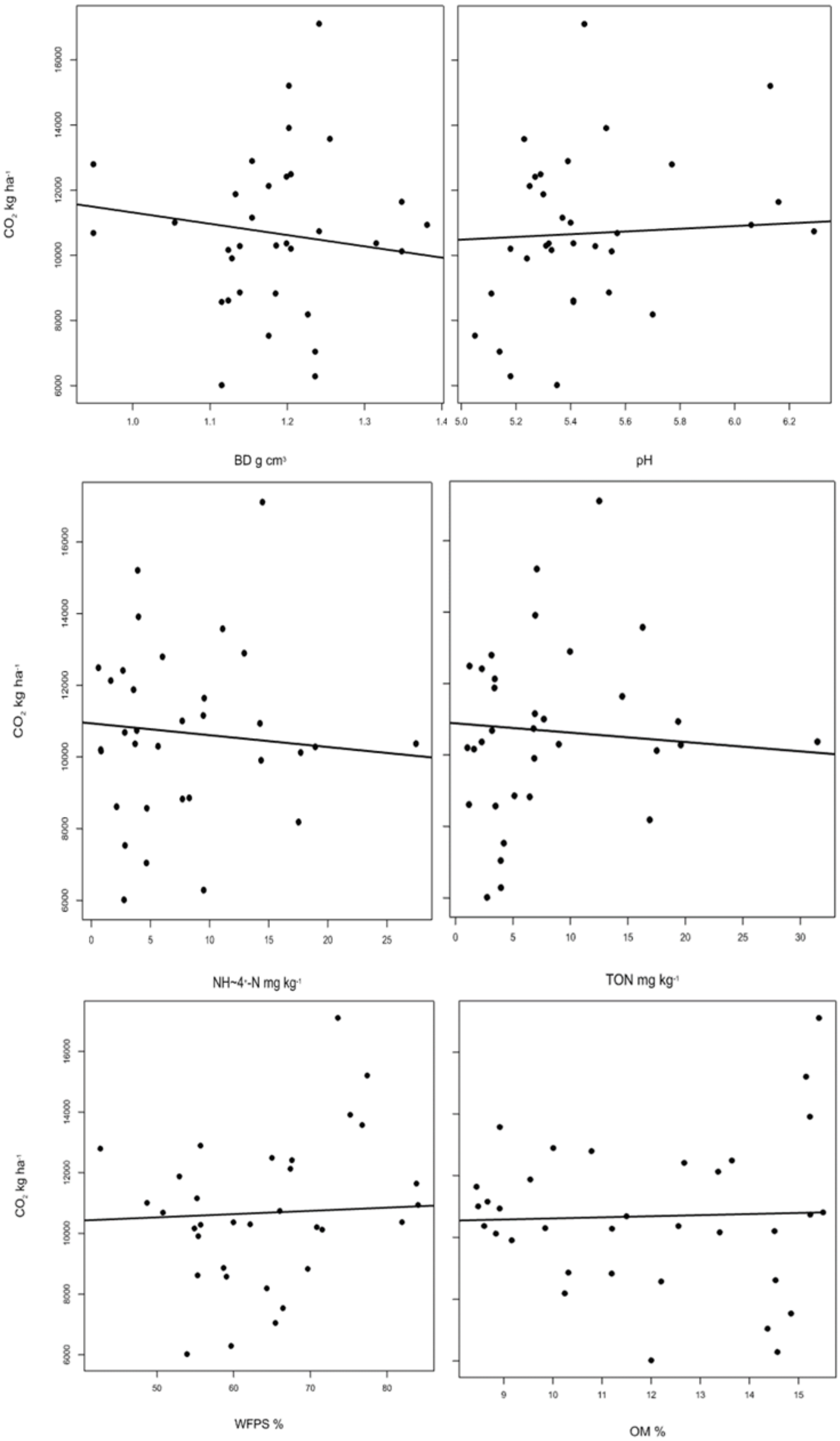

Figure 6. 4: Relationships between cumulative CO2 emissions and each of the explanatory soil variables.

6.4 Discussion

6.4.1 Soil and environmental variables and soil CO_2 fluxes

Soil moisture is well documented as one of the major drivers of soil CO_2 fluxes by a number of authors, particularly Reth *et al.* (2005), Dlamini *et al.* (2020), Ray *et al.* (2020) and Adams *et al.* (2021). Similar to the aforementioned authors, large soil CO_2 fluxes in all the treatments followed immediately after increases in soil %WFPS particularly in the first four months of the current study. The previous authors, particularly Dlamini *et al.* (2020) reported that denitrification; induced by high soil moisture conditions, is carried-out by facultative anaerobes, producing free energy, N_2, and CO_2, as a result of electron transfer between NO_3^- and C. This process is known to be dependent on soil C-supply and accounts for about 37% of CO_2 produced in the soil respiration system (Rastogi *et al.*, 2002). Also, Ray *et al.* (2020) found that CO_2-producing soil respiration increased with soil moisture following rainfall events, similar to observations of the current study. The previous author credited such CO_2 increase after rainfall and subsequent soil moisture increase to stimulated microbial activities, including soil respiration.

Soil temperature is one of the most important factors of soil CO_2 production through the respiration process (Hou *et al.*, 2014; Wang *et al.*, 2019). Similar to the previous authors, in all the treatments of the current study, a majority of the higher CO_2 fluxes coincided with higher atmospheric and soil surface temperatures, and fluxes decreased with decreasing temperatures (Figures 5.1 A and 6.1). The previous authors reported that high soil temperatures drove CO_2-producing soil microbial reactions including soil respiration.

6.4.2 Soil CO_2 emissions in upslope pasture and different riparian buffers

The woodland riparian buffer had larger cumulative CO_2 emissions compared to the remainder of the treatments as a result of its relatively higher soil OM, similar to reports by other authors, particularly Ussiri and Lal (2009) and Setia *et al.* (2011). The previous authors reported high CO_2 as a result of OM mineralization, hence vegetation that recycles higher OM is most likely to produce higher CO_2. Also, soil NH_4^+-N is known to inhibit soil methane oxidation into CO_2 (Bian *et al.*, 2019; Wang *et al.*, 2014), thus the higher soil CO_2 fluxes were expected in the woodland riparian buffer since the vegetated riparian buffers were not directly fertilized. The values observed in the current study are in line with other authors, particularly Tufekcioglu *et al.* (2001) and Jacinthe *et al.* (2015), who reported higher cumulative soil CO_2 values in riparian buffers compared to immediately adjacent croplands. For example, Jacinthe *et al.* (2015) found soil CO_2 emissions of 4850 and 8630 kg ha^{-1} $year^{-1}$ in tree and grass riparian buffers, respectively, and 2560 and 4540 kg ha^{-1} $year^{-1}$ in their respective immediately adjacent croplands in a Humid Subtropical and Cold Continental climates respectively.

6.5 Conclusion

The findings of the current study show that the woodland riparian buffers emitted larger soil CO_2 compared to the other riparian buffer vegetation, as well as the upslope pasture it serves. Thus, these findings suggest that the woodland riparian buffers may not be the best choice for water quality services as it may risk trading its water quality functions for CO_2 emissions, but the willow riparian buffer which had the lowest emissions. A further investigation also required on permanent pasture and riparian buffers in different climatic settings as this study found no evidence of a statistically significant difference between treatments. Further investigations are suggested with different crops, particularly in sites of different soils and environmental conditions, in order to validate the current findings. The findings of the current study are useful in developing CO_2 mitigation through careful riparian buffer vegetation selection and calibrating mechanistic models that explore CO_2 mitigation measures in cropping systems with different riparian buffers.

6.6 References

Adams, T., Ashworth A.J., Sauer T., 2021. Soil CO_2 evolution is driven by forage species, soil moisture, grazing pressure, poultry litter fertilization, and seasonality in silvopastures. *Agrosystems Geosciences & Environment*, 4:e20179.

Bian, R., Shi W., Duan Y., Chai X., 2019. Effect of soil types and ammonia concentrations on the contribution of ammonia-oxidizing bacteria to CH_4 oxidation. *Waste Management & Research*, 37:698-705.

Blazejewski, G.A., Stolt M.H., Gold A.J., Gurwick N., Groffman P.M., 2009. Spatial distribution of carbon in the subsurface of riparian zones. *Soil Science Society of America Journal*, 73:1733-1740.

Capon, S.J., Chambers L.E., Mac Nally R., Naiman R.J., Davies P., Marshall N., Pittock J., Reid M., Capon T., Douglas M., 2013. Riparian ecosystems in the 21st century: hotspots for climate change adaptation? *Ecosystems*, 16:359-381.

De Carlo, N., Oelbermann M., Gordon A., 2019. Carbon dioxide emissions: Spatiotemporal variation in a young and mature riparian forest. *Ecological Engineering*, 138:353-361.

Dlamini, J., Chadwick D., Hawkins J., Martinez J., Scholefield D., Ma Y., Cárdenas L., 2020. Evaluating the potential of different carbon sources to promote denitrification. *Journal of Agricultural Sciences*, 158:194-205.

Franzluebbers, A., Haney R., Honeycutt C., Schomberg H.-H., Hons F., 2000. Flush of carbon dioxide following rewetting of dried soil relates to active organic pools. *Soil Science Society of America Journal*, 64:613-623.

Harrison-Kirk, T., Beare M., Meenken E., Condron L., 2013. Soil organic matter and texture affect responses to dry/wet cycles: Effects on carbon dioxide and nitrous oxide emissions. *Soil Biology & Biochemistry*, 57:43-55.

Hou, R., Ouyang Z., Wilson G., Li Y., Li H., 2014. Response of carbon dioxide emissions to warming under no-till and conventional till systems. *Soil Science Society of America Journal*, 78:280-289.

Jacinthe, P.-A., Vidon P., Fisher K., Liu X., Baker M., 2015. Soil methane and carbon dioxide fluxes from cropland and riparian buffers in different hydrogeomorphic settings. *Journal of Environmental Quality*, 44:1080-1090.

Jaynes, D.B., Isenhart T.M., 2014. Reconnecting tile drainage to riparian buffer hydrology for enhanced nitrate removal. *Journal of Environmental Quality*, 43:631-638.

Lundquist, E., Scow K., Jackson L., Uesugi S., Johnson C., 1999. Rapid response of soil microbial communities from conventional, low input, and organic farming systems to a wet/dry cycle. *Soil Biology & Biochemistry*, 31:1661-1675.

Mitsch, W.J., Day J.W., Gilliam J.W., Groffman P.M., Hey D.L., Randall G.W., Wang N., 2001. Reducing Nitrogen Loading to the Gulf of Mexico from the Mississippi River Basin: Strategies to Counter a Persistent Ecological Problem: Ecotechnology-the use of natural ecosystems to solve environmental problems-should be a part of efforts to shrink the zone of hypoxia in the Gulf of Mexico. *AIBS Bulletin,* 51:373-388.

Naiman, R.J., Decamps H., 1997. The ecology of interfaces: riparian zones. *Annual Review of Ecology, Evolution, & Systematics*, 28:621-658.

Rastogi, M., Singh S., Pathak H., 2002. Emission of carbon dioxide from soil. *Current Science*, 82:510-517.

Ray, R.L., Griffin R.W., Fares A., Elhassan A., Awal R., Woldesenbet S., Risch E., 2020. Soil CO_2 emission in response to organic amendments, temperature, and rainfall. *Scientific Reports*, 10:1-14.

Reth, S., Reichstein M., Falge E., 2005. The effect of soil water content, soil temperature, soil pH-value and the root mass on soil CO_2 efflux–a modified model. *Plant & Soil*, 268:21-33.

Sabater, S., Butturini A., Clement J.-C., Burt T., Dowrick D., Hefting M., Matre V., Pinay G., Postolache C., Rzepecki M., 2003. Nitrogen removal by riparian buffers along a European climatic gradient: patterns and factors of variation. *Ecosystems*, 6:0020-0030.

Setia, R., Marschner P., Baldock J., Chittleborough D., Verma V., 2011. Relationships between carbon dioxide emission and soil properties in salt-affected landscapes. *Soil Biology & Biochemistry*, 43:667-674.

Soosaar, K., Mander Ü., Maddison M., Kanal A., Kull A., Lõhmus K., Truu J., Augustin J., 2011. Dynamics of gaseous nitrogen and carbon fluxes in riparian alder forests. *Ecological Engineering*, 37:40-53.

Tonderski, A., 1996. Landuse-based nonpoint source pollution. A threat to water resources in developing countries. *Water Science & Technology*, 33:53-61.

Tufekcioglu, A., Raich J.W., Isenhart T.M., Schultz R.C., 2001. Soil respiration within riparian buffers and adjacent crop fields. *Plant & Soil*, 229:117-124.

Ussiri, D.A., Lal R., 2009. Long-term tillage effects on soil carbon storage and carbon dioxide emissions in continuous corn cropping system from an alfisol in Ohio. *Soil & Tillage Research*, 104:39-47.

Valkama, E., Usva K., Saarinen M., Uusi-Kämppä J., 2019. A meta-analysis on nitrogen retention by buffer zones. *Journal of Environmental Quality*, 48:270-279.

Vidon, P., Marchese S., Welsh M., McMillan S., 2016. Impact of precipitation intensity and riparian geomorphic characteristics on greenhouse gas emissions at the soil-atmosphere interface in a water-limited riparian zone. *Water, Air, & Soil Pollution*, 227:8.

Wang, W., Akhtar K., Ren G., Yang G., Feng Y., Yuan L., 2019. Impact of straw management on seasonal soil carbon dioxide emissions, soil water content, and temperature in a semi-arid region of China. *Science of the Total Environment*, 652:471-482.

Wang, Y., Cheng S., Fang H., Yu G., Xu M., Dang X., Li L., Wang L., 2014. Simulated nitrogen deposition reduces CH_4 uptake and increases N_2O emission from a subtropical plantation forest soil in southern China. *PloS One*, 9:e93571.

CHAPTER 7.0

SOIL N_2O AND CH_4 EMISSIONS FROM FODDER MAIZE PRODUCTION WITH AND WITHOUT RIPARIAN BUFFER STRIPS OF DIFFERING VEGETATION

This chapter is *published* in the journal "**Plant and Soil**" as:

Dlamini JC, Cardenas LM, Tesfamariam EH, Dunn RM, Evans J, Hawkins JMB, Blackwell MSA, Collins AL. **2022**. Soil N_2O and CH_4 emissions from fodder maize production with and without riparian buffer strips of varying vegetation. *Plant and Soil*, 2022. DOI: https://doi.org/10.1007/s11104-022-05426-0

Corresponding author: JCD

Author contributions:

JCD, JE, EHT, LMC, RD, MSAB, ALC: Conceptualization, Methodology, Software. **JCD:** Data curation, Writing- Original draft preparation. **JD, JE:** Visualization, Investigation. **EHT, LMC:** Supervision. **JCD, JE:** Software, Validation. **EHT, LMC, RD, MSAB, ALC:** Writing- Reviewing and Editing.

Abstract

Nitrous oxide and CH_4 are some of the most critical greenhouse gases of the 21st century. Vegetated riparian buffers are primarily implemented for their water quality functions in agroecosystems, and their location in the agricultural landscape allows them to intercept and process pollutants from immediately adjacent agricultural land. They recycle OM, which increases soil C, intercept N-rich runoff from adjacent croplands, and are seasonally anoxic, promoting processes producing environmentally harmful gases, including N_2O and CH_4. Against this context, the study quantified these atmospheric losses between a cropland and vegetated riparian buffers of varying vegetation that serve it. The current study used the static chamber technique to measure N_2O and CH_4 emissions simultaneously. Gas measurements were done simultaneously with soil and environmental variables for a 6-month period in a replicated plot-scale facility comprising of maize cropping served by three vegetated riparian buffers, namely: (i) a novel grass riparian buffer; (ii) a willow riparian buffer, and (iii) a woodland riparian buffer. These buffered treatments were compared with a no-buffer control. The no-buffer control generated the largest cumulative N_2O emissions of 18 929 g N ha^{-1} (95% confidence intervals: 524.1 - 63 643) whilst the maize crop upslope generated the largest cumulative CH_4 emissions of 5 050 ± 875 g C ha^{-1}. Soil N_2O and CH_4-based GWP were lower in the willow (1223.5 ± 362.0 and 134.7 ± 74.0 kg CO_2-eq. ha^{-1} $year^{-1}$, respectively) and woodland (1771.3 ± 800.5 and 3.4 ± 35.9 kg CO_2-eq. ha^{-1} $year^{-1}$, respectively) riparian buffers. The current findings suggest that maize production in general, and in situations where such cropping is not undertaken in tandem with a riparian buffer strip, result in atmospheric CH_4 and N_2O concerns.

7.1 Introduction

Nitrous oxide and CH_4 are important GHGs that contribute more than 21% of radiative forcing of the greenhouse effect (IPCC, 2006). Although N_2O and CH_4 are less abundant than CO_2 in the atmosphere, their respective GWPs over a 100-year horizon are ~310 and ~28 times, respectively, that of CO_2 (IPCC, 2014; Ramaswamy *et al.*, 2001). Soils play a vital role in the global N_2O and CH_4 cycles (Conrad, 2007; Firestone, 1982; IPCC, 2008). Soils of natural and semi-natural agroecosystems, including croplands, grasslands, and forests, are significant global sources/sinks of N_2O and CH_4, and thus play a significant role in balancing atmospheric concentrations of these gases (Dutaur and Verchot, 2007; Smith *et al.*, 2000; Stehfest and Bouwman, 2006).

In soils N_2O and CH_4 are produced and/or consumed as a result of microbial processes (Ball *et al.*, 1999; Conrad, 2007; Yao *et al.*, 2017). N_2O is predominantly produced as a by-product of two microbial processes; nitrification and denitrification (Bowden, 1986; Davidson, 2009). In the case of CH_4, production occurs due to organic material decomposition under anaerobic conditions by methanogens in soils (Smith *et al.*, 2018b; Yamulki and Jarvis, 2002). However, under such conditions and some aerobic conditions, atmospheric CH_4 diffusing into the topsoil can be oxidized by methanotrophs which subsequently result to CO_2 (Jacinthe *et al.*, 2015; Le Mer and Roger, 2001).

Agronomic management practices associated with annual row crops may result in soil disturbances that affect soil microbial communities (Friedel *et al.*, 1996), soil physical (Gronle *et al.*, 2015), chemical properties (Neugschwandtner *et al.*, 2014; Wang *et al.*, 2008), soil temperature (Shen *et al.*, 2018), and moisture content (Ouattara *et al.*, 2006). These changes in agricultural land often result in substantial soil and nutrient runoff losses (Bechmann and Bøe, 2021; Ulén, 1997), including, where they are implemented, into riparian buffer strips. The implementation of riparian buffers may further affect soil processes such as N-mineralization, N-uptake, leaching, gaseous N emissions (particularly nitrification and denitrification) (Firestone, 1982; Müller *et al.*, 2004; Reinsch *et al.*, 2018), CH_4 oxidation, and methanogenesis (Le Mer and Roger, 2001; Luo *et al.*, 2013; Megonigal and Guenther, 2008); all of which are responsible for N_2O and CH_4 production and/or uptake and subsequent exchanges between the soil and atmosphere. Previous studies on N_2O Jacinthe *et al.* (2012) and CH_4 (Zhang *et al.*, 2016) emissions from riparian buffers have focused on buffer vegetation type and the understanding of soil and environmental drivers of these gases. Despite previous work, understanding of N and C trace gas fluxes from adjacent cropped land in comparison to fluxes from riparian buffer strips serving that land remain elusive. Therefore, this study aimed to evaluate the unintended emissions of N_2O and CH_4 from maize production which had both buffered and un-buffered downslope.

7.2 Materials and Methods

Information on the chapter's (i) study site description, (ii) experimental design and treatments, and (iii) field measurements are detailed in Chapter 3 (section 3.2). The previous chapters (4, 5 and 6) described N_2O, CH_4, and CO_2 dynamics in a permanent pasture which had been planted in 2016. And the current chapter describes N_2O and CH_4 dynamics in an upslope maize and downslope riparian buffers of varying vegetation. The maize crop was planted in plots that had been planted with permanent pasture after ripping and ploughing on the 14th of May 2019 and the riparian buffer vegetation areas remained untouched. Maize (*Zea mays* L.) was planted on the 17th of May 2019 for the experiment reported herein. Cattle slurry and inorganic fertilizer were applied at times and rates summarised in Table 7.1.

Table 7. 1: Application rates of cattle slurry and inorganic fertilizer during the cropping season.

Date	**Source**	**N-input (kg ha^{-1})**	**P-input (kg ha^{-1})**	**K-input (kg ha^{-1})**
14 May 2019	Cattle slurry	20.8	12	46
17 May 2019	Inorganic fertilizer	100†	85¥	205‡

Nutrient sources: Nitrogen; †Nitram (Ammonium nitrate), Phosphorus; ¥ triple superphosphate (P_2O_5), Potassium‡ muriate of potash (K_2O)

7.2.1 Data processing and statistical analysis

Linear mixed models in Genstat 20 (VSN International, Hemel Hempstead, United Kingdom) were used to determine whether cumulative N_2O and CH_4 differed with treatment. The random structure of each model (accounting for the experiment structure) was *block/plot/chamber*. The fixed structure (accounting for treatment effects) was *treatment type/(treatment*distance).* This model gives the following four tests in the output: (i) *Treatment type* – tests main maize cropped area vs. no-buffer control vs. riparian buffers, (ii) *Treatment type*treatment* – tests for differences between grass, willow, and woodland riparian buffers, (iii) *Treatment type*buffer distance* – tests for the difference between upper and lower riparian buffer areas, and (iv) *Treatment type*treatment*buffer distance* – tests for interaction between riparian buffer type and distance. A transformation was required to satisfy the equal variance assumption of the analysis of N_2O. Due to the large negative values present for N_2O, a modified square root transformation was used; $SIGN\ (N_2O)\ *\sqrt{\ }\ (abs\ (N_2O))$. No transformation was required for CH_4 analysis.

Linear mixed models with the same random and fixed structures as those used for N_2O and CH_4 were used to determine whether any measured soil variables (BD, pH, NH_4^+-N, TON, %WFPS, and OM) differed with treatment. Pearson's correlation coefficient (r) was used to indicate the strength of relationships between soil and environmental factors and N_2O/CH_4 emissions. This was tested more formally in the linear mixed models described above. If linear mixed models indicated the presence of treatment differences, LSDs were calculated to determine which specific treatment pairs resulted in the significant differences in N_2O/CH_4 emissions. All graphs were generated using Sigma Plot (Systat Software Inc., CA, USA).

7.3 Results

7.3.1 Meteorological and soil characteristics

7.3.1.1 Rainfall patterns

Figure 7.1 shows the total monthly rainfall during the experimental period. The total rainfall for the whole experimental period was 492.2 mm, and the highest rainfall event of 118.2 mm fell in October 2019. Before the highest rainfall in October, the second-highest rainfall events of 96.6 and 96.2 mm were recorded in June and September 2019, respectively.

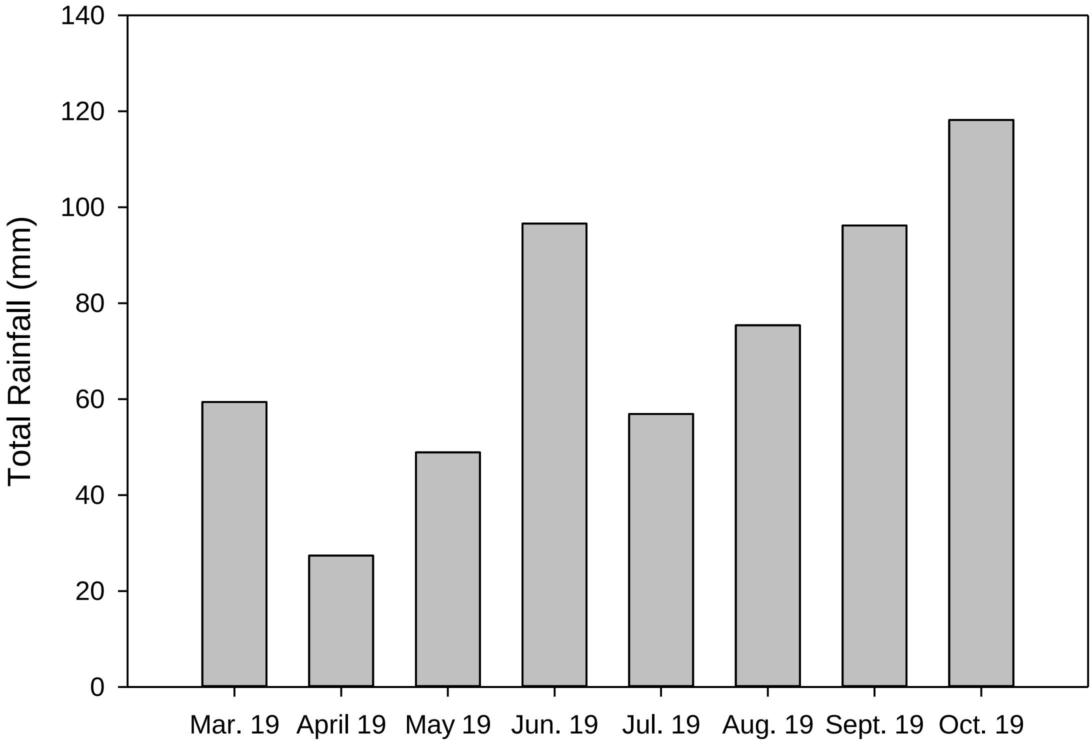

Figure 7. 1: Total monthly rainfall during the experimental period.

7.3.1.2 Soil variables

Table 7.2 presents the average soil variable data during the experimental period. Soil pH ranged from 5.1 ± 0.17 and 5.5 ± 0.17, with the highest pH of 5.5 ± 0.17 (willow riparian buffer), which was however, not significantly (*LSD=0.29*) different to the grass or woodland riparian buffers. The largest soil BD of 1.2 ± 0.05 g cm^{-3} was recorded in the no-buffer control, which was not significantly different from the upslope maize and the different vegetated riparian buffers (*LSD=0.19*). Soil OM ranged from 9.0 ± 3.2 to 17.8 ± 2.3%, with the largest %OM of 17.8 ± 2.3% recorded in the willow riparian buffer, which was, however, not significantly (*LSD=8.6*) different to the woodland riparian buffer (15.98 ± 2.3%).

Table 7. 2: Summary of soil parameters (mean ± standard error) in the upslope maize and downslope riparian buffers with different vegetation (upslope maize: *n*=12, no-buffer control: *n*=3 and grass, willow, and woodland riparian buffers: *n*=6) before the commencement of the current experiment in May 2019.

Parameter	**Upslope maize**	**No-buffer control**	**Grass buffer**	**Willow buffer**	**Woodland buffer**	**LSD**
pH	5.1 ± 0.17	5.1 ± 0.19	5.4 ± 0.17	5.5 ± 0.17	5.4 ± 0.17	0.29
BD (g cm^{-3})	1.21 ± 0.03	1.21 ± 0.05	1.1 ± 0.04	1.2 ± 0.04	1.2 ± 0.04	0.19
OM (% w/w)	9.9 ± 1.3	9.0 ± 3.2	12.2 ± 2.3	17.8 ± 2.3	16.0 ± 2.3	8.6
NH_4^+-N (mg kg^{-1} dry soil)	27.4 ± 2.98	20.6 ± 4.6	6.4 ± 2.7	13.6 ± 2.7	9.1 ± 2.7	7.8
TON (mg kg^{-1} dry soil)	55.7 ± 1.7	42.8 ± 3.7	13.6 ± 3.0	4.99 ± 3.0	10.9 ± 3.0	10.0
%WFPS (%)	86.9 ± 5.3	81.7 ± 9.9	86.7 ± 7.2	102.9 ± 7.2	98.2 ± 7.2	18.6

7.3.1.3 Soil mineral N-dynamics

Figure 7.2 shows soil mineral N dynamics during the experimental period. At the commencement of the experiment, NH_4^+-N was < 17 mg kg^{-1} dry soil in all of the treatments, with the largest of 16.7 ± 3.5 mg kg^{-1} dry soil observed in the upslope maize. However, after the second sampling event, which had been preceded by two fertilizer application events (Table 7.1), NH_4^+-N increased by almost 3-fold in the no-buffer control and upslope maize but remained relatively low in the three vegetated riparian buffers. Despite the high NH_4^+-N values in the no-buffer control and upslope maize after fertilization, values dropped to <30 mg kg^{-1} dry soil after the fourth sampling event and remained low until the end of the experimental period (Figure 7.2 A). The average NH_4^+-N for the whole experimental period ranged from 6.4 ± 2.8 to 27.4 ± 2.8 mg kg^{-1} dry soil, with the largest value of 27.4 ± 2.8 mg kg^{-1} dry soil obtained from the upslope maize, which was however, not significantly (*LSD=7.8*) different to the no-buffer control. It was, however, significantly different (*LSD=7.8*) to the three vegetated riparian buffers (Table 7.2).

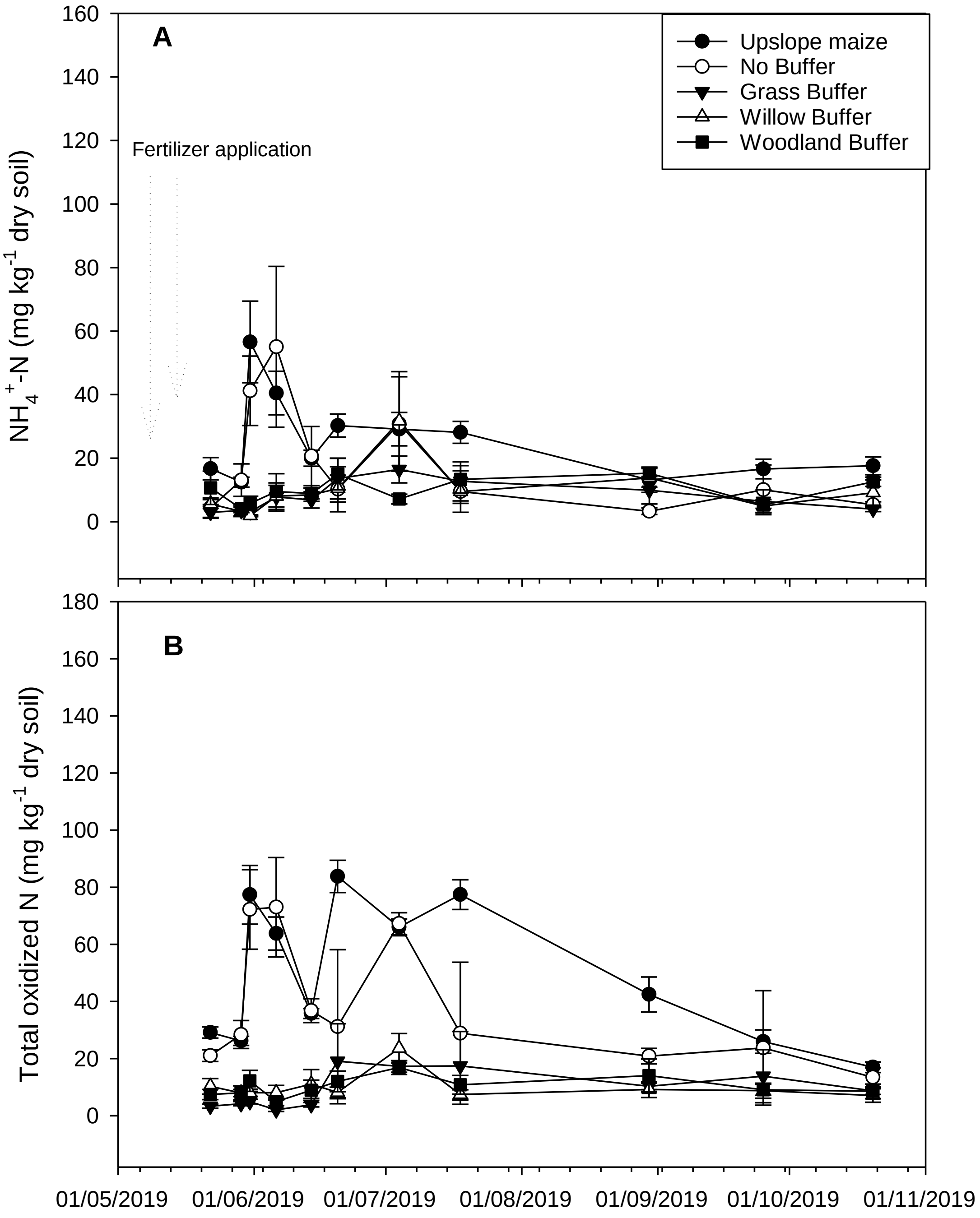

Figure 7. 2: Soil NH_4^+ and TON in the upslope maize and downslope riparian buffers during the experimental period.

Total oxidized N was <30 mg kg^{-1} dry soil in all the treatments at the commencement of the experiment (Figure 7.2 B). However, after the second sampling event, TON increased 4-fold in the upslope maize and no-buffer control but remained low in the three vegetated riparian buffers. Despite a drop to ~35 mg kg^{-1} dry soil in the upslope maize and no-buffer control during the fifth sampling event, the upslope maize emerged with the highest TON of ~81 mg kg^{-1} dry soil during the sixth sampling event. However, these values dropped gradually up until the end of the experiment. Average TON for the whole experimental period ranged from 4.99 ± 3.0 to 55.7 ± 1.7 mg kg^{-1} dry soil, with the highest value of 55.7 ± 1.7 mg kg^{-1} dry soil obtained from the upslope maize. This value was significantly different (*LSD = 10.0*) to all other treatments, except for the no-buffer control (Table 7.2).

7.3.1.4 Water filled-pore spaces

Soil %WFPS trends during the experimental period are shown in Figure 7.3 (A), and Table 7.2 shows the average %WFPS for the whole season. The highest %WFPS was observed during the fifth sampling event, with the overall highest estimate observed in the woodland riparian buffer. The woodland riparian buffer maintained higher %WFPS values than the remainder of the treatments during the experiment. The average %WFPS for the whole experimental period ranged from 81.7 ± 9.9 to 102.9 ± 7.2%, with the highest value recorded in the willow riparian buffer, which was however not significantly (*LSD = 18.6*) different to the woodland riparian buffer treatment, or any of the other treatments.

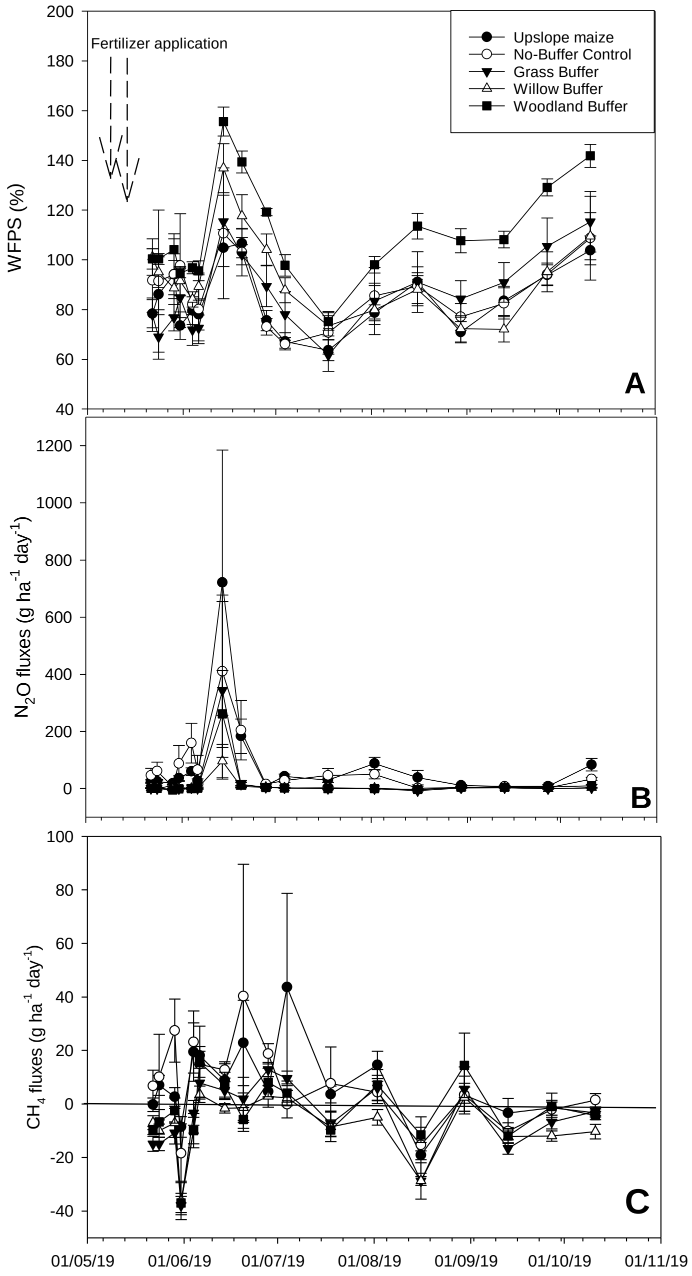

Figure 7. 3: Daily (A) soil water-filled pore spaces, and (B) N_2O, (C) CH_4, in the upslope maize and downslope riparian buffers. Data points and error bars represent the treatment means (upslope maize: *n*=12, no-buffer control: *n* = 3, grass, woodland, and willow riparian buffers: *n*=6) and SE during each sampling day. The vertical line in CH_4 marks 0 fluxes.

7.3.2 Treatment effects on explanatory variables

Table 7.3 shows that soil OM differed between sampling areas; upslope and downslope chambers ($p < 0.05$), but there was no evidence of any other differences between treatments. Soil OM in the vegetated riparian buffer strips was different from the upslope maize but not to the no-buffer control, which was not different from the upslope maize. Soil NH_4^+-N also differed between areas, but there was no evidence of any other differences between treatments. The NH_4^+-N in the vegetated riparian buffers was different from the upslope maize and no-buffer control, and the upslope maize and no-buffer control were not different from each other. Soil pH was different between sampling areas, and there was an interaction between treatments and the upper and lower riparian buffer areas. The pH in the vegetated riparian buffers was different from the upslope maize and no-buffer control; but they were not different to each other. Soil pH was different in the upper and lower areas of the willow and woodland riparian buffer strips but not in the grass riparian buffer. TON was different between areas, but there was no evidence of any other treatment differences. All three riparian buffer vegetation types were different, and there was no evidence of any treatment differences for BD or %WFPS (Table 7.2).

Table 7. 3: *p*-values for tests from LMMs on each of the measured soil variables.

Factors and interactions	OM	BD	NH_4-N	pH	TON	%WFPS
Area	0.04	0.29	<0.001	<0.001	<0.001	0.23
Area * Treatment crop	0.31	0.13	0.16	0.238	0.173	0.24
Area * Buffer area	0.551	1	0.97	0.959	0.349	0.9
Area * Treatment crop * Buffer area	0.079	1	0.77	0.05	0.5	0.84

7.3.3 Gas emissions

7.3.3.1 Gas fluxes

a. Nitrous oxide

Nitrous oxide fluxes measured during each sampling event are shown in Figure 7.3 (B). The commencement of the experiment was marked by relatively low fluxes in all of the treatments. These low fluxes were immediately followed by the highest peak in all the treatments; observed after both fertilizer application events, with a maximum mean flux of 721.1 ± 464.3 g ha^{-1} day^{-1} observed in the upslope maize. There was also a smaller peak of up to 204 ± 5.7 g ha^{-1} day^{-1} observed in the upslope maize at around the 1st of August 2019. After that, fluxes remained < 10 g ha^{-1} day^{-1} in all the treatments, with the upslope maize and no-buffer control maintaining predominantly larger fluxes until the end of the experiment.

b. Methane

Daily CH_4 fluxes, which were mostly positive and sometimes negative, are illustrated in Figure 7.3 (C). Similar to N_2O fluxes, the commencement of the experiment was marked by low CH_4 fluxes, which increased up to ~40 g ha^{-1} day^{-1} (in the upslope maize and no-buffer control) immediately after fertilizer application. After these peaks, CH_4 fluxes remained low and mostly negative in all the treatments until the end of the experiment.

7.3.3.2 Cumulative gas emissions

a. Nitrous oxide

There was no evidence of significant treatment differences in N_2O emissions between the upslope maize, no-buffer control and the three vegetated riparian buffers ($p = 0.67$) (Figure 7.4 A). Cumulative N_2O emissions had a descending order: no-buffer control;

18 929 g ha^{-1} (95% confidence intervals: 524.1 - 63 643 g ha^{-1}) > upslope maize; 6 523 g ha^{-1} (95% CI: 550.7 – 19 060) > woodland riparian buffer; 2 641 g ha^{-1} (95% CI: -267.9-14 195 g ha^{-1}), willow riparian buffer; 2 324 g ha^{-1} (95% CI: -382.1-13 448) > grass riparian buffer; 375 g ha^{-1} (95% CI: -2 340.6 – 7 592 g ha^{-1}).

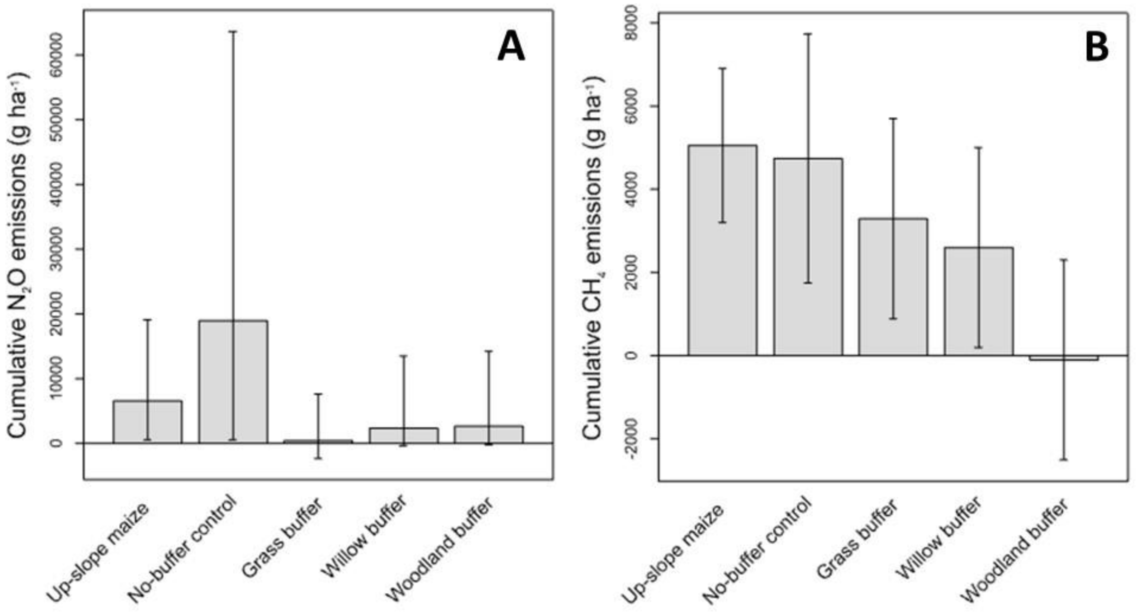

Figure 7. 4: Cumulative (A) N_2O and (B) CH_4 emissions for the whole experimental period from the upslope maize and different downslope buffer vegetation. Error bars represent 95% confidence intervals (upslope maize: *n*=12, no-buffer control: *n*=3, grass, woodland, and willow riparian buffers: *n* = 6). Vertical lines are 95% confidence intervals.

b. Methane

The upslope maize and the no-buffer control (not significantly different from each other) emitted significantly higher cumulative soil CH_4 fluxes than the three vegetated riparian buffers (*p* = 0.02) (Figure 7.4 B). Cumulative soil CH_4 fluxes were in the descending order: upslope maize: 5050 ± 875 g ha^{-1} > no-buffer control: 4740 ±

1411 g ha^{-1} > grass riparian buffer: 3289 ± 1135 g ha^{-1} > willow riparian buffer: 2597 ± 1135 g ha^{-1} > woodland riparian buffer: -102 ± 1135 g ha^{-1}.

7.3.3.3 Relationships between gas emissions and measured soil variables

Table 7.4 and Figure 7.5 show that none of the measured soil variables had a significant relationship with cumulative N_2O, but a slight relationship with TON (r = 0.32; *p=0.065*). N_2O emissions were shown to increase with an increase in soil BD, NH_4^+-N, TON, and %WFPS and to decrease with an increase in pH and OM (Figure 7.6).

Table 7. 4: *p*-values for the slope of the fitted line of the model for N_2O and measured soil variables.

Variable	Intercept	Standard error intercept	Slope	Standard error slope	*p*-value
BD	-172.6	142.1	201.9	119.98	0.126
pH	122.9	191.9	-10.56	36.194	0.786
NH_4^+	38.29	23.48	1.58	1.1513	0.18
TON	33.97	18.18	1.068	0.555	0.065
%WFPS	44.16	69.45	0.2518	0.75597	0.742
OM	69.7	29.76	-.2556	2.05029	0.902

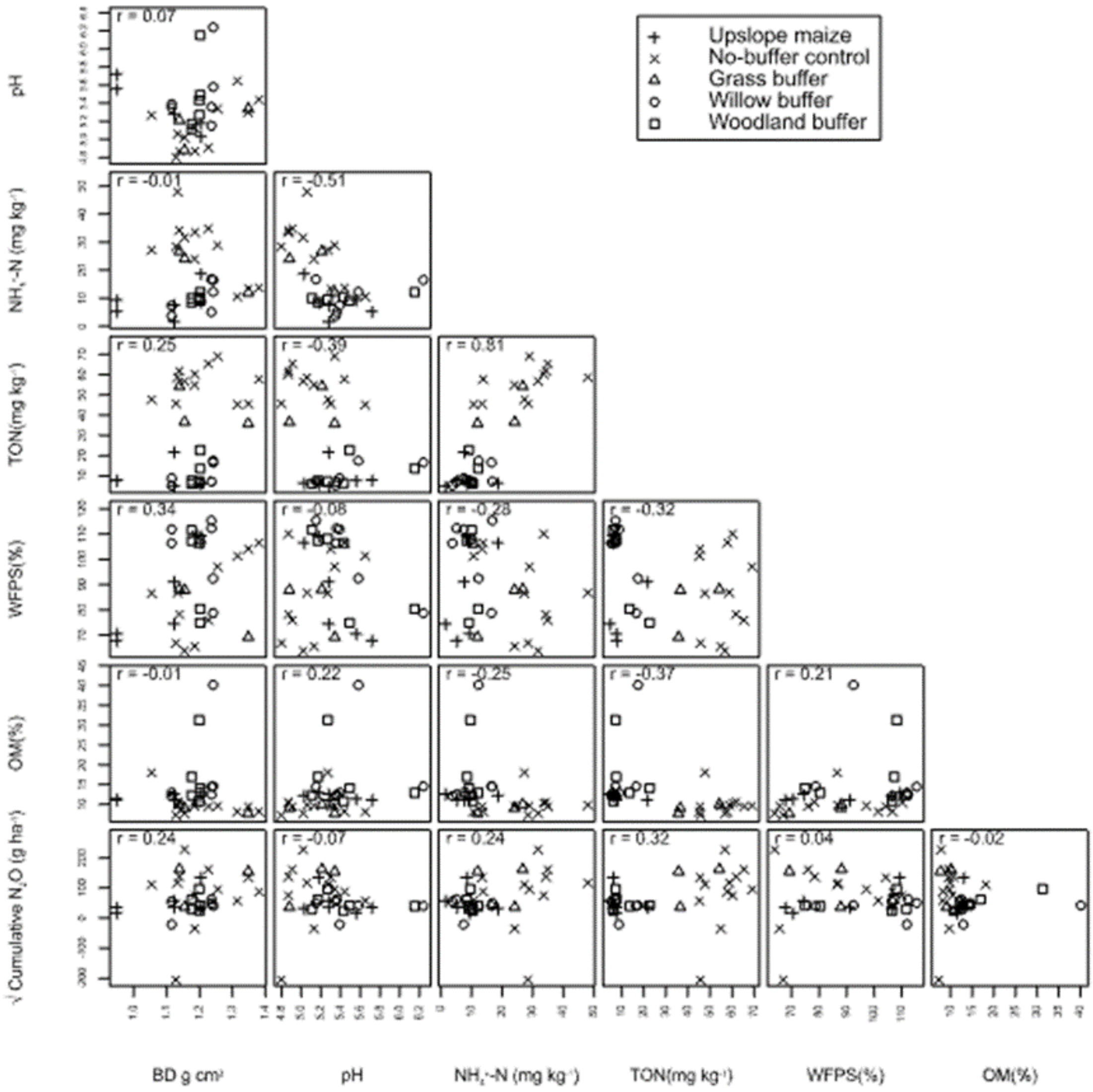

Figure 7. 5: Scatterplot showing the relationships between the variables soil pH, NH$_4^+$-N, TON, %WFPS, OM, BD and cumulative N$_2$O emissions for the upslope maize and the downslope riparian buffers with different vegetation treatments. r = Pearson's correlation coefficient.

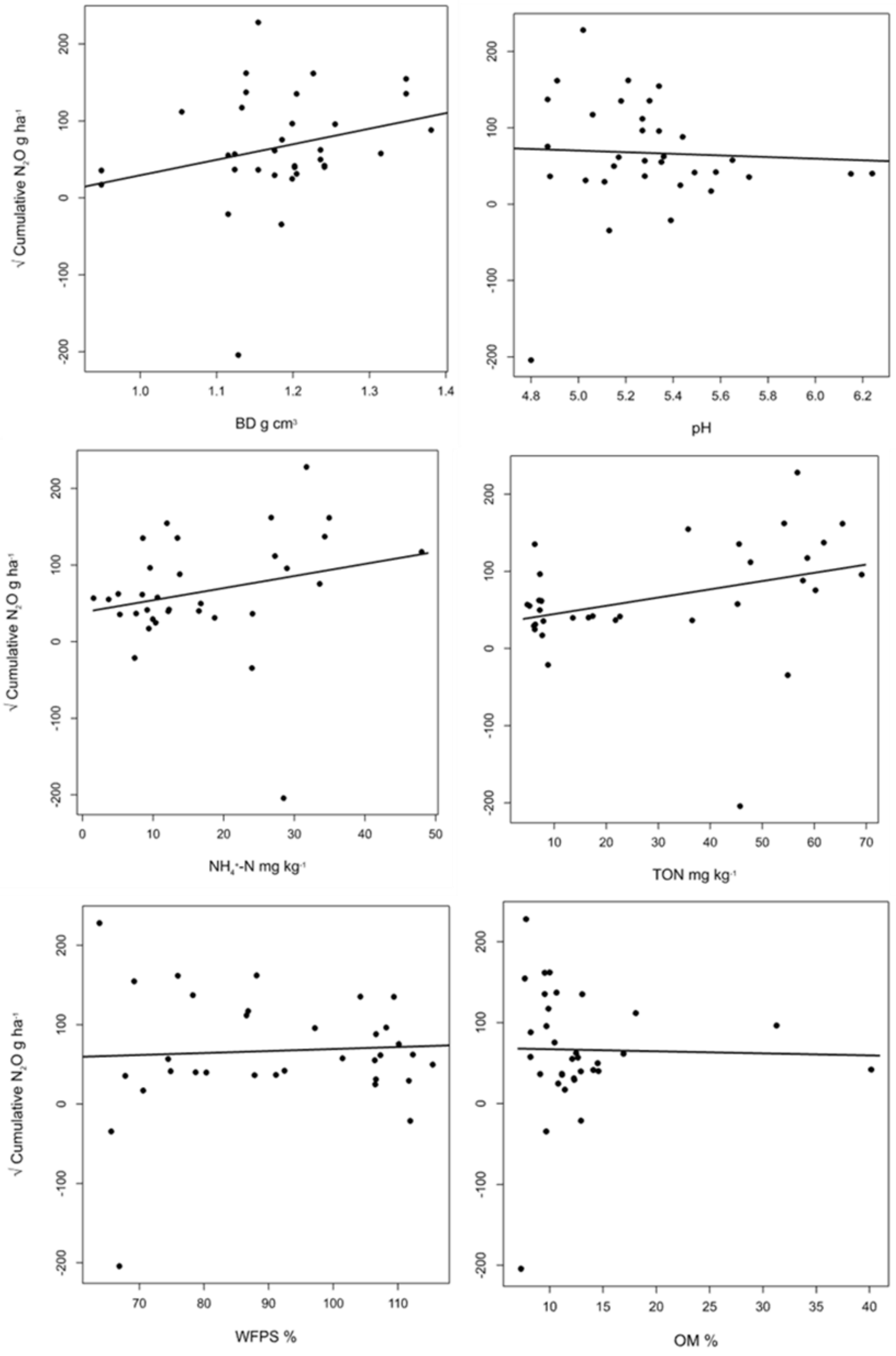

Figure 7. 6: Relationships between cumulative N_2O emissions and each of the explanatory soil variables.

Table 7.5 and Figure 7.7 show that pH (r = -0.44; *p* = 0.042), TON (r = 0.44; *p* = 0.005), and NH_4^+-N (r = 0.33; *p* = 0.056) had significant relationships with cumulative CH_4 emissions. Soil CH_4 emissions increased with increasing soil BD, NH_4^+-N, and TON and decreased with increasing in soil pH, %WFPS, and OM (Figure 7.8).

Table 7. 5: *p*-values for the slope of the fitted line of the model for CH_4 and measured soil variables.

Variable	Intercept	Standard error intercept	Slope	Standard error slope	*p*-value
BD	-4469	6524	6575	5467.2	0.24
pH	26829	5813	-4447	1094.7	0.042
NH_4^+	1901	918.6	84.33	42.303	0.056
TON	1663	925.3	56.41	18.574	0.005
%WFPS	5265	2916	-21.41	30.548	0.489
OM	4861	1197	-122	74.55	0.113

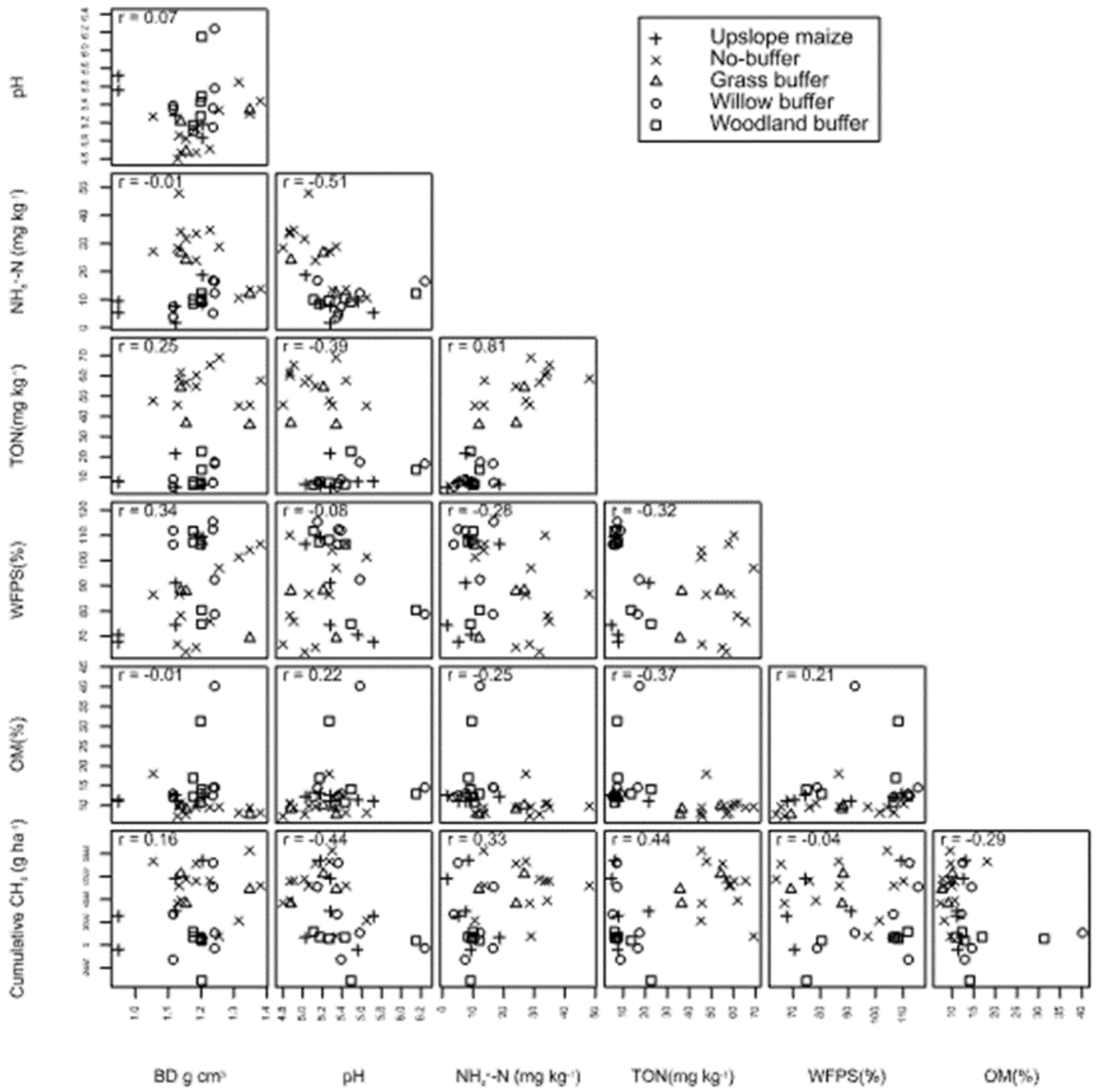

Figure 7. 7: Scatterplot showing the relationships between the variables soil pH, NH_4^+-N, TON, %WFPS, OM, BD and cumulative CH_4 emissions for the upslope maize and the downslope riparian buffers with different vegetation treatments. r = Pearson’s correlation coefficient.

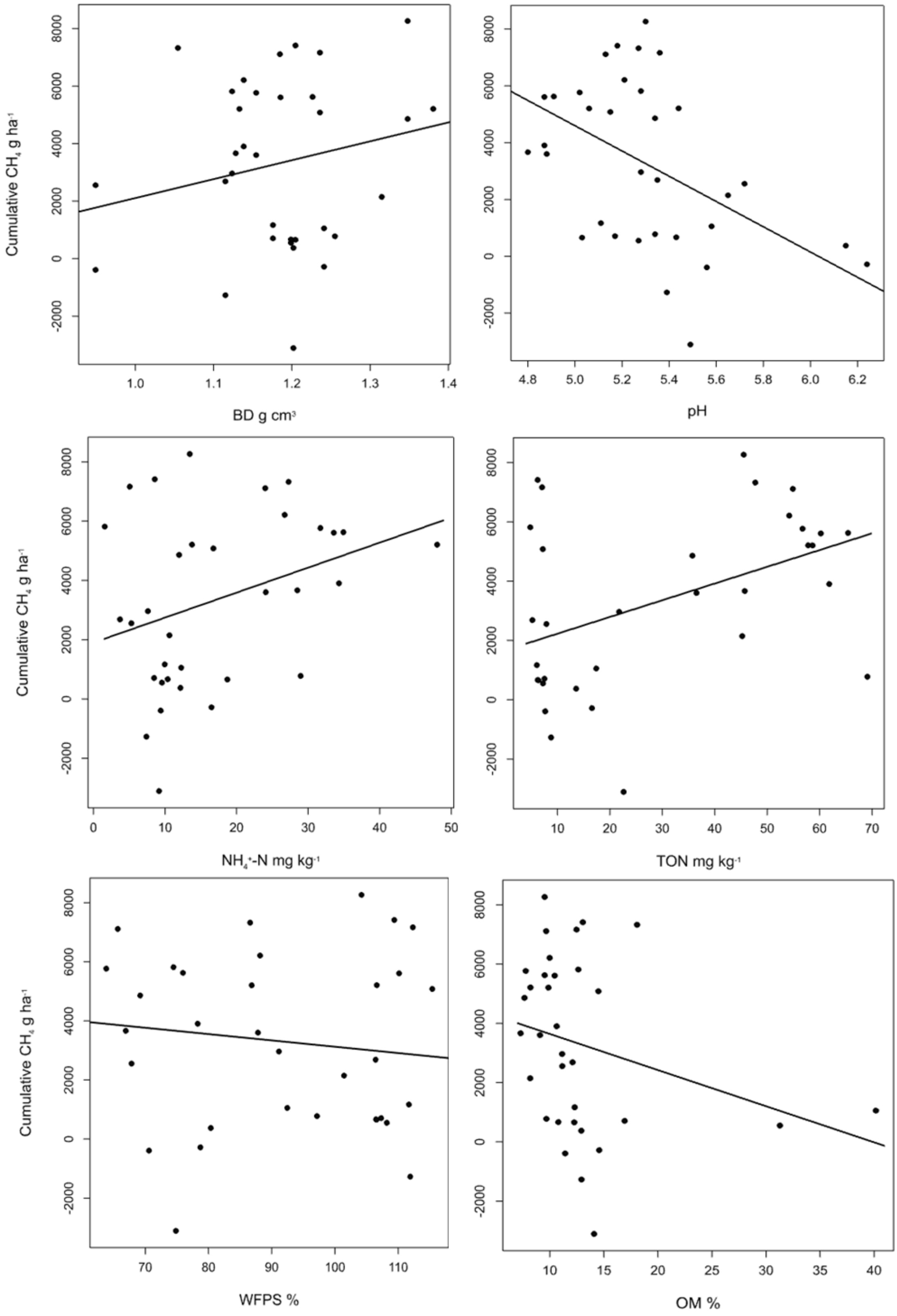

Figure 7. 8: Relationships between cumulative CH_4 emissions and each of the explanatory soil variables.

7.3.3.4 Global warming potential

Soil N_2O-based GWP ranged from 1223.5 ± 362.0 (willow riparian buffer) to 10 225.1 ± 4735.7 (no buffer control) kg CO_2-eq. ha^{-1} $year^{-1}$ (Table 7.6). Significantly the highest GWP was generated from the no-buffer control, which was, however not significantly different from the upslope maize. On the other hand, soil CH_4-based GWP ranged from 3.4 ± 35.9 (woodland riparian buffer) to 282.9 ± 33.4 (no buffer control) kg CO_2-eq. ha^{-1} $year^{-1}$. Despite the large GWP found in the no buffer control, it was not significantly different to the other treatments, but to the woodland riparian buffer. (Table 7.6).

Table 7. 6: Land-use effects on global warming potential.

	GWP (kg CO_2-C equivalent ha^{-1} $year^{-1}$)	
Land-use	**N_2O**	**CH_4**
Upslope maize	6181.7 ± 3545.5 ab	282.9 ± 33.4 a
No-buffer control	10225.1 ± 4735.6 a	273.8 ± 42.2 a
Grass Buffer	2518.3 ± 1689.3 bc	177.5 ± 68.1 a
Willow Buffer	1223.5 ± 362.0 c	134.7 ± 74.0 ab
Woodland Buffer	1771.3 ± 800.5 bc	3.4 ± 35.9 b

†All values are mean ± standard error (upslope maize: *n* = 12, no-buffer control: *n* = 3, grass, woodland and willow riparian buffers: *n* = 6).

‡Values with the same letter in a row are not statically different at 5% significance level.

7.4 Discussion

7.4.1 Gas emissions

7.4.1.1 Soil and environmental controls of gas fluxes

a. Nitrous oxide

The largest peak N_2O flux observed in the upslope maize coincided largest %WFPS in the treatment and followed N fertilizer application events in the upslope maize and no buffer control (Figure 7.3 A and B). Soil N_2O fluxes following N fertilizer application events are known to increase with increasing soil water content; most rapidly above

70% WFPS, wherein denitrification is a dominant process (Abbasi and Adams, 2000; Dobbie *et al.*, 1999; Granli and Bockman, 1994; Skiba and Ball, 2002). As one of the major drivers of N_2O production, soil moisture directly affects N_2O production and consumption through its influence on the N-substrate availability, soil aeration and metabolic activity of N_2O-producing microorganisms; all controlling the capacity of soil to produce N_2O (Di *et al.*, 2014; Khalil and Baggs, 2005; Simona *et al.*, 2004). Fertilizer N increases soil mineral N availability; a substrate for dominant N_2O microbial producing reactions; nitrification and denitrification (Butterbach-Bahl *et al.*, 2013; Dobbie *et al.*, 1999). Thus, the higher fluxes were expected after fertilizer N application in the no-buffer control and the upslope maize of the current study, similar to other studies; particularly Halvorson *et al.* (2008) and Van Groenigen *et al.* (2004), who reported that soil N_2O emissions increased linearly with increasing fertilizer N. This was further attested to by an increase in N_2O emissions with increasing soil TON and NH_4^+-N (Figure 7.6). This was also in agreement with previous work, particularly Mosier (1994), Mosier *et al.* (1996), and Barton and Schipper (2001). Notably, the woodland and willow riparian buffers had the highest %WFPS but were characterised by lower N_2O emissions during the peak flux. On top of the low N substrate due to the fact that the riparian buffers were not fertilized, this could have been due to reduced diffusion in the high soil moisture causing a further reduction of N_2O to N_2 (Balaine *et al.*, 2013; Hamonts *et al.*, 2013). On the other hand, the no-buffer control and upslope maize had larger fluxes; which further highlights the interactive role of soil moisture and mineral N in enhanced N_2O production (Klemedtsson *et al.*, 1988). The no buffer control emitted 15.6% while the upslope maize 5.4%, which means that of the total fertilizer N added, 21% was lost as N_2O in the 6-month experimental period. The current study, however, did not use stable isotopes to ascertain this.

b. Methane

The overall positive CH_4 emissions from all treatments are most likely the result of the high %WFPS experienced during most of the experimental period. The upper values (~5 kg C ha^{-1}) are similar to those reported by Groh *et al.* (2015). A number of field investigations have identified soil water content as one of the critical controls of CH_4 production and consumption in soils from different ecosystems (Butterbach-Bahl and Papen, 2002; Khalil and Baggs, 2005; Kim *et al.*, 2010; Wu *et al.*, 2010). Similarly, in the current study, the peak CH_4 fluxes followed immediately after the highest %WFPS (Figure 7.3 C). High soil moisture contents are documented drivers of CH_4 production and emissions in soils; as a group of strictly anaerobic bacteria biologically produce a majority of CH_4 in reduced environments (Ehhalt *et al.*, 2001; Ehhalt and Schmidt, 1978; Yang and Chang, 1998). Soil moisture directly affects the production of soil CH_4 through its influence on C-substrate availability, soil aeration, and metabolic activity of CH_4 producing microorganisms; all affecting the capacity of soil to produce or consume CH_4 (Khalil and Baggs, 2005; Simona *et al.*, 2004). Further, the role of soil moisture in CH_4 production and subsequent emissions was attested to by the low (sometimes negative) CH_4 fluxes we observed; coinciding with low soil %WFPS at the end of August (Figure 6.3 A); similar to Luo *et al.* (2013). The latter work observed that soil moisture affected soil CH_4 consumption through its effect on substrate availability and redistribution, soil aeration, and the metabolic activity of microorganisms.

7.4.1.2 Gas emissions in upslope maize and downslope riparian buffers

a. Nitrous oxide

For a riparian buffer to be considered an atmospheric concern, it must emit more N_2O than the cropland it serves (Fisher *et al.*, 2014). In the current study, the no-buffer control proved to be an atmospheric concern, since it generated the highest N_2O

emissions compared to the upslope maize and the three vegetated riparian buffers (Figure 7.4 A). The maximum cumulative emissions of 20 kg N_2O (~12 kg N ha^{-1}) are similar to Kim *et al.* (2009) (2-year study) and Groh *et al.* (2015) (1-year study), who observed 24 and 14.8 kg N_2O ha^{-1}, respectively, in maize in a Humid Continental climate. The high N_2O emissions observed in the no-buffer control could have been due to applied fertilizer N (particularly readily available inorganic N); which increased mineral N availability for the N_2O-producing nitrification and denitrification processes, similar to the responses reported by other authors; particularly Dobbie *et al.* (1999) and Butterbach-Bahl *et al.* (2013). In fact, the high N_2O emissions in the no-buffer control shows a downward movement of the fertilizer applied N with rainwater. This was further attested to by the high mineral N (both TON and NH_4^+) in the no-buffer control compared to the remainder of the treatments (Table 7.2) and an increase in N_2O emissions with every increase in mineral N (Figure 7.7). The fact that the vegetated riparian buffers had low N_2O emissions shows that they served their purpose of intercepting and processing N to N_2 through denitrification induced by their high soil moisture (Groffman *et al.*, 1991; Knowles, 1982) before it was delivered off-site. Interestingly, the vegetated riparian buffers had ideal conditions to promote full denitrification, reducing N to N_2, especially at the high moisture and in the case of willow and woodland the high organic matter and potentially available C which explains their low N_2O compared to the upslope pasture and no buffer control. The low N_2O emissions in the vegetated riparian buffers could also be a result of the fact that the riparian buffer strips were not directly fertilized; further highlighting the role of fertilizer N in increasing mineral N availability for N_2O producing processes; similar to Davis *et al.* (2019), Hefting *et al.* (2003) and Iqbal *et al.* (2015). The second highest N_2O

emissions observed in the upslope maize could have also been due to the N fertilizer applied.

b. Methane

The fact that the upslope maize and no-buffer control treatments exhibited high CH_4 emissions may have been a result of NH_4^+-N based fertilizer N applied in the two treatments, since NH_4^+-N has been shown to inhibit CH_4 oxidation to CO_2 (Hütsch, 1998; Kravchenko *et al.*, 2002; Tlustos *et al.*, 1998); which often results in a net increase in CH_4 emitted from soil (Bronson and Mosier, 1994). This inhibition is thought to be either a general salt effect (Gulledge and Schimel, 1998), a competition between ammonia (NH_3) and CH_4 for methane monooxygenase enzymes (Bédard and Knowles, 1989), or non-competitive inhibition by hydroxylamine (NH_2OH) or NO_2^- produced during NH_3 oxidation (King and Schnell, 1994). To further emphasize the role of mineral N in inhibiting CH_4 oxidation, the three vegetated and unfertilized riparian buffers had significantly lower CH_4 emissions than the upslope maize and the no-buffer control (Figure 7.4 B).

7.4.1.3 Global warming potential

The high N_2O and CH_4-based GWP observed in the no buffer control shows that growing a maize crop without implementing riparian buffer vegetation may increase the risk of global warming potential. On a positive note, implementing the willow and woodland riparian buffers in tandem with a maize crop may reduce the risk of global warming potential while addressing water quality problems for which they are usually implemented.

7.4.2 Implications of the findings

The findings of the current study have a number of implications especially in research and environmental policy. Although riparian buffer strips are conventionally implemented to help tackle the widespread water quality issues in the UK, and elsewhere globally, associated with intensive farming, the current work demonstrates the co-benefits of their uptake for gaseous emissions. Many countries globally are focussing on the urgent need to tackle the climate emergency and robust evidence on the efficacy of interventions for reducing harmful gaseous emissions is critical for engaging stakeholders including farmers.

The current findings also have implications for the calibration of process-based models to simulate N_2O and CH_4 emissions from croplands and/ or riparian buffer areas with varying vegetation, which has been challenging in the past due to lack of data availability. Process-based models including the Riparian Ecosystem Management Model (REMM) (Lowrance *et al.*, 2000) have been calibrated to simulate soil processes under riparian buffers. For example, REMM has been used to simulate groundwater movement, water table depths, surface runoff and annual hydrological budgets (Inamdar *et al.*, 1999b) and N, P, and C cycling (Dukes and Evans, 2003; Inamdar *et al.*, 1999a) interactions between varying riparian buffer systems. Other watershed models, such as the Soil and Water Assessment Tool (SWAT), have been calibrated to assess the effectiveness of riparian buffers for reducing total organic N in a watershed (Lee *et al.*, 2020). A landscape model, the Morgan-Morgan-Finney topographic wetness index (MMF-TWI), has been calibrated to simulate erosion reduction using riparian buffers (Smith *et al.*, 2018a). But, to the best knowledge, none of these mechanistic models have been calibrated to simulate N_2O and CH_4 emissions from riparian buffers and further compared with emissions from croplands. Whilst some process-based models, e.g., Denitrification-Decomposition (DNDC), have been calibrated to simulate biogeochemical cycles including N_2O emissions from different grass riparian buffers in Illinois, USA (Gopalakrishnan *et al.*, 2012), to the best of our knowledge, this model has not been being calibrated to simulate N_2O and CH_4 emissions from riparian buffers in the UK.

7.4.3 Limitations of the study

One of the significant limitations of the current study is that it was based on a replicated plot-scale experimental facility. This means that the findings represent the climate, soil, and environmental conditions prevailing at the experimental site at North Wyke, Devon, UK. Similar conditions in terms of annual rainfall, soils and farming systems, are present in 1843 km^2 of farmed land across England (Collins *et al.*, 2021). The results provide robust data on short-term N and C gaseous emissions and clearly, longer-term measurements would help in confirming the current findings. Although the static chamber is cheaper and easy to use, further shortcomings may be associated with it as it was used to trap the gases in the field for the current experiment. For instance Healy *et al.* (1996) and Rochette (2011) reported that insertion of chambers into the soil may limit lateral gas exchange. However, Rochette (2011) suggested that such limitations may be overcome by inserting the chamber collars prior to chamber use. But the same author argued that this practice may affect soil temperature by shading the soil and affect soil moisture by preventing soil run-off as well as affect gas exchange through formation of shrinkage cracks at the collar-soil interface.

7.5 Conclusion

The replicated plot-scale facility experiment showed that the N-fertilized no-buffer control and upslope areas used for maize cropping are significant N_2O and CH_4 sources, respectively. Furthermore, the low N_2O and CH_4-based GWP from the willow (11 and 49% that of no buffer control, respectively) and woodland (17 and 1.2% that of no-buffer control) riparian buffers show that the willow mitigated global warming potential when implemented for water quality protection purposes in this maize crop. Accordingly, the results attest to the unintended benefits of riparian buffers for reducing gaseous emissions, despite primarily being implemented as water quality protection measures. The type of work undertaken in the current experiment herein demonstrates the importance of gathering data for co-benefits and trade-offs associated with the management of agroecosystems.

7.6 References

Abbasi, M., Adams W., 2000. Estimation of simultaneous nitrification and denitrification in grassland soil associated with urea-N using ^{15}N and nitrification inhibitor. *Biology & Fertility of Soils*, 31:38-44.

Balaine, N., Clough T.J., Beare M.H., Thomas S.M., Meenken E.D., Ross J.G., 2013. Changes in relative gas diffusivity explain soil nitrous oxide flux dynamics. *Soil Science Society of America Journal*, 77:1496-1505.

Ball, B.C., Scott A., Parker J.P., 1999. Field N_2O, CO_2 and CH_4 fluxes in relation to tillage, compaction and soil quality in Scotland. *Soil & Tillage Research*, 53:29-39.

Barton, L., Schipper L., 2001. Regulation of nitrous oxide emissions from soils irrigated with dairy farm effluent. *Journal of Environmental Quality*, 30:1881-1887.

Bechmann, M.E., Bøe F., 2021. Soil tillage and crop growth effects on surface and subsurface runoff, loss of soil, phosphorus and nitrogen in a cold climate. *Land*, 10:77.

Bédard, C., Knowles R., 1989. Physiology, biochemistry, and specific inhibitors of CH_4, NH_4^+, and CO oxidation by methanotrophs and nitrifiers. *Microbiology & Molecular Biology Reviews*, 53:68-84.

Bowden, W.B., 1986. Gaseous nitrogen emmissions from undisturbed terrestrial ecosystems: An assessment of their impacts on local and global nitrogen budgets. *Biogeochemistry*, 2:249-279.

Bronson, K., Mosier A., 1994. Suppression of methane oxidation in aerobic soil by nitrogen fertilizers, nitrification inhibitors, and urease inhibitors. *Biology & Fertility of Soils*, 17:263-268.

Butterbach-Bahl, K., Baggs E.M., Dannenmann M., Kiese R., Zechmeister-Boltenstern S., 2013. Nitrous oxide emissions from soils: how well do we understand the processes and their controls? *Philosophical Transactions of the Royal Society B-Biological Sciences*, 368. DOI: 10.1098/rstb.2013.0122.

Butterbach-Bahl, K., Papen H., 2002. Four years continuous record of CH_4-exchange between the atmosphere and untreated and limed soil of a N-saturated spruce and beech forest ecosystem in Germany. *Plant & Soil*, 240:77-90.

Collins, A., Zhang Y., Upadhayay H., Pulley S., Granger S., Harris P., Sint H., Griffith B., 2021. Current advisory interventions for grazing ruminant farming cannot close exceedance of modern background sediment loss–Assessment using an instrumented farm platform and modelled scaling out. *Environmental Science & Policy*, 116:114-127.

Conrad, R., 2007. Microbial ecology of methanogens and methanotrophs. *Advances in Agronomy*, 96:1-63.

Davidson, E.A., 2009. Microbial processes of production and consumption of nitric oxide, nitrous oxide and methane, In: PA Matson and RC HArris (Eds.), Biogenic Trace Gases : Measuring Emisions from Soil and Water, Wiley-Blackwell, Oxford.

Davis, M.P., Groh T.A., Jaynes D.B., Parkin T.B., Isenhart T.M., 2019. Nitrous oxide emissions from saturated riparian buffers: Are we trading a water quality problem for an air quality problem? *Journal Environmental Quality*, 48:261-269.

Di, H.J., Cameron K.C., Podolyan A., Robinson A., 2014. Effect of soil moisture status and a nitrification inhibitor, dicyandiamide, on ammonia oxidizer and denitrifier growth and nitrous oxide emissions in a grassland soil. *Soil Biology & Biochemistry*, 73:59-68.

Dobbie, K., McTaggart I.P., Smith K., 1999. Nitrous oxide emissions from intensive agricultural systems: variations between crops and seasons, key driving variables, and mean emission factors. *Journal of Geophysical Research: Atmospheres*, 104:26891-26899.

Dukes, M., Evans R., 2003. Riparian ecosystem management model: Hydrology performance and sensitivity in the North Carolina middle coastal plain. *Transactions of the American Society of Agricultural & Biological Engineers*, 46:1567. DOI: doi: 10.13031/2013.15645.

Dutaur, L., Verchot L.V., 2007. A global inventory of the soil CH_4 sink. *Global Biogeochemical Cycles*, 21.

Ehhalt, D., Prather M., Dentener F., Derwent R., Dlugokencky E.J., Holland E., Isaksen I., Katima J., Kirchhoff V., Matson P., 2001. Atmospheric chemistry and greenhouse gases, Pacific Northwest National Lab.(PNNL), Richland, WA (United States).

Ehhalt, D., Schmidt U., 1978. Sources and sinks of atmospheric methane. *Pure & Applied Geophysics*, 116:452-464.

Firestone, M*.,* 1982. Biological denitrification, In: F Stevenson (Ed.), Nitrogen in agricultural soils, American Society of Agronomy, Inc. Crop Science Society of America, Inc. Soil Science Society of America Inc., Madison, Wisconsin, USA. pp. 289-326.

Fisher, K., Jacinthe P., Vidon P., Liu X., Baker M., 2014. Nitrous oxide emission from cropland and adjacent riparian buffers in contrasting hydrogeomorphic settings. *Journal of Environmental Quality*, 43:338-348.

Friedel, J., Munch J., Fischer W., 1996. Soil microbial properties and the assessment of available soil organic matter in a haplic luvisol after several years of different cultivation and crop rotation. *Soil Biology & Biochemistry*, 28:479-488.

Gopalakrishnan, G., Cristina Negri M., Salas W., 2012. Modeling biogeochemical impacts of bioenergy buffers with perennial grasses for a row-crop field in Illinois. *Global Change Biology - Bioenergy*, 4:739-750.

Granli, T., Bockman O.C., 1994. Nitrous oxide from agriculture. *Norwegian Journal of Agricultural Sciences*, 12:94-128.

Groffman, P.M., Axelrod E.A., Lemunyon J.L., Sullivan W.M., 1991. Denitrification in grass and forest vegetated filter strips. *Journal of Environmental Quality*, 20:671-674.

Groh, T.A., Gentry L.E., David M.B., 2015. Nitrogen removal and greenhouse gas emissions from constructed wetlands receiving tile drainage water. *Journal of Environmental Quality*, 44:1001-1010.

Gronle, A., Lux G., Böhm H., Schmidtke K., Wild M., Demmel M., Brandhuber R., Wilbois K.-P., Heß J., 2015. Effect of ploughing depth and mechanical soil loading on soil physical properties, weed infestation, yield performance and grain quality in sole and intercrops of pea and oat in organic farming. *Soil & Tillage Research*, 148:59-73.

Gulledge, J., Schimel J.P., 1998. Moisture control over atmospheric CH_4 consumption and CO_2 production in diverse Alaskan soils. *Soil Biology & Biochemistry*, 30:1127-1132.

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*, 37:1337-1344.

Hamonts, K., Balaine N., Moltchanova E., Beare M., Thomas S., Wakelin S.A., O'Callaghan M., Condron L.M., Clough T.J., 2013. Influence of soil bulk density and matric potential on microbial dynamics, inorganic N transformations, N_2O and N_2 fluxes following urea deposition. *Soil Biology & Biochemistry*, 65:1-11.

Healy, R.W., Striegl R.G., Russell T.F., Hutchinson G.L., Livingston G.P., 1996. Numerical Evaluation of Static-Chamber Measurements of Soil—Atmosphere Gas Exchange: Identification of Physical Processes. *Soil Science Society of America Journal*, 60:740-747.

Hefting, M.M., Bobbink R., de Caluwe H., 2003. Nitrous oxide emission and denitrification in chronically nitrate-loaded riparian buffer zones. *Journal of Environmental Quality*, 32:1194-1203.

Hütsch, B., 1998. Methane oxidation in arable soil as inhibited by ammonium, nitrite, and organic manure with respect to soil pH. *Biology & Fertility of Soils*, 28:27-35.

Inamdar, S., Lowrance R., Altier L., Williams R., Hubbard R., 1999a. Riparian Ecosystem Management Model (REMM): II. Testing of the water quality and nutrient cycling component for a coastal plain riparian system. *Transactions of the ASABE*, 42:1691.

Inamdar, S., Sheridan J., Williams R., Bosch D., Lowrance R., Altier L., Thomas D., 1999b. Riparian ecosystem management model (REMM): I. Testing of the hydrologic component for a coastal plain riparian system. *Transactions of the ASABE*, 42:1679.

IPCC, 2006. 2006 IPCC guidelines for national greenhouse gas inventories Institute for Global Environmental Strategies Hayama, Japan.

IPCC, 2008. IPCC, 2007: climate change 2007: synthesis report, IPCC.

IPCC, 2014. Climate change 2014: synthesis report. Contribution of Working Groups I, II and III to the fifth assessment report of the Intergovernmental Panel on Climate Change IPCC.

Iqbal, J., Parkin T.B., Helmers M.J., Zhou X., Castellano M.J., 2015. Denitrification and nitrous oxide emissions in annual croplands, perennial grass buffers, and restored perennial grasslands. *Soil Science Society of America Journal*, 79:239-250.

Jacinthe, P.-A., Vidon P., Fisher K., Liu X., Baker M., 2015. Soil methane and carbon dioxide fluxes from cropland and riparian buffers in different hydrogeomorphic settings. *Journal of Environmental Quality*, 44:1080-1090.

Jacinthe, P., Bills J., Tedesco L., Barr R., 2012. Nitrous oxide emission from riparian buffers in relation to vegetation and flood frequency. *Journal of Environmental Quality*, 41:95-105.

Khalil, M., Baggs E., 2005. CH_4 oxidation and N_2O emissions at varied soil water-filled pore spaces and headspace CH_4 concentrations. *Soil Biology & Biochemistry*, 37:1785-1794.

Kim, D.-G., Isenhart T.M., Parkin T.B., Schultz R.C., Loynachan T.E., 2010. Methane flux in cropland and adjacent riparian buffers with different vegetation covers. *Journal of Environmental Quality*, 39:97-105.

Kim, D., Isenhart T.M., Parkin T.B., Schultz R.C., Loynachan T.E., Raich J.W., 2009. Nitrous oxide emissions from riparian forest buffers, warm-season and cool-season grass filters, and crop fields. *Biogeosciences Discussions*, 6:607.

King, G.M., Schnell S., 1994. Ammonium and nitrite inhibition of methane oxidation by Methylobacter albus BG8 and Methylosinus trichosporium OB3b at low methane concentrations. *Applied and Environmental Microbiology*, 60:3508-3513.

Klemedtsson, L., Svensson B., Rosswall T., 1988. Relationships between soil moisture content and nitrous oxide production during nitrification and denitrification. *Biology & Fertility of Soils*, 6:106-111.

Knowles, R., 1982. Denitrification. *Microbiology Review*, 46:43.

Kravchenko, I., Boeckx P., Galchenko V., Van Cleemput O., 2002. Short-and medium-term effects of NH_4^+ on CH_4 and N_2O fluxes in arable soils with a different texture. *Soil Biology & Biochemistry*, 34:669-678.

Le Mer, J., Roger P., 2001. Production, oxidation, emission and consumption of methane by soils: a review. *European Journal of Soil Biology*, 37:25-50.

Lee, S., McCarty G.W., Moglen G.E., Li X., Wallace C.W., 2020. Assessing the effectiveness of riparian buffers for reducing organic nitrogen loads in the Coastal Plain of the Chesapeake Bay watershed using a watershed model. *Journal of Hydrology*, 585:124779.

Lowrance, R., Altier L., Williams R., Inamdar S., Sheridan J., Bosch D., Hubbard R., Thomas D., 2000. REMM: The riparian ecosystem management model. *Journal of Soil & Water Conservation*, 55:27-34.

Luo, G., Kiese R., Wolf B., Butterbach-Bahl K., 2013. Effects of soil temperature and moisture on methane uptake and nitrous oxide emissions across three different ecosystem types. *Biogeosciences*, 10:3205-3219.

Megonigal, J.P., Guenther A.B., 2008. Methane emissions from upland forest soils and vegetation. *Tree Physiology*, 28:491-498.

Mosier, A., 1994. Nitrous oxide emissions from agricultural soils. *Fertilizer Research*, 37:191-200.

Mosier, A., Duxbury J., Freney J., Heinemeyer O., Minami K., 1996. Nitrous oxide emissions from agricultural fields: Assessment, measurement and mitigation, Progress in Nitrogen Cycling Studies, Springer. pp. 589-602.

Müller, C., Stevens R., Laughlin R., Jäger H.-J., 2004. Microbial processes and the site of N_2O production in a temperate grassland soil. *Soil Biology & Biochemistry*, 36:453-461.

Neugschwandtner, R., Liebhard P., Kaul H., Wagentristl H., 2014. Soil chemical properties as affected by tillage and crop rotation in a long-term field experiment. *Plant, Soil & Environment*, 60:57-62.

Ouattara, K., Ouattara B., Assa A., Sédogo P.M., 2006. Long-term effect of ploughing, and organic matter input on soil moisture characteristics of a Ferric Lixisol in Burkina Faso. *Soil & Tillage Research*, 88:217-224.

Ramaswamy, V., Boucher O., Haigh J., Hauglustine D., Haywood J., Myhre G., Nakajima T., Shi G., Solomon S., 2001. Radiative forcing of climate. *Climate Change,* 349.

Reinsch, T., Loges R., Kluß C., Taube F., 2018. Renovation and conversion of permanent grass-clover swards to pasture or crops: Effects on annual N_2O emissions in the year after ploughing. *Soil & Tillage Research*, 175:119-129.

Rochette, P., 2011. Towards a standard non-steady-state chamber methodology for measuring soil N_2O emissions. *Animal Feed Science & Technology,* 166:141-146.

Shen, Y., McLaughlin N., Zhang X., Xu M., Liang A., 2018. Effect of tillage and crop residue on soil temperature following planting for a Black soil in Northeast China. *Scientific Reports*, 8:1-9.

Simona, C., Ariangelo D.P.R., John G., Nina N., Ruben M., Jose S.J., 2004. Nitrous oxide and methane fluxes from soils of the Orinoco savanna under different land uses. *Global Change Biology*, 10:1947-1960.

Skiba, U., Ball B., 2002. The effect of soil texture and soil drainage on emissions of nitric oxide and nitrous oxide. *Soil Use & Management*, 18:56-60.

Smith, H.G., Peñuela A., Sangster H., Sellami H., Boyle J., Chiverrell R., Schillereff D., Riley M., 2018a. Simulating a century of soil erosion for agricultural catchment management. *Earth Surface Processes & Landforms*, 43:2089-2105.

Smith, K., Ball T., Conen F., Dobbie K., Massheder J., Rey A., 2018b. Exchange of greenhouse gases between soil and atmosphere: interactions of soil physical factors and biological processes. *European Journal of Soil Science*, 69:10-20.

Smith, K., Dobbie K., Ball B., Bakken L., Sitaula B., Hansen S., Brumme R., Borken W., Christensen S., Priemé A., 2000. Oxidation of atmospheric methane in Northern European soils, comparison with other ecosystems, and uncertainties in the global terrestrial sink. *Global Change Biology*, 6:791-803.

Stehfest, E., Bouwman L., 2006. N_2O and NO emission from agricultural fields and soils under natural vegetation: summarizing available measurement data and modeling of global annual emissions. *Nutrient Cycling in Agroecosystems*, 74:207-228.

Tlustos, P., Willison T., Baker J., Murphy D., Pavlikova D., Goulding K., Powlson D., 1998. Short-term effects of nitrogen on methane oxidation in soils. *Biology & Fertility of Soils*, 28:64-70.

Ulén, B., 1997. Nutrient losses by surface run-off from soils with winter cover crops and spring-ploughed soils in the south of Sweden. *Soil & Tillage Research*, 44:165-177.

Van Groenigen, J., Kasper v.G., Velthof G., Van den Pol-van Dasselaar A., Kuikman P., 2004. Nitrous oxide emissions from silage maize fields under different mineral nitrogen fertilizer and slurry applications. *Plant & Soil*, 263:101-111.

Wang, Q., Bai Y., Gao H., He J., Chen H., Chesney R., Kuhn N., Li H., 2008. Soil chemical properties and microbial biomass after 16 years of no-tillage farming on the Loess Plateau, China. *Geoderma*, 144:502-508.

Wu, X., Yao Z., Brüggemann N., Shen Z., Wolf B., Dannenmann M., Zheng X., Butterbach-Bahl K., 2010. Effects of soil moisture and temperature on CO_2 and CH_4 soil–atmosphere exchange of various land use/cover types in a semi-arid grassland in Inner Mongolia, China. *Soil Biology & Biochemistry*, 42:773-787.

Yamulki, S., Jarvis S., 2002. Short-term effects of tillage and compaction on nitrous oxide, nitric oxide, nitrogen dioxide, methane and carbon dioxide fluxes from grassland. *Biology & Fertility of Soils*, 36:224-231.

Yang, S.-S., Chang H.-L., 1998. Effect of environmental conditions on methane production and emission from paddy soil. *Agriculture, Ecosystems, & Environment*, 69:69-80.

Yao, P., Li X., Nan W., Li X., Zhang H., Shen Y., Li S., Yue S., 2017. Carbon dioxide fluxes in soil profiles as affected by maize phenology and nitrogen fertilization in the semiarid Loess Plateau. *Agriculture, Ecosystems, & Environment*, 236:120-133.

Zhang, T., Huang X., Yang Y., Li Y., Dahlgren R.A., 2016. Spatial and temporal variability in nitrous oxide and methane emissions in urban riparian zones of the Pearl River Delta. *Environmental Science & Pollution Research*, 23:1552-1564.

CHAPTER 8.0

SOIL CO_2 EMISSIONS IN FODDER MAIZE WITH AND WITHOUT RIPARIAN BUFFER STRIPS OF DIFFERING VEGETATION

This chapter is *published* in the journal “**Agroforestry Systems**” as:

Dlamini JC, Tesfamariam EH, Dunn RM, Evans J, Hawkins JMB, Blackwell MSA, Collins AL, Cardenas LM. Soil carbon dioxide (CO_2) fluxes in permanent upslope pasture and downslope riparian buffers with varying vegetation. *Agroforestry Systems*, 2022. DOI: https://doi.org/10.1007/s10457-022-00756-5

Corresponding author: JCD

Author contributions:

JCD, JE, EHT, LMC, RD, MSAB, ALC: Conceptualization, Methodology, Software. **JCD:** Data curation, Writing- Original draft preparation. **JCD, JE:** Visualization, Investigation. **EHT, LMC:** Supervision. **JCD, JE:** Software, Validation. **EHT, LMC, RD, MSAB, ALC:** Writing- Reviewing and Editing.

Abstract

Vegetated land areas play a significant role in determining the fate of carbon in the global carbon cycle. Riparian buffer vegetation is primarily implemented for water quality purposes as they attenuate pollutants from immediately adjacent croplands before reaching freshwater systems. However, their prevailing conditions promote processes that produce soil CO_2. Despite this, the understanding of soil CO_2 emissions from riparian buffer vegetation and a direct comparison with adjacent croplands they serve remain elusive. In order to quantify the extent of CO_2 emissions in such an agro system, soil CO_2 emissions were measured simultaneously with soil and environmental variables for six months in a replicated plot-scale facility comprising of maize cropping served by three vegetated riparian buffers, namely: (i) a novel grass riparian buffer; (ii) a willow riparian buffer, and (iii) a woodland riparian buffer. These buffered treatments were compared with a no-buffer control. The woodland (322.9 ± 3.1 kg ha^{-1}) and grass (285 ± 2.7 kg ha^{-1}) riparian buffer treatments (not significant to each other) generated significantly ($p =< 0.0001$) the largest CO_2 compared to the remainder of the treatments. The results of the current study suggest that during maize production in general, the woodland and grass riparian buffers serving a maize crop pose a CO_2 threat. The results of the current study further point to the need to consider the disbenefits of CO_2 emissions when choosing riparian buffer vegetation primarily for improving the sustainability of water resources.

8.1 Introduction

Vegetated land areas play a pivotal role in understanding C dynamics in the global C cycle (Stauch *et al.*, 2008). Vegetated riparian buffer strips are primarily introduced between croplands and waterbodies to attenuate NPS pollutants from agricultural lands from reaching freshwater ecosystems (Jaynes and Isenhart, 2014; Lowrance *et al.*, 2002; Valkama *et al.*, 2018). The vegetated riparian buffers usually recycle high organic matter that elevates soil C and are usually anoxic since they sustain high soil moisture from seasonally high water tables (Jacinthe, 2015). These conditions, as mentioned above, and the processing of the pollutants promote biological processes including denitrification, mineralization, and fermentation, produce greenhouse gases, including CO_2 (Kayranli *et al.*, 2010; Thangarajan *et al.*, 2013).

Soil CO_2 production and subsequent emissions indicate soil respiration in the biota, as both are influenced by factors controlling CO_2 movement in the soil (Raich and Potter, 1995; Raich and Schlesinger, 1992). Soil temperature and moisture are considered the most dominant factors influencing soil CO_2, as they influence CO_2-producing soil biological activities (Davidson *et al.*, 1998). Soil organic matter provides a substrate for soil CO_2 producing microbial activities, and its decomposition result in CO_2 emissions (Harrison-Kirk *et al.*, 2013); thus, it is expected that vegetation that recycles the most organic matter might have high CO_2 emissions. However, this may be highly dependent on the labile C fraction in the organic matter, as Dlamini *et al.* (2020) observed that soils containing highly labile C result in high CO_2.

Previous studies, De Carlo *et al.* (2019) and Jacinthe (2015), have compared CO_2 emissions from different riparian buffer vegetation types. Despite previous works, understanding of CO_2 fluxes and their controlling soil and environmental variables riparian buffer strips and a direct comparison with the cropland they serve remain elusive. Therefore, this study aimed to evaluate the unintended emissions of CO_2 and enrich the understanding of their soil and environmental controls from maize production, which had both buffered and un-buffered downslope.

8.2 Materials and Methods

Information on the chapter's (i) study site description, (ii) experimental design and treatments, and (iii) field measurements are detailed in Chapter 3 (section 3.2). The methodology described below (Statistical analysis) is specific to this chapter and is not presented in Chapter 3. Further details on the management of the upslope maize crop from which the soil CO_2 was measured in conjunction with the different riparian buffer vegetation are detailed in Chapter 7 (section 7.2).

8.2.1 Data processing and statistical analysis

Linear mixed models in Genstat 20 (VSN International, Hemel Hempstead, United Kingdom) were used to determine whether cumulative CO_2 differed with treatment. The random structure of each model (accounting for the experiment structure) was *block/plot/chamber*. The fixed structure (accounting for treatment effects) was *treatment type/ (treatment*distance.* This model gives the following four tests in the output: (i) *Treatment type* – tests main maize cropped area vs. no-buffer control vs. riparian buffers, (ii) *Treatment type*treatment* – tests for differences between grass, willow, and woodland riparian buffers, (iii) *Treatment type*buffer distance* – tests for the difference between upper and lower riparian buffer areas, and (iv) *Treatment type*treatment*buffer distance* – tests for interaction between riparian buffer type and distance.

Linear mixed models with the same random and fixed structures as those used for CO_2 were used to determine whether any measured soil variables (BD, pH, NH_4^+, TON, %WFPS, and OM) differed with treatment. Pearson's correlation coefficient (r) was used to indicate the strength of relationships between soil and environmental factors and CO_2 emissions. This was tested more formally in the linear mixed models described above. If linear mixed models indicated that treatment differences were present, LSDs were calculated to determine which specific treatment pairs resulted in the significant differences in CO_2 emissions. All graphs were generated using Sigma Plot (Systat Software Inc., CA, USA).

8.3 Results

8.3.1 Soil CO_2 fluxes

Figure 8.1 (B) shows daily CO_2 fluxes for the different treatment during the experimental period. Soil CO_2 fluxes were < 289.3 kg $ha^{-1}day^{-1}$ at the commencement of the experiment, with the largest of 289.3 ± 14.5 kg $ha^{-1}day^{-1}$ recorded in the woodland riparian buffer. The woodland and grass riparian buffers maintained predominately larger (up to 547.9 ± 33.9 kg $ha^{-1}day^{-1}$ from the woodland buffer on the 13th of September 2019) whilst the willow riparian buffer, no-buffer control and upslope maize maintained lower fluxes throughout the experimental period. Prior to the larger peak, two smaller peaks of 449 ± 76.6 and 516.9 ± 57.9 kg $ha^{-1}day^{-1}$ were observed in the woodland riparian buffer on the 4th of July and the 2nd of August 2019, respectively.

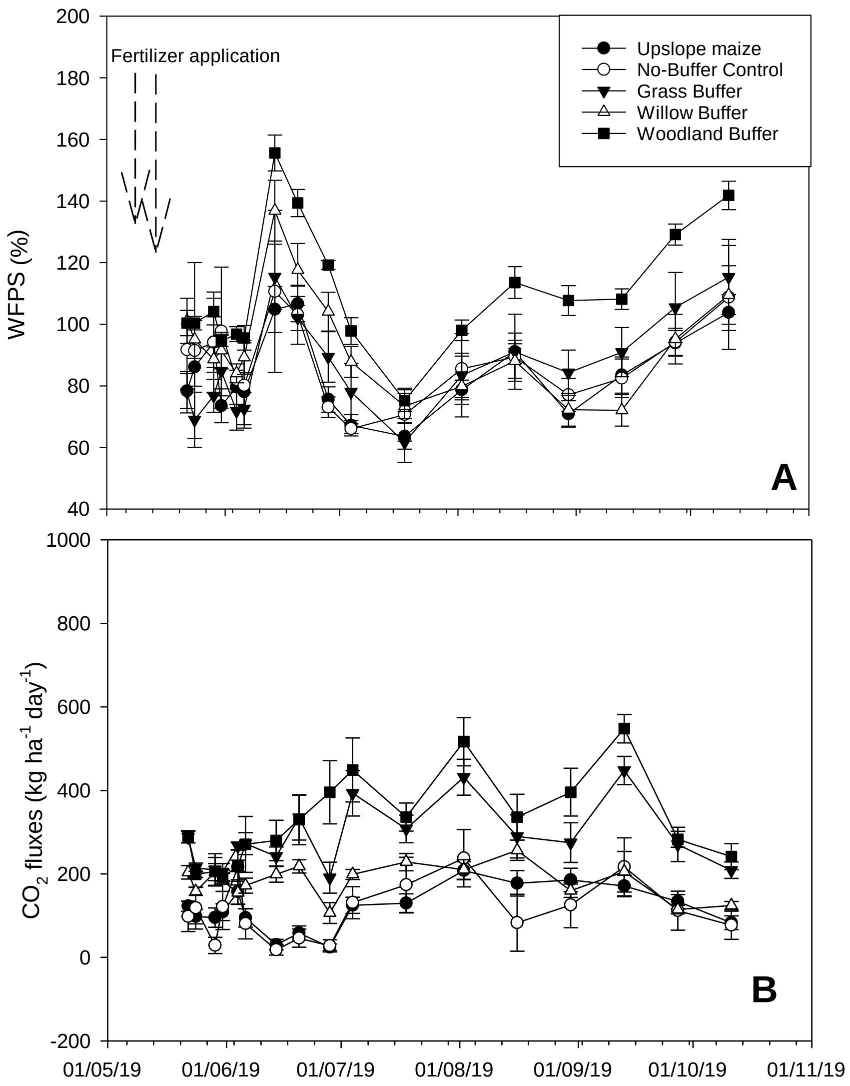

Figure 8. 1: Daily (A) soil %WFPS, and (B) soil CO_2 fluxes, in the upslope maize and downslope riparian buffers. Data points and error bars represent the treatment means (upslope maize: *n*=12, no-buffer control: *n* = 3, grass, woodland and willow riparian buffers: *n*=6) and SE during each sampling day.

8.3.2 Cumulative CO_2 emissions

Figure 8.2 shows cumulative CO_2 emissions in the descending order: woodland riparian buffer: 322.9 ± 3.1 kg ha^{-1} > grass riparian buffer: 285 ± 2.7 kg ha^{-1} > 182 ± 1.9 kg ha^{-1} > upslope maize: 118 ± 2.0 kg ha^{-1} > no buffer control: 112.7 ± 3.6 kg ha^{-1}. Significantly large ($p =<0.0001$) emissions were obtained from the woodland and grass riparian buffer treatments (not significant to each other) compared to the remainder of the treatments.

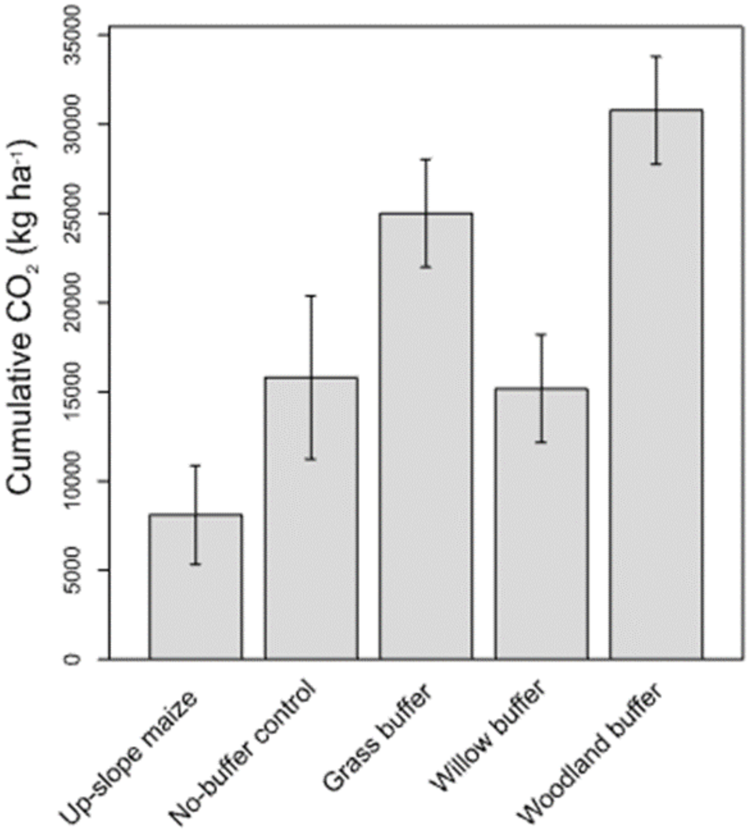

Figure 8. 2: Cumulative CO_2 emissions for the whole experimental period from the upslope maize and different downslope buffer vegetation. Error bars represent 95% confidence intervals (upslope maize: *n*=12, no-buffer control: *n*=3, grass, woodland and willow riparian buffers: *n*=6). Vertical lines are 95% confidence intervals.

8.3.3 Relationships between CO_2 emissions and measured soil variables

Soil pH (r = 0.14; *p = 0.03*), NH_4^+-N (r =-0.44; *p = 0.003*), and TON (r = -0.58; *p = <0.0001*) had significant relationships with cumulative CO_2 (Table 8.1 and Figure 8.3).

Table 8. 1: *p*-values for the slope of the fitted line of the model for CO_2 and measured soil variables.

Variable	Intercept	Standard error intercept	Slope	Standard error slope	*p*-value
BD	51694	24844	-29098	20934.2	0.177
pH	-74174	40215	17262	7531.9	0.030
NH_4	26065	4046	-513.5	158.81	0.003
TON	25805	2916	-289.4	71.08	<0.001
%WFPS	-417.9	10318	194.4	111.72	0.098
OM	10385	4328	543.2	287.85	0.071

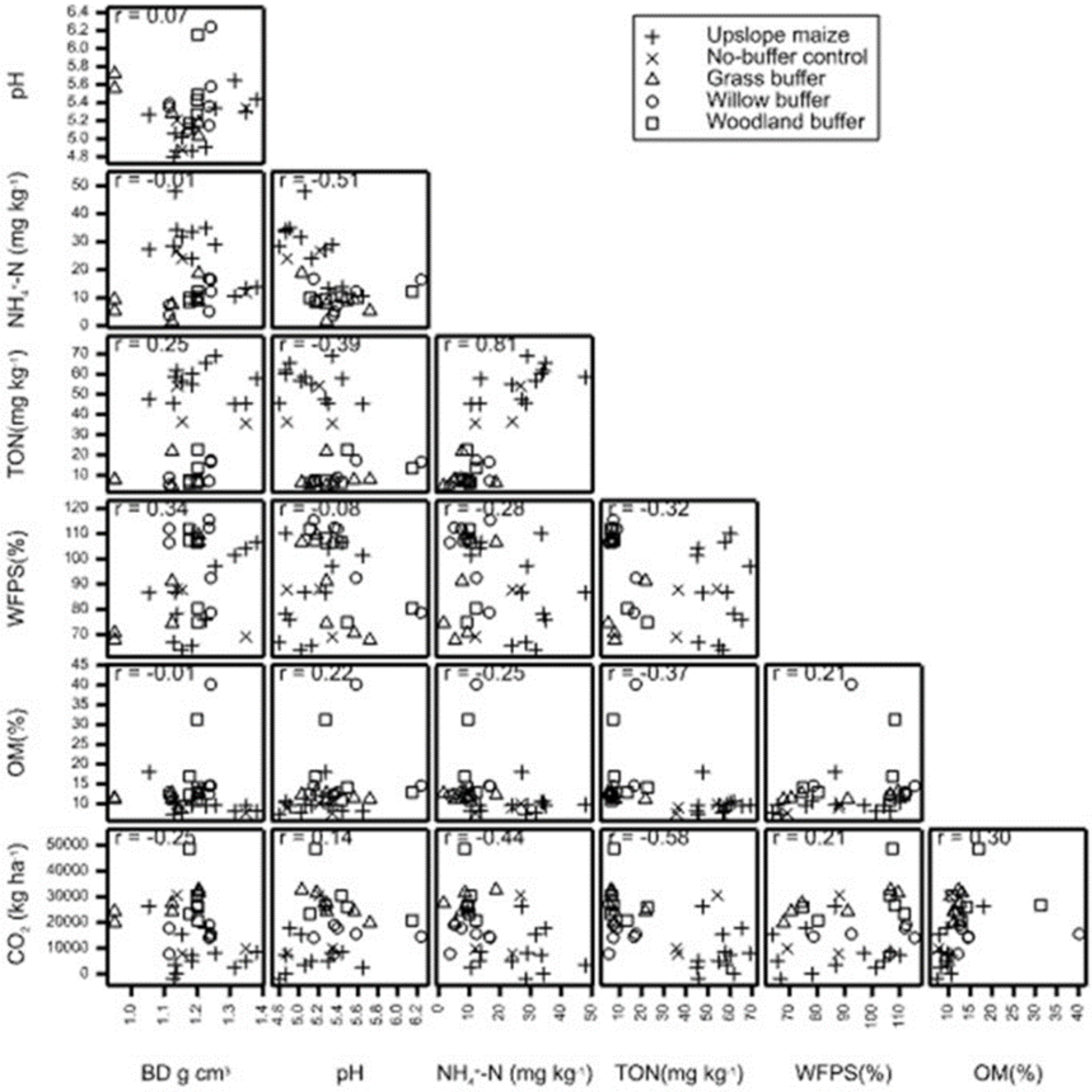

Figure 8. 3: Scatterplot showing the relationships between the variables soil pH, NH_4^+-N, TON, %WFPS, OM, BD and cumulative CO_2 emissions for the upslope maize and the downslope riparian buffers with different vegetation treatments. r = Pearson’s correlation coefficient.

Soil CO_2 emissions increased with increasing soil pH, OM, and %WFPS, and decreased with increasing soil BD, NH_4^+-N, and TON (Figure 8.4).

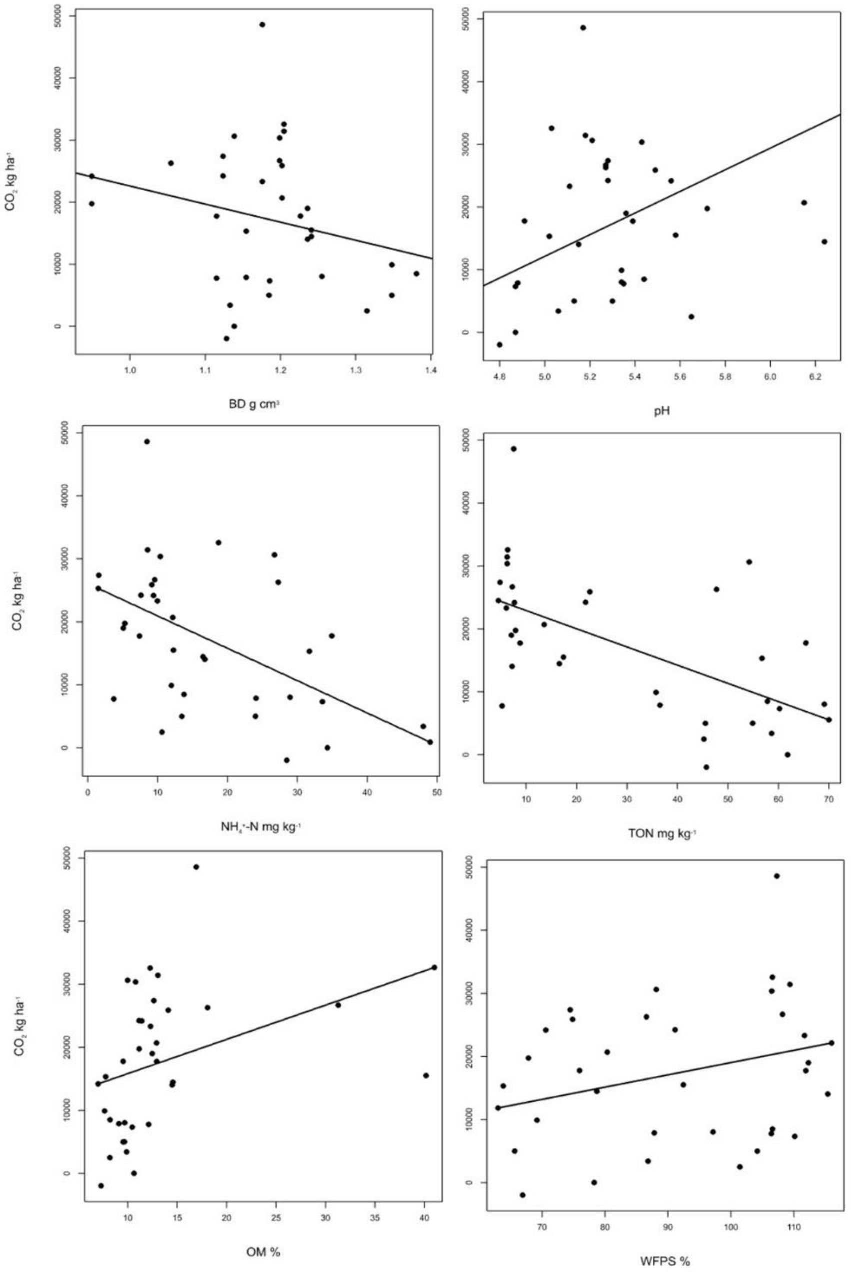

Figure 8. 4: Relationships between cumulative CO_2 emissions and each of the explanatory soil variables.

8.4 Discussion

8.4.1 Soil CO_2 emissions

8.4.1.1 Soil CO_2 and environmental controls

Significantly higher CO_2 were consistently measured in the grass and woodland riparian buffers similar to previous studies which compared soil respiration between croplands and riparian buffer systems, particularly Tufekcioglu *et al.* (2001), and Jacinthe *et al.* (2015). The previous authors primarily linked the high CO_2 fluxes in the vegetated riparian buffers compared to croplands to soil moisture and temperature differences as influenced by land-use differences of the two systems. In the current study, the consistently high CO_2 fluxes in the woodland riparian buffer is linked to the higher soil moisture it maintained throughout the experimental period (Figure 8.1 A and B). The findings of the current study are consistent with other authors particularly Singh and Gupta (1977), Davidson *et al.* (1998), and Reth *et al.* (2005) who observed that high soil moisture regulated soil CO_2 diffusion, hence its pronounced influence on soil respiration. Also, Sainju *et al.* (2010) reported a peak of CO_2 fluxes immediately after a rainfall event (>10 mm), which further highlights the role of soil moisture in CO_2 production. The current study also observed an increase in CO_2 with increasing soil moisture (Figure 8.4).

Soil temperature is an environmental factor controlling CO_2-producing microbial reactions provided that other factors including soil moisture and C contents are not limiting. For instance, Li *et al.* (2013) observed that only 26-34% of the seasonal variations in soil CO_2 fluxes could be explained by soil temperature in exponential equations, implying that there were other factors affecting soil CO_2. In the current experiment the upslope maize and no-buffer control had a row crop which was mostly bare and hence prone to higher temperatures compared to the permanently ground covered-riparian buffers, but the latter treatments had low soil OM and consequently low CO_2 fluxes. This then highlight the interactive role of soil C addition, temperature and soil moisture in CO_2 production, similar to other authors, particularly Davidson *et al.* (1998), Epron *et al.* (1999), and Šimek *et al.* (2004)

Denitrification is a process carried out by facultative anaerobes and free energy, N_2, and CO_2 are produced as a result of electron transfer between NO_3^- and C (Hume *et al.*, 2002; Tusneem, 1970). The process is highly dependent on the supply of readily available C and accounts for about 37% of the CO_2 from the soil respiration systems (Ingersoll and Baker, 1998; Rastogi *et al.*, 2002). Thus, the predominantly higher soil moisture in the woodland riparian buffer coupled with high OM compared to the remainder of the treatments during the experimental period (Figure 8.1 A and B) could have promoted denitrification in the treatment which consequently increased CO_2 fluxes similar to other authors, particularly Beauchamp *et al.* (1989) and Dlamini *et al.* (2020).

8.4.1.2 Soil CO_2 emissions in upslope maize and downslope riparian buffers

High CO_2 emissions from the riparian buffers compared to croplands are linked to differences in biomass, C inputs and density of plant roots in the two systems (Jacinthe *et al.*, 2015; Tufekcioglu *et al.*, 2001). The relatively high soil OM in the woodland riparian buffer may have resulted to increased C-priming effect hence the high CO_2 emissions in the treatment, similar to findings by Šimek *et al.* (2004). Despite having the largest amount of soil OM, the willow riparian buffer had low CO_2 emissions, which could imply that the treatment had a low labile C fraction similar to other studies including Dlamini *et al.* (2020), but C fractions were not quantified in the current study. The previous author reported that compounds with highly labile C (readily available for microbial reactions) result to high CO_2 compared to those with less labile C. Soil respiration is an indicator of total soil biological activity, and therefore an indicator of overall soil quality (Tufekcioglu *et al.*, 2001; Visser and Parkinson, 1992), and vegetated riparian buffers have been reported to improve soil quality characteristics compared to croplands (Musfiq-Us-Salehin *et al.*, 2020; Seobi *et al.*, 2005; Udawatta *et al.*, 2009). Thus, the resultant higher soil CO_2 emission from the grass and woodland riparian buffers compared to the upslope maize and no-buffer control was expected in the current experiment.

8.5 Conclusion

The replicated plot-scale facility experiment showed that when different riparian buffer vegetation are introduced for water quality purposes in maize production, the woodland and grass riparian buffers may pose a CO_2 threat. Accordingly, the results attest to the unintended effects of some riparian buffer vegetation in emitting soil CO_2, particularly when primarily implemented for water quality protection measures. The type of work undertaken in the experiment herein demonstrates the importance of gathering data for co-benefits and trade-offs associated with the management of agroecosystems.

8.6 References

Beauchamp, E.G., Trevors J.T., Paul J.W., 1989. Carbon Sources for Bacterial Denitrification, In: BA Stewart (Ed.), Advances in Soil Science, Springer., New York. pp. 113-142.

Davidson, E.A., Belk E., Boone R.D., 1998. Soil water content and temperature as independent or confounded factors controlling soil respiration in a temperate mixed hardwood forest. *Global Change Biology*, 4:217-227.

De Carlo, N., Oelbermann M., Gordon A., 2019. Carbon dioxide emissions: Spatiotemporal variation in a young and mature riparian forest. *Ecological Engineering*, 138:353-361.

Dlamini, J., Chadwick D., Hawkins J., Martinez J., Scholefield D., Ma Y., Cárdenas L., 2020. Evaluating the potential of different carbon sources to promote denitrification. *Journal of Agricultural Sciences*, 158 (3) :1-12.

Epron, D., Farque L., Lucot É., Badot P.-M., 1999. Soil CO_2 efflux in a beech forest: dependence on soil temperature and soil water content. *Annals of Forest Science*, 56:221-226.

Harrison-Kirk, T., Beare M., Meenken E., Condron L., 2013. Soil organic matter and texture affect responses to dry/wet cycles: Effects on carbon dioxide and nitrous oxide emissions. *Soil Biology & Biochemistry*, 57:43-55.

Hume, N.P., Fleming M.S., Horne A.J., 2002. Denitrification potential and carbon quality of four aquatic plants in wetland microcosms. *Soil Science Society of America Journal*, 66:1706-1712.

Ingersoll, T.L., Baker L.A., 1998. Nitratfe removal in wetland microcosms. *Water Research*, 32:677-684.

Jacinthe, P.-A., Vidon P., Fisher K., Liu X., Baker M., 2015. Soil methane and carbon dioxide fluxes from cropland and riparian buffers in different hydrogeomorphic settings. *Journal of Environmental Quality*, 44:1080-1090.

Jacinthe, P., 2015. Carbon dioxide and methane fluxes in variably-flooded riparian forests. *Geoderma*, 241:41-50.

Jaynes, D.B., Isenhart T.M., 2014. Reconnecting tile drainage to riparian buffer hydrology for enhanced nitrate removal. *Journal of Environmental Quality*, 43:631-638. DOI: 10.2134/jeq2013.08.0331.

Kayranli, B., Scholz M., Mustafa A., Hedmark Å., 2010. Carbon storage and fluxes within freshwater wetlands: a critical review. *Wetlands*, 30:111-124. DOI: DOI 10.1007/s13157-009-0003-4.

Li, L.-J., You M.-Y., Shi H.-A., Ding X.-L., Qiao Y.-F., Han X.-Z., 2013. Soil CO_2 emissions from a cultivated Mollisol: Effects of organic amendments, soil temperature, and moisture. *European Journal of Soil Biology*, 55:83-90.

Lowrance, R., Dabney S., Schultz R., 2002. Improving water and soil quality with conservation buffers. *Journal of Soil & Water Conservation*, 57:36A-43A.

Musfiq-Us-Salehin, S., Ghimire R., Angadi S.V., Idowu O.J., 2020. Grass buffer strips improve soil health and mitigate greenhouse gas emissions in center-pivot irrigated cropping systems. *Sustainability*, 12:6014.

Raich, J.W., Potter C.S., 1995. Global patterns of carbon dioxide emissions from soils. *Global Biogeochemical Cycles*, 9:23-36.

Raich, J.W., Schlesinger W.H., 1992. The global carbon dioxide flux in soil respiration and its relationship to vegetation and climate. *Tellus B: Chemical & Physical Meteorology*, 44:81-99.

Rastogi, M., Singh S., Pathak H., 2002. Emission of carbon dioxide from soil. *Current Science*, 82:510-517.

Reth, S., Reichstein M., Falge E., 2005. The effect of soil water content, soil temperature, soil pH-value and the root mass on soil CO_2 efflux–a modified model. *Plant & Soil*, 268:21-33.

Sainju, U.M., Jabro J.D., Caesar-TonThat T., 2010. Tillage, cropping sequence, and nitrogen fertilization effects on dryland soil carbon dioxide emission and carbon content. *Journal of Environmental Quality*, 39:935-945.

Seobi, T., Anderson S., Udawatta R., Gantzer C., 2005. Influence of grass and agroforestry buffer strips on soil hydraulic properties for an Albaqualf. *Soil Science Society of America Journal*, 69:893-901.

Šimek, M., Elhottová D., Klimeš F., Hopkins D.W., 2004. Emissions of N_2O and CO_2, denitrification measurements and soil properties in red clover and ryegrass stands. *Soil Biology & Biochemistry*, 36:9-21.

Singh, J.S., Gupta S., 1977. Plant decomposition and soil respiration in terrestrial ecosystems. *The Botanical Review*, 43:449-528.

Stauch, V.J., Jarvis A.J., Schulz K., 2008. Estimation of net carbon exchange using eddy covariance CO_2 flux observations and a stochastic model. *Journal of Geophysical Research : Atmospheres*, 113.

Thangarajan, R., Bolan N.S., Tian G., Naidu R., Kunhikrishnan A., 2013. Role of organic amendment application on greenhouse gas emission from soil. *Science of the Total Environment*, 465:72-96.

Tufekcioglu, A., Raich J.W., Isenhart T.M., Schultz R.C., 2001. Soil respiration within riparian buffers and adjacent crop fields. *Plant & Soil*, 229:117-124.

Tusneem, M.E., 1970. *Nitrogen transformations in waterlogged soil*, PhD Thesis, Louisiana State University, Louisiana, United States.

Udawatta, R.P., Kremer R.J., Garrett H.E., Anderson S.H., 2009. Soil enzyme activities and physical properties in a watershed managed under agroforestry and row-crop systems. *Agriculture, Ecosystems, & Environment*, 131:98-104.

Valkama, E., Usva K., Saarinen M., Uusi-Kämppä J., 2018. A meta-analysis on nitrogen retention by buffer zones. *Journal of Environmental Quality,* 48 (2): 270-279.

Visser, S., Parkinson D., 1992. Soil biological criteria as indicators of soil quality: soil microorganisms. *American Journal of Alternative Agriculture*, 7(1-2):33-37.

CHAPTER 9.0

EMISSIONS OF NO, N_2O, N_2 AND CO_2 FROM INCUBATED SOILS FROM A CROPLAND AND RIPARIAN BUFFERS

This chapter is *prepared* for submission in the journal “**Soil Use and Management**” as:

Dlamini JC, Tesfamariam EH, Verbeeck M, Loick N, Louro-Lopez A, Hawkins JMB, Blackwell MSA, Dunn R, Collins AL, Cardenas LM. Comparison of NO, N_2O, N_2, and CO_2 fluxes in incubated soils from cropland, and varying riparian buffers

Corresponding author: JCD

Author contribution:

JCD, JE, EHT, LMC, RD, MSAB, NL ALC: Conceptualization, Methodology, Software. **JCD:** Data curation, Writing- Original draft preparation. **JD, JE, NL:** Visualization, Investigation. **EHT, LMC:** Supervision. **JCD, JE:** Software, Validation. **EHT, LMC, RD, MSAB, ALC, MV, ALL, NL:** Writing- Reviewing and Editing.

Abstract

Vegetated riparian buffer areas are implemented as an intervention to intercept and retain diffuse NPS pollutants emanating from adjacent agricultural lands. Their location in the agricultural landscapes allows riparian buffers areas to process pollutants that would otherwise reach freshwater bodies and further maintain soil conditions promoting soil processes including denitrification and respiration. The processes dominant in the riparian buffer areas produce soil gases, including NO, N_2O, N_2 and CO_2, some of which are environmentally harmful. To investigate the magnitude of the emissions of the previous gases and further understand their soil drivers, soil samples were collected from upslope cropland and downslope grass, willow, and woodland riparian buffers in a replicated plot scale experimental facility. The soils were re-packed into cores, an amendment containing potassium nitrate (KNO_3^-) and glucose (labile C) added, and after that incubated in a specialized laboratory DENItrification System (DENIS). The resulting NO, N_2O, N_2, and CO_2 emissions were measured simultaneously, with the highest NO (2.9 ± 0.31 mg N m^{-2}), and N_2O (1413.4 ± 448.3 mg N m^{-2}) losses generated by the grass riparian buffer treatment and the highest N_2 (698.1 ± 270.3 mg N m^{-2}) and CO_2 (27558.3 ± 128.9 mg C m^{-2}) produced by the willow riparian buffer treatment. Under the given soil conditions (high soil moisture, N, and readily available C source), the results of the current study showed that the grass riparian buffer produced 88.6%, 94.5%, and 92.4% more NO, and 99.9%, 99.2 and 98.6% more N_2O than the cropland, and willow and woodland riparian buffers treatments, respectively. On the other hand, the willow riparian buffer generated 19.8%, 13.1%, and 87.7% more CO_2 and 29.9%, 11.6%, 9.8% more N_2 than the cropland, and grass and woodland riparian buffers treatments, respectively. Thus, the results show that careful selection of riparian buffer vegetation is essential

for co-addressing water and air quality, especially in areas with similar conditions to the current study. Further experiments are suggested at field setting and natural environmental conditions can help understand the extent of NO, N_2O, N_2, and CO_2 emissions in soils developing under varying land management practices.

9.1 Introduction

A drastic increase in the loss of N compounds from agricultural land into surface and shallow groundwater has been reported for many settings globally (Olsthoorn and Fong, 1998; Xia *et al.*, 2020). The installation of vegetated riparian buffer strips, defined as transitionary boundaries disconnecting direct interaction between freshwater ecosystems and agricultural land (Naiman *et al.*, 2010), is a widely-used mitigation measure for NPS pollution on the premise that such features can intercept and remove N-inputs before delivery to freshwater ecosystems (Valkama *et al.*, 2019; Xia *et al.*, 2020). The distinctive location of riparian buffer strips in the landscape is vital for retaining excessive NO_3^- loads transferred from agricultural land (Gundersen *et al.*, 2010; Jaynes and Isenhart, 2014). Riparian buffers would likely have high denitrification rates because of the high C, their high moisture content and the relatively high supply of mineral N (particularly NO_3^-) from the intensively managed upslope agricultural land they serve (Dlamini *et al.*, 2020; Groffman and Crawford, 2003; Schultz *et al.*, 2000; Valkama *et al.*, 2019). Processes including C-mineralisation and microbial respiration have been reported to increase CO_2 production in riparian buffers (Jacinthe *et al.,* 2015: Tufekcioglu *et al.,* 2001).

The production and subsequent emissions of gases have been studied in riparian buffer systems (Lowrance, 1992; Silverthorn and Richardson, 2021; Watts and Seitzinger, 2000); however, it has been mainly overlooked in the case of the actual riparian buffer areas themselves, which receive substantial NO_3^- (an additional pollutant) loads from neighbouring agricultural land (Groffman *et al.*, 1998). Moreover, direct comparisons of soil drivers of these gases between agricultural land and riparian buffers have received little attention (Davis *et al.*, 2019; Iqbal *et al.*, 2015) thereby underscoring the need to address this important evidence gap.

Compared to agricultural land, riparian buffers improve soil characteristics, for instance they increase soil C sequestration, soil physical (i.e., bulk density and hydraulic conductivity), chemical (i.e., total N), and biological properties (i.e., enzymatic activity and microbial biomass N and C) (Paudel *et al.*, 2011; Seobi *et al.*, 2005; Udawatta *et al.*, 2009; Weerasekara *et al.*, 2016) which affect soil gas production and their subsequent emissions. It is well known that, significant NO_3^- loads from agricultural lands seep into C-rich (increased by high OM deposited through plant litter), and predominantly wet vegetated riparian buffers, and NO_3^- is further removed through denitrification (Fisher *et al.*, 2014; Groffman *et al.*, 1991; Groh *et al.*, 2015; Iqbal *et al.*, 2015). For example, in a forest riparian buffer, Pinay *et al.* (1993) observed that denitrification was mediated by organic C energy source, anaerobiosis, and NO_3^- supply; which are controlled by vegetation cover, soil moisture saturation and topography. Also, Groh *et al.* (2019) observed that the potential for increased C decomposition, mineralisation, and availability promoted denitrification in an established grass riparian buffer. Denitrification is a bacterially-mediated process whereby NO_3^- is transformed to NO_2^-, NO, N_2O and finally N_2, under limited O_2 by facultative anaerobes (Robertson and Groffman, 2007; Stevens *et al.*, 1997). Most denitrifying bacteria couple NO_3^- reduction with organic C oxidation to gain energy, making C-supply a usual requirement for denitrification to occur, a process which further produces CO_2 (Beauchamp *et al.*, 1989). Furthermore, the OM decomposition in vegetated riparian buffer may promote CO_2 production in such agro systems (Tufekcioglu *et al.,* 2001).

Considering the role of soil characteristics developed under different riparian buffer vegetation and its prevailing environmental conditions in promoting the production and the subsequent emissions of gases including NO, N_2O, N_2 and CO_2, through various processes i.e., denitrification, may result in their unintended trade-offs between emissions to water and the atmosphere (Groffman *et al.,* 2000; Jacinthe *et al.,* 2015).Further, Groffman *et al.* (2002) previously suggested the IPCC's inventories may be improved by including measurements from riparian buffer strips . Despite this, there is still limited evidence in existing literature on GHG measurements from riparian buffer areas and a concomitant lack of direct comparisons with corresponding emissions from neighbouring agricultural land.

Given this important evidence gap, this study aimed to (i) compare NO, N_2O, N_2 and CO_2 emissions from incubated soils sourced from upslope cropland and downslope grass, willow and woodland riparian buffer areas, in a replicated plot scale experimental facility, and (ii) correlate emissions with soil properties to better understand the underlying processes driving the emissions, by measuring potential denitrification under high soil water conditions (i.e., 85% WFPS). It was hypothesized that high NO, N_2O and N_2 emissions will result in soil sourced from the cropland as a result of residual N fertilizer from the permanent pasture and the grass riparian buffer treatment will generate larger CO_2 due to higher organic matter cycling and soil moisture retention.

9.2 Materials and Methods

Information on the chapter's (i) study site description, (ii) experimental design and treatments, and (iii) field measurements are detailed in Chapter 3 (section 3.2). The methodology used in this chapter is related to soil collection, experimental setup of the incubation system, soil, and gas measurements, and statistical analyses used in this chapter which is not presented in Chapter 3.

9.2.1 Soil collection and preparation

Soil samples were collected at site and plots described in section 3.2.2 and Figure 3.1. Two weeks before the experiment, soil samples (enough soil to fill a 25 kg plastic bag per treatment) were collected along a zigzag pattern (Wollenhaupt and Wolkowski, 1994) from each replicated plot area (cropland: 340-m^2 and each riparian buffer strip: 100-m^2) and the plots with no-buffer control were omitted for the current study (Figure 3.1). Samples were collected up to a depth of 10-cm using a soil corer, with a semi-cylindrical gouge auger (2-3 cm diameter and 10-cm in length) (Poulton *et al.*, 2018). Samples from the different plots of the same treatment were mixed to generate four composite samples that generated the following treatments: (i) cropland soil; (ii) grass riparian buffer soil; (iii) willow riparian buffer soil, and (iv) woodland riparian buffer soils. After sampling, plant roots and residues and stones were removed, and the soils were sieved to <2 mm using a wire-mesh sieve. Subsequently, samples were air-dried at room temperature until the gravimetric soil moisture; a method that determines the weight of water contained in the soil samples relative to weight of dry soil, reached ~30% H_2O before core-packing, amendment application and subsequently the vessel incubation. The gravimetric soil moisture analysis involved taking six sub-samples from each of the sieved composite soils, accurately weighing them, completely drying them out in an oven (i.e., 105°C until constant dry weight), and thereafter reweighing the dry samples. Thereafter, moisture content in subsamples samples was determined and expressed percentage (Equation 9.1).

$$\%SM = 100 * \frac{W_{w} - D_{w}}{D_{w}} \qquad (Eq. 9.1)$$

Where, *%SM* is the soil moisture content, W_w is soil wet weight, and D_w is soil dry weight.

9.2.2 Experimental set-up

The experiment was carried out using a specialized gas-flow-soil-core incubation system; the DENitrification Incubation System (DENIS) (Cárdenas *et al.*, 2003) in which environmental conditions can be controlled. The different soils were packed into 12-cylindrical stainless-steel vessels with a diameter of 14 cm up to a height of 6 cm and to BD values to simulate those prevailing in the field of 1.3 g cm^{-3} (cropland soil), 1.0 g cm^{-3} (grass riparian buffer soil), and 1.2 g cm^{-3} (willow and woodland riparian buffer soils). After core packing, soil moisture was adjusted to 85% WFPS; taking the amendment that was to be applied later into consideration, similar to values used in other authors (Bergstermann *et al.*, 2011; Loick *et al.*, 2017; Loick *et al.*, 2016; Meijide *et al.*, 2010) studying potential denitrification. The native atmosphere was removed by flushing the soil cores from the bottom using a mixture of He: O_2 (80:20) at a flow rate of 30 ml min^{-1} for 14 hours, in order to facilitate N_2 measurement. Thereafter, flow rates were decreased to 12 ml min^{-1}, and the flow re-directed over the surface of the soil cores for three days before amendment application in order to measure baseline emissions. Since the objective of the study was to investigate potential denitrification as a result of high %WFPS, O_2 was kept at atmospheric levels in the gas mixture (20%).

In order to promote potential denitrification, KNO_3 was added as an N source and glucose as a C source (Morley and Baggs, 2010). The amendment was applied at a rate equivalent to 400 kg C ha^{-1} (i.e., 1583.6 mg kg^{-1} dry soil) and N at a rate equivalent to 75 kg N ha^{-1} (i.e., 857.3 mg kg^{-1} dry soil), similar to previous studies (Bergstermann *et al.*, 2011; Loick *et al.*, 2017; Loick *et al.*, 2016; Meijide *et al.*, 2010).

The C and N amendments were applied to each vessel with 45 ml distilled water (taking into consideration the amount of water added earlier, thus making-up the 85% WFPS incubation soil moisture) and vessels incubated at 20°C for the 16-day experimental period (NO analysis was terminated at day-15 as a result of equipment malfunction).

9.2.3 Gas analyses

The DENIS is a flow-through system, where continuously flowing gas samples are analysed from each incubation vessel in turn. A new vessel was sampled every 8-minutes for the duration of the experimental period resulting in the same vessel being measured every 96 minutes. CO_2 and N_2O fluxes were quantified using a Perkin Elmer Clarus 500 gas chromatograph (Perkin Elmer Instruments, Beaconsfield, UK), equipped with an ECD. Concentrations of NO were determined by chemiluminescence (Sievers NOA280i, GE Instruments, Colorado, USA), and N_2 fluxes measured by gas chromatography fitted with a helium ionization detector (VICI AG International, Schenkon, Switzerland) (Cárdenas *et al.*, 2003). Concentrations for each gas were corrected for the core surface area, and the daily-measured flow rates passing through each vessel. Gas fluxes and emissions were calculated on an mg C and N m^{-2} hr^{-1} and mg C and N m^{-2} (cumulative for the whole experimental period) basis, respectively.

9.2.4 Soil analyses

Before incubation, three replicate samples were taken from each of the sieved composite soils (cropland, and grass, willow and woodland riparian buffers), and, after incubation, soils from each vessel (corresponding with each treatment) were mixed and a sub-sample was taken and analysed as a replicate. From each replicate soil pH, OM, TON, and NH_4^+-N were determined. Soil pH [within-lab precision: 0.015] was measured in a soil: water suspension of 1:2.5 (Jenway pH meter, Staffordshire, UK) and OM was determined using the LOI technique (Wilke, 2005). TON [comprised of NO_2^- and NO_3^-, the former considered to be negligible] and NH_4^+-N [within-lab precision (RSD%): 7.2%] were quantified following the method by Searle (1984). For this, 20 g moist soil samples were mixed with 2 M KCl at a ratio of 1:5, filtered using Whatman 2V filter paper, and thereafter soil extracts colometrically analysed using Aquakem^{TM} analyser (Thermo Fisher Scientific, Finland).

9.2.5 Data processing and statistical analysis

Genstat 20th edition (VSN International Ltd, Hemel Hempstead, UK) was used to perform statistical analysis. The cumulative CO_2, N_2O, NO, and N_2 emissions were estimated by calculating the area under the curve after linear interpolation between sampling points for the length of the peak of gas fluxes (i.e., 0-48 hours for NO, 0-72 hours for N_2O, 60-384 hours for N_2 and 0-144 hours for CO_2). Prior to statistical tests, the data was checked for normal distribution using the Shapiro-Wilk test (D'Agostino, 2017; Welham *et al.*, 2014). ANOVA at $p < 0.05$ was performed according to the GLM procedure when the Shapiro-Wilk test was significant ($p > 0.05$) in order to assess differences in cumulative emissions of each gas and measured soil characteristics between treatments. Fisher's LSD test was used to ascertain differences among treatments when treatment effects proved to be significant. The relationships between cumulative gas emissions and measured soil variables (OM, TO-N, NH_4^+-N, pH, BD, and %WFPS) were investigated using Pearson correlation (Statistix. Inc., Talahassee, USA). All tests were performed at the 5% probability level.

9.3 Results

9.3.1 Soil characteristics

Before incubation, the soil pH was higher (*$p = 0.0001$*) in the woodland riparian buffer (5.1 ± 0.01), compared to the cropland, and the grass and the willow riparian buffer treatments (Table 9.1). Similar to the status before incubation, at post-incubation, the woodland riparian buffer (5.1 ± 0.02) maintained higher (*$p = 0.0003$*) soil pH compared to the cropland, and the grass and the willow riparian buffer treatments. Soil BD did not change before and after incubation, with values of 1.3 g cm^{-3} (cropland), 1.0 g cm^{-3} (grass riparian buffer), and 1.2 g cm^{-3} (willow and woodland riparian buffers) (Table 8.1). Prior to incubation, the soil TON was greater (*$p = 0.0003$*) in the cropland (62.5 ± 1.3 mg kg^{-1} dry soil) compared to all the three riparian buffer treatments. Even after incubation, the soil TON remained higher (*$p = 0.0001$*) in the cropland (156.7 ± 2.2 mg kg^{-1} dry soil) compared to the three riparian buffer treatments. Also, after incubation, soil TON had increased by 2.5 and 19 to 22.5-fold for the cropland and the three different riparian buffer treatments, respectively, from the status before incubation. Compared to the status before incubation, soil TON in the cropland had increased by 9.4% and the increase in riparian buffer treatments were almost similar, with the grass, willow, and woodland riparian buffers increasing by 124%, 134% and 115%, respectively. Notably, the riparian buffer treatments started from much lower values at around 5 mg N kg^{-1} dry soil whilst the cropland had values >60 mg N kg^{-1} dry soil (Table 8.1). Also, after incubation, the soil TON was significantly correlated with OM (r = - 0.70; $p = 0.012$).

Similar to soil TON before incubation, soil NH_4^+ was higher (*$p = 0.0001$*) in the cropland (27.1 ± 0.58 mg kg^{-1} dry soil), compared to the three riparian buffer treatments (ranging between 93.6 ± 7.2 and 106.4 ± 1.6 mg N kg^{-1} dry soil). After incubation, the soil NH_4^+ in the cropland treatment decreased by 6.9%, whilst, in the riparian buffer treatments NH_4^+ increases between 5% and 16% were observed. The soil NH_4^+ was higher (*p = 0.0003*) in the willow riparian buffer (14.6 ± 0.32 mg N kg^{-1} dry soil) compared to other treatments and the increase was 3.5-fold from the soil NH_4^+ status pre-incubation (Table 9.1).

Table 9. 1: Soil characteristics before and after the incubation experiment.

Parameter	**Treatment**			
	Cropland	**Grass buffer**	**Willow buffer**	**Woodland buffer**
Before Incubation				
pH Water (1:2.5)	4.7 ± 0.04[†] d[‡]	5.0 ± 0.02 b	4.9 ± 0.02 c	5.1 ± 0.01 a
BD (g cm^{-3})	1.3 ± 0.0 a	1.0 ± 0.0 c	1.2 ± 0.0 b	1.2 ± 0.0 b
TON (mg kg^{-1} dry soil)	62.5 ±1.3 a	4.5 ± 0.22 b	4.6 ± 1.30 b	5.5 ± 0.78 b
NH_4^+-N (mg kg^{-1} dry soil)	27.1 ± 0.58 a	3.1 ± 0.07 b	4.1 ± 0.23 b	3.6 ± 0.24 b
OM (% w/w)	10.1 ± 0.09 c	11.4 ± 0.32 b	12.8 ± 0.04 a	12.7 ± 0.04 a
%WFPS (%)	85.0 ± 0.0 a	85.0 ± 0.0 a	85.0 ± 0.0 a	85.0 ± 0.0 a
After Incubation				
pH water (1:2.5)	4.6 ± 0.01 c	4.9 ± 0.03 b	4.9 ± 0.01 b	5.0 ± 0.02 a
BD (g cm^{-3})	1.3 ± 0.0 a	1.0 ± 0.0 c	1.2 ± 0.0 b	1.2 ± 0.0 b
TON (mg kg^{-1} dry soil)	156.7 ± 2.2 a	93.6 ± 7.2 c	103.5 ± 2.30 b	106.4 ± 1.6 b
NH_4^+-N (mg kg^{-1} dry soil)	13.5 ± 0.28 b	5.7 ± 0.08 d	14.6 ± 0.32 a	6.7 ± 0.29 c
OM (% w/w)	10.1 ± 0.17 c	11.7 ± 0.17 b	12.8 ± 0.06 a	12.4 ± 0.07 a
%WFPS (%)	82.3 ± 0.61 a	82.8 ± 1.21 a	83.7 ± 0.68 a	81.4 ± 0.71 a

[†] Mean ± standard error (*n*=3).

[‡] Different letters within a row indicate significant differences between treatments (*n*=3, p<0.05).

The soil OM before incubation was the highest in the willow (12.8 ± 0.04%) and the woodland (12.7 ± 0.04%) riparian buffer treatments (not different from each other), but both treatments had higher (*p = 0.0001*) soil OM than the cropland and grass riparian buffer treatments (Table 9.1). After incubation, soil OM remained within the same range (between 10.1 ± 0.17% and 12.8 ± 0.06%) in all the treatments as the status before incubation, with the willow and woodland riparian buffers maintaining the highest (*p = 0.0001*) soil OM (Table 9.1). All treatments had 85.0 ± 0.0% %WFPS before incubation, whilst post-incubation, they were at 82.3 ± 0.61, 82.8 ± 1.21, 83.7 ± 0.68, and 81.4 ± 0.71% for the cropland, and the grass, willow and woodland riparian buffers, respectively and all treatments were not different from each other (Table 9.1).

9.3.2 Gases

9.3.2.1 Gas fluxes

Soil NO fluxes peaked within the first 24-hours after amendment application in all the treatments, with the largest flux of 0.123 ± 0.011 mg N m^{-2} hr^{-1} observed in the grass riparian buffer treatment at 17.3-hours after amendment application (Figure 9.1). While the grass riparian buffer had a large NO flux, fluxes stayed below 0.02 ± 0.0003 mg N m^{-2} hr^{-1} in the other treatments. The times of the NO maxima were 2.9, 6.5, 6.5, and 17.3-hours after amendment application for the willow riparian buffer, cropland, woodland riparian buffer and grass riparian buffer treatments, respectively. At 24 hours after amendment application, NO fluxes were negligible in all treatments until the end of the experimental period.

Soil N_2O fluxes increased immediately after amendment application; in almost a similar pattern to the NO fluxes (Figure 9.1). N_2O fluxes peaked at 10.1-hours after amendment application and showed only small peaks of 0.26 ± 0.003, 0.25 ± 0.098 and 0.77 ± 0.32 mg N m^{-2} hr^{-1}, for the cropland, and the willow and woodland riparian buffers, respectively. In contrast to this, the grass riparian buffer treatment showed much larger values in a double peak, reaching a first high at 35-hours after amendment application with 10 ± 1.5 mg N m^{-2} hr^{-1} (close in time to the NO peak), followed by a second high at 69.1-hours after amendment application reaching 17.4 ± 5.6 mg N m^{-2} hr^{-1} .

Gaseous N_2 fluxes followed a similar pattern in all treatments from the day of amendment application until the end of the experiment (Figure 9.1). In all the treatments, soil N_2 fluxes above 2.4 ± 1.8 mg N m^{-2} hr^{-1} were observed within the first 60-hours after amendment application, which then declined to 0. After this period, the cropland, and the grass and willow riparian buffer treatments had fluxes not exceeding 2.3 ± 1 mg N m^{-2} hr^{-1} in, and the willow riparian buffer treatment had fluxes not exceeding 0.5 ± 0.1 mg N m^{-2} hr^{-1}, until the end of the experiment.

Carbon dioxide fluxes increased immediately after the amendment application in all the treatments (Figure 9.1). The largest peak of 430 ± 17 mg C m^{-2} hr^{-1} was observed in the willow riparian buffer treatment at 28-hours after amendment application. Thereafter, fluxes decreased gradually until the grass, willow, and woodland riparian buffer treatments maintained fluxes of ~100 ± 11 mg C m^{-2} hr^{-1} and the cropland with fluxes of ~50 ± 5 mg C m^{-2} hr^{-1} from 72-hours after amendment application until the end of the experiment.

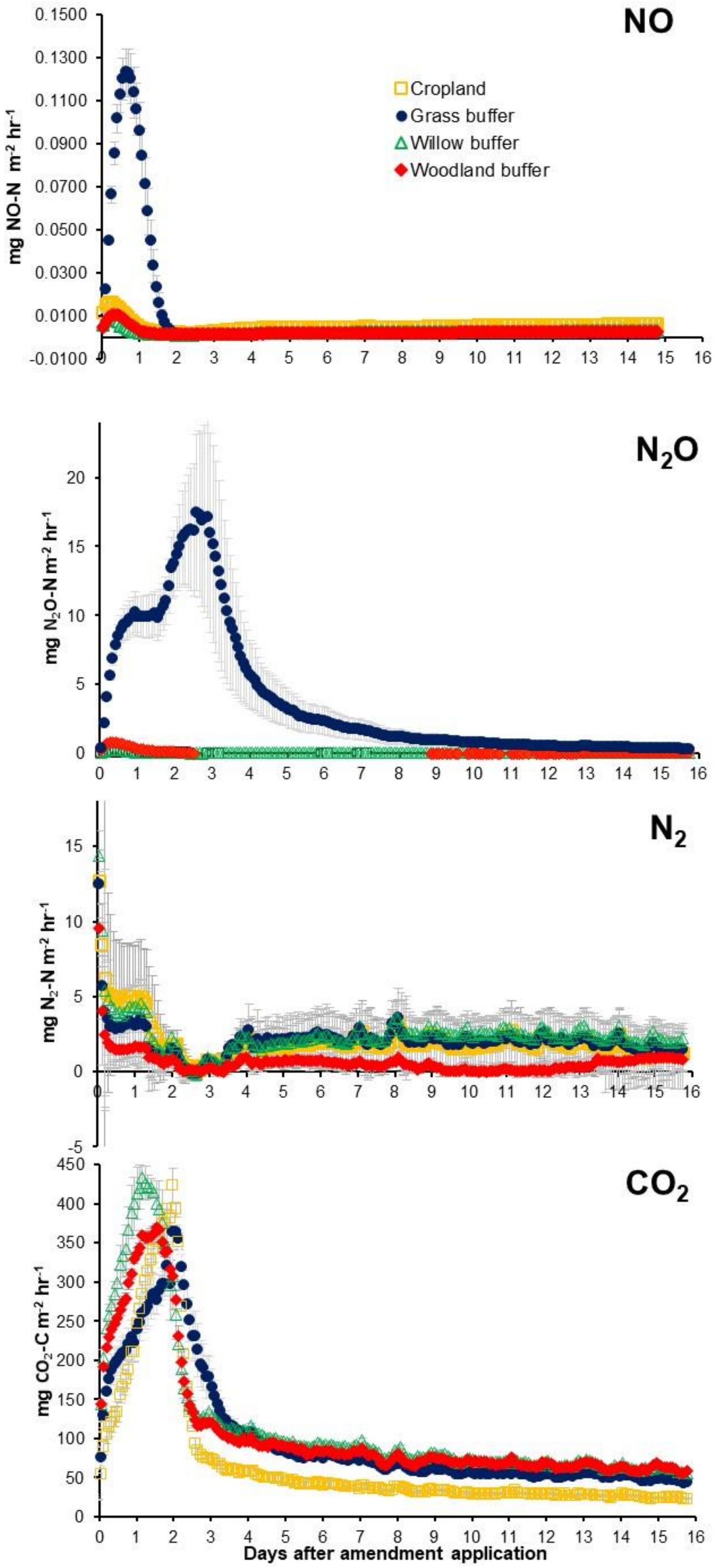

Figure 9. 1: Gaseous emissions during the experimental period. Error bars are standard errors of treatment mean (*n*=3).

9.3.2.2 Cumulative gas emissions

Table 9.2 shows cumulative emissions of the measured gases in the cropland, and the grass, willow, and woodland riparian buffer treatments. Total NO emissions ranged from 0.16 ± 0.023 to 2.9 ± 0.31 mg N m^{-2} and were greater ($p = 0.0002$) from the grass riparian buffer treatment (2.9 ± 0.31 mg N m^{-2}) compared to the cropland and the other riparian buffer treatments. Cumulative NO emissions were significantly correlated with OM (r = 0.70; p = 0.012), TO-N (r = - 0.59; p = 0.042), and BD (r = - 0.89; p = 0.0001) (Figure 9.2).

Table 9. 2: Cumulative emissions of NO, N_2O, N_2 and CO_2 for each treatment.

	Treatment			
Gas	**Cropland**	**Grass buffer**	**Willow buffer**	**Woodland buffer**
NO (mg N m^{-2})	0.33 ± 0.005† b‡	2.9 ± 0.31 a	0.16 ± 0.023 b	0.22 ± 0.074 b
N_2O (mg N m^{-2})	0.39 ± 0.48 b	1413.4 ± 448.3 a	10.3 ± 6.9 b	18.4± 9.8 b
N_2 (mg N m^{-2})	559.2 ± 476.9 a	606.6 ± 488.9 a	698.1 ± 270.3 a	113.6 ± 47.1 a
CO_2 (mg C m^{-2})	19310 ± 735.3 c	24372.6 ± 233.2 b	27558.3 ± 128.9 a	24842.8 ± 503.7 b

† Mean ± standard error (n=3).

‡ Different letters indicate a significant difference between treatments for each measured gas (n=3, p < 0.05).

Similar to NO emissions, cumulative N_2O emissions were significantly greater ($p = 0.0178$) in the grass riparian buffer treatment (1413.4 ± 448.3 mg N m^{-2}) compared to the cropland (0.39 ± 0.48 mg N $m^{-2}m^{-2}$), and the willow (10.3 ± 6.9 mg N m^{-2}), and woodland (18.4± 9.8 mg N m^{-2}) riparian buffer treatments (Table 9.2). The cumulative N_2O emissions were significantly correlated with OM (r = 0.7; p = 0.012), TO-N (r = - 0.74; p = 0.006), and BD (r = - 0.83; p = 0.0008) (Figure 9.2). The cumulative N_2O emissions during the experiment represented 0.0052, 18.8%, 0.13% and 0.24% of the amendment applied N in the cropland, and the grass, willow, and woodland riparian buffer treatments, respectively. Cumulative N_2 ranged from 113.6 ± 47.1 to 698.1 ±

270.3 mg N m^{-2} there were no differences ($p = 0.93$) between all the treatments (Table 9.2). The willow riparian buffer (27558.3 ± 128.9 mg C m^{-2}) had significantly the highest ($p = 0.0001$) CO_2 emissions compared to the cropland, and the grass, and woodland riparian buffer treatments (Table 9.2). Cumulative CO_2 emissions were significantly correlated with NH_4^+-N (r = 0.98; p = 0.0) after incubation (Figure 9.2).

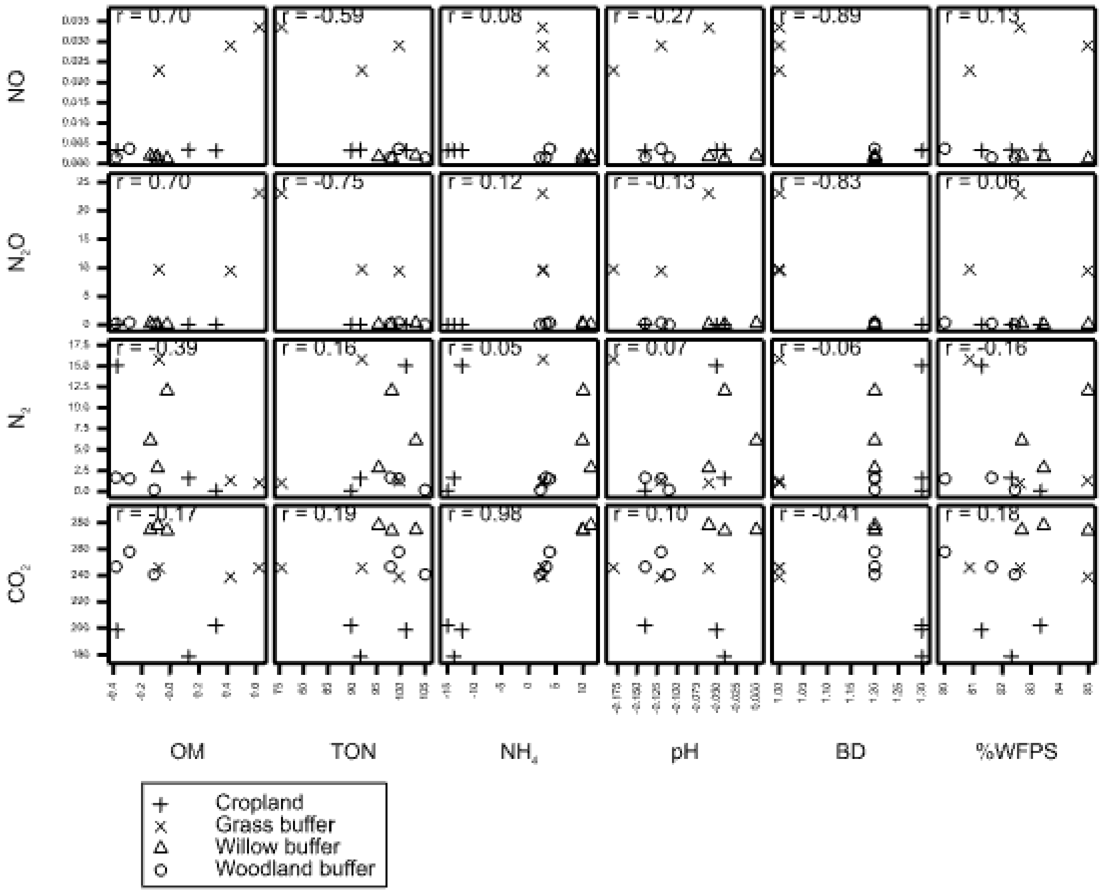

Figure 9. 2: Pearson correlation coefficients between cumulative gas emissions and soil parameters after incubation for all the treatments.

9.4 Discussion

9.4.1. Soil C and N

The increase in soil TON in all the treatments was primarily as a result of the NO_3^- introduced with the amendment. This increase in soil TON in all the treatments could also indicate mineralisation of soil OM to NH_4^+ followed by small amount of nitrification to NO_2^- and further to NO_3^- immediately after the incubation (since the headspace volume was having 20% O_2), however, this amount would have been small due to high %WFPS causing primarily favouring anaerobic N_2O production (Bridgham and Ye, 2013; Burt and Haycock, 1991). Since soil extraction for TON analysis was done on the day the experiment was terminated, it would not be assumed that nitrification had much influence on TON immediately after incubation. The decrease in soil NH_4^+ in the cropland treatment did not correspond to the change in soil TON (increase was 7 times larger; Table 9.1); which partially confirms that a majority of the TON came from the addition of NO_3^- with the amendment. It is also possible that the current study did not observe the decrease in soil NH_4^+ as it was being produced simultaneously from mineralisation while it was being slightly nitrified immediately after incubation. The slight increase in soil NH_4^+ in the grass, willow and woodland riparian buffer treatments could have been as a result of dissimilatory nitrate reduction to NH_4^+ of the NO_3^- introduced by the amendment during incubation, as described by Tiedje (1988). The previous author described this process as one regulated by O_2, thus, well suited to anaerobic environments, similar to conditions of the current study. This slight increase in soil NH_4^+ in the buffer treatments could also have been as a result of soil OM mineralisation that did not proceed to nitrification due to anaerobic conditions, similarly to other authors, particularly Clark *et al.* (2020) and (Højberg *et al.*, 1996). The previous authors studied mineralisation and nitrification in soils under grasslands

(Clark *et al.*, 2020) and young barley (Højberg *et al.*, 1996), and reported nitrification after mineralisation to be a two-step oxidation process of NH_4^+-N or NH_3 to NO_3^-; which does not seem to have been the case in the current study, since NH_4^+ accumulated instead.

9.4.2 Land uses and gases

9.4.2.1 Nitric oxide

The NO increase observed immediately after N application in all the treatments of the current study (Figure 9.1) indicates that the majority of NO was a result of denitrification of NO_3^- at the relatively high soil moisture content (85% WFPS) during the experiment. In soils, NO is produced by microbial nitrification and denitrification processes (Medinets *et al.*, 2015; Skiba *et al.*, 1997). During denitrification, NO is an obligatory intermediate between NO_2^- and N_2O (Ye *et al.*, 1994). In line with findings of the current study, studies by Russow *et al.* (2009) and Wang *et al.* (2011) also established that NO emissions from soils are promoted by denitrification. Several studies have also previously observed increasing NO emissions immediately after N fertilizer/amendment application under high soil moisture conditions (Cui *et al.*, 2012; Liu *et al.*, 2011; Loick *et al.*, 2016), similarly to the current study. The current study observed a significant correlation between NO emissions and OM ($p = 0.012$) after incubation (Figure 8.2), in line with studies by Stüven *et al.* (1992) and Homyak *et al.* (2017) which reported that soils with increased OM were vulnerable to N losses via NO as soil OM may be composed of organic substances that are suitable electron donors for NO production by some denitrifiers.

The fact that all the treatments had the same %WFPS and received the same amount of N shows that soil BD was a major driver of NO emissions in the current study, as the grass riparian buffer strip with the lowest soil BD had the highest cumulative NO emissions and vice versa for the treatments with high soil BD. Also, the riparian buffers had the same (statistically) TON and NH_4^+-N at the start, so there was no influence of inorganic N on these three treatments, but it was different in the cropland. OM was different between treatments at the start, so this would have made an impact, as the current study found a correlation between OM and NO. The negative correlation between NO and BD was consistent with previous authors, particularly Skiba *et al.* (1997), Stehfest and Bouwman (2006), and Zhang *et al.* (2016) that reported that high soil BD restricts gas diffusivity in the soil and may consequently reduce NO emissions. This then explains the significantly high NO emissions from the grass riparian buffer treatment compared to the remainder of the treatments as it had the lowest BD (Table 9.2). The results show that soil BD was a major driver of NO emissions in the current study, as the grass riparian buffer strip with the lowest soil BD had the highest cumulative NO emissions.

9.4.2.2 Nitrous oxide

The peak N_2O fluxes in all the treatments immediately after incubation are in line with field (Bouwman *et al.*, 2002; Scheer *et al.*, 2008) and laboratory (Wang *et al.*, 2011) studies, which observed peak N_2O immediately after N-fertilisation and at high soil moisture contents; conditions prevailing in our study. As a substrate for N_2O producing microorganisms, mineral N content is one of the significant drivers of N_2O emissions in soils (Ball, 2013; Schmid *et al.*, 2001). In addition to stimulating soil microbes, soil moisture influences gas diffusivity, which controls the movement of gas between the soil and the atmosphere, thus influencing the capacity of soil to produce and consume N_2O (Smith *et al.*, 2003). When high %WFPS prevails and soil gas diffusivity is impeded, NO is further reduced to N_2O before reaching the atmosphere (Russow *et al.*, 2009; Smith *et al.*, 2003), thus the larger N_2O fluxes in the current study. The large peak in all treatments immediately after incubation could mean both nitrification and denitrification contributed to the N_2O flux; but this was not confirmed in the current study.

Soil BD is widely recognized as one of the major drivers of soil N_2O emissions, since low BD is known to facilitate N_2O diffusivity from production microsites to the soil surface (Balaine *et al.*, 2013; Skiba and Ball, 2002; Smith *et al.*, 2018). Similarly, to the previous authors, the significantly large soil N_2O emissions in the grass riparian buffer treatment of the current study were driven by low soil BD, since the treatment had lower soil BD compared to the remainder of the treatments. These findings are further supported by the significant relationships between N_2O and BD in the current experiment (Figure 9.2). A high soil BD is known to increase the chances of N_2O being reduced to N_2 (Del Grosso *et al.*, 2000; Hamonts *et al.*, 2013). These findings are in line with findings by Ball (2013) and Smith *et al.* (2018), which reported that N_2O emissions decreased with increasing soil BD since it reduces soil gas diffusivity. The current study further shows a significant correlation between N_2O emissions and OM ($P = 0.012$) after incubation (Figure 9.2), in agreement with Harrison-Kirk *et al.* (2013), who reported that higher N_2O emissions were associated with higher soil OM. Despite the significant correlation observed between N_2O and OM in the current study (Figure 9.3), the grass riparian buffer treatment which had significantly higher N_2O emissions had relatively lower OM. Thus, it is evident that low BD was a major driver of N_2O emissions in the current study, similar to other authors including Ball (2013) and Smith *et al.* (2018).

Regarding the source processes, denitrification was likely to be the main source, but some N_2O could have also been due to some small nitrification immediately after incubation near the surface due to the aerobic headspace; a process limited in anaerobic conditions similar to conditions prevailing in the current study (Abbasi and Adams, 2000; Khalil *et al.*, 2004), but this was not ascertained since stable isotopes like other authors who confirmed this using isotope techniques i.e., Loick *et al.* (2016). However, the double N_2O peak observed could have been that, initially there was a small contribution to N_2O from nitrification, followed by a larger pulse of N_2O from denitrification; an N_2O producing process dominant in anaerobic conditions similar to the current study (Abbasi and Adams, 2000; Dlamini *et al.*, 2020; Li *et al.*, 2016). This could also be as a result of insufficient denitrifying bacteria present at the commencement of the experiment, which then took advantage of the presence of readily available NO_3^- to reproduce and multiply within the first two days of the experiment.

9.4.2.3 Nitrogen gas

The high N_2 fluxes in all treatments immediately after the amendment application were most likely due to the release of N_2 dissolved in the amendment into the vessels, which was being flushed-out during the first 60-hours, and decreasing N_2 concentrations to background levels, before an actual N_2 peak commenced. Although the current study did not use a ^{15}N labelled amendment to confirm the source of the N_2, but previous authors particularly Bergstermann *et al.* (2011), Cardenas *et al.* (2007), and Meijide *et al.* (2010) used labelled amendments to confirm that most of the dissolved N_2 in the amendment gets flushed-out within 2.5-3 days after incubation. After flushing the amendment dissolved N_2 (48 hours), the willow riparian maintained relatively larger N_2 fluxes compared to the remainder of the treatments, which could mean that its relatively high soil BD could have facilitated complete denitrification to N_2 (Aulakh *et al.,* 1992; Firestone, 1982). Nonetheless, high N_2 fluxes and subsequent emissions were expected from the cropland soil which had a higher soil BD compared to the remainder of the treatments. The findings of the current study were consistent with those by Smith *et al.* (2018b), who reported that if an N_2O molecule cannot readily diffuse from a site of production into an oxygenated pore, it has a good chance of being reduced into N_2 before being emitted into the atmosphere.

The addition of an available C-source, the addition of N and as well as high soil moisture content favoured N_2 production through potential denitrification in all treatments in the current study, similar to other authors, particularly Bergstermann *et al.* (2011) and Obia *et al.* (2015). This was expected, since N_2 is the final product of denitrification and the wet soil conditions (85% WFPS in the current study) favoured N_2 production through denitrification. The N_2O: (N_2 + N_2O) ratios are typically around 0.1 (less for the grass riparian buffer), which indicated that about 90% (or more for the grass riparian buffer) of denitrification tends to be complete denitrification to N_2 (Ciarlo *et al.,* 2008).

9.4.2.4 Carbon dioxide

The initial increase in CO_2 fluxes in all the treatments within the first 72-hours after incubation reflects aerobic respiration in the current study, similar to Lopez-Aizpun *et al.* (2018) and Loick *et al*. (2021). The previous authors reported that high CO_2 fluxes and emissions indicate microbial respiration and activity. The large CO_2 flux in all the treatments within the first 72-hours after amendment application was also as a result of a “priming effect”; accelerated soil OM mineralization when stimulated by the addition of new substrates (i.e., labile C source in the current case), similar to the review of field and laboratory studies by Kuzyakov *et al.* (2000). Some authors, including Kudeyarov, (1988) and Pascual *et al*., (1998) reported that priming effect arose shortly or immediately after addition of a specific subtance to the soil. This then explains the peak CO_2 fluxes immediatley after amendment application, which curved downwards and remained low until the end of the experiment at about 2 days post amendment application before decreasing to what was assumend to be baseline emissions; which could mean that the majority of the added labile C which resulted to the priming effect was exhausted within the first 72-hours of the experiment. The findings of the current study were similar to other authors, particularly Dlamini *et al.* (2020) who reported that highly labile C compounds including glucose get exhausted within the first 3 days after incubation under high soil moisture conditions.

The priming effect is known to be larger in C and N-rich soils as opposed to C and N-poor soils (Hart *et al.,* 1986) and NH_4^+-N causes significant priming effects compared to NO_3^- -N in soils (Steele *et al.,* 1980; Stout, 1995). Since the same N and C was added across treatments in the current experiment, the larger OM in the willow riparian buffer (Table 9.1) explains the significantly large CO_2 emissions in the treatment (i.e., Šimek *et al.,* 2004) compared the cropland and the grass riparian buffers but not to the woodland riparian buffer, as there were no significant differences in OM between these two treatments (Table 9.2). The significantly large CO_2 emissions in the willow treatment (Table 9.2) compared to the remainder of the treatments is explained by the significantly large NH_4^+-N (known to increase priming effect) in the willow riparian buffer compared to the remainder of the treatments (Table 9.1). The findings of the current study are in line with other authors, particularly Steele *et al.* (1980), who reported that NH_4^+ -N caused more priming effects compared to NO_3^- -N in soils.

9.4.3 Implications of the findings

The findings of the current study have several implications for an array of research fields. This study suggests that there is potential for higher NO and N_2O emissions from the grass riparian buffer, and larger N_2 and CO_2 from the willow riparian buffer under these conditions, however these may be different in field setting.

In the UK, some of the most commonly used riparian buffer vegetation include single stands or a mixture of grass, trees and woodlands (DEFRA, 2019; Natural England, 2013). Given that the grass riparian buffer displayed a larger potential to produce environmentally harmful gases i.e., NO and N_2O through in the current study. And the evidence that the grass riparian buffer is amongst the widely used buffer vegetation in England, shows that there is a need for intervention. Thus, the findings may also be useful in the recommending mitigation measures through careful buffer choices i.e., avoiding the use of grass riparian buffers in order to mitigate NO and N_2O production in similar agroecosystems with prevailing high soil moisture.

9.5 Conclusion

The study hypothesized that high NO, N_2O and N_2 emissions in soil from the cropland would occur as a result of residual N fertilizer while the riparian buffer treatments generally have lower labile N concentrations, also that the grass riparian buffer treatment will generate larger CO_2 due to higher organic matter cycling compared to the remainder of the treatments. The hypotheses were rejected since the results showed that larger NO and N_2O were produced in the grass riparian buffer treatment and high N_2 and CO_2 generation in the willow riparian buffer treatment. These results provide some information to help address an evidence gap previously highlighted by Groffman *et al.* (2002) to the IPCC. The results of the current study further highlight the need for similar research in a range of environmental conditions and field settings to enrich the understanding of the extent of NO, N_2O, N_2 and CO_2 emissions as a result of certain soil properties affected by various land management practices. Further, future research combing molecular tools with isotopic analyses may be useful to expand the findings of the current study.

9.6 References

Abbasi, M., Adams W., 2000. Gaseous N emission during simultaneous nitrification–denitrification associated with mineral N fertilization to a grassland soil under field conditions. *Soil Biology & Biochemistry*, 32:1251-1259.

Balaine, N., Clough T.J., Beare M.H., Thomas S.M., Meenken E.D., Ross J.G., 2013. Changes in relative gas diffusivity explain soil nitrous oxide flux dynamics. *Soil Science Society of America Journal*, 77:1496-1505.

Ball, B., 2013. Soil structure and greenhouse gas emissions: a synthesis of 20 years of experimentation. *European Journal of Soil Science*, 64:357-373.

Beauchamp, E.G., Trevors J.T., Paul J.W., 1989. Carbon Sources for Bacterial Denitrification, In: BA Stewart (Ed.), Advances in Soil Science, Springer., New York. pp. 113-142.

Bergstermann, A., Cárdenas L., Bol R., Gilliam L., Goulding K., Meijide A., Scholefield D., Vallejo A., Well R., 2011. Effect of antecedent soil moisture conditions on emissions and isotopologue distribution of N_2O during denitrification. *Soil Biology & Biochemistry*, 43:240-250.

Bouwman, A., Boumans L., Batjes N., 2002. Modeling global annual N_2O and NO emissions from fertilized fields. *Global Biogeochemical Cycles*, 16:28-1-28-9.

Bridgham, S., Ye R., 2013. Methods in Biogeochemistry of Wetlands, In: R DeLaune, et al. (Eds.), Organic Matter Mineralization and Decomposition, SSSA Book Series, Madison, Wisconsin. pp. 185-202.

Burt, T., Haycock N., 1991. Farming and nitrate pollution. *Geography*, 76:60-63.

Cardenas, L.M., Chadwick D., Scholefield D., Fychan R., Marley C.L., Jones R., Bol R., Well R., Vallejo A., 2007. The effect of diet manipulation on nitrous oxide and methane emissions from manure application to incubated grassland soils. *Atmospheric Environment*, 41:7096-7107.

Cárdenas, L.M., Hawkins J.M.B., Chadwick D., Scholefield D., 2003. Biogenic gas emissions from soils measured using a new automated laboratory incubation system. *Soil Biology & Biochemistry*, 35:867-870.

Clark, D.R., McKew B.A., Dong L.F., Leung G., Dumbrell A.J., Stott A., Grant H., Nedwell D.B., Trimmer M., Whitby C., 2020. Mineralization and nitrification: Archaea dominate ammonia-oxidising communities in grassland soils. *Soil Biology & Biochemistry,* 143:107725.

Cui, F., Yan G., Zhou Z., Zheng X., Deng J., 2012. Annual emissions of nitrous oxide and nitric oxide from a wheat–maize cropping system on a silt loam calcareous soil in the North China Plain. *Soil Biology & Biochemistry*, 48:10-19.

D'Agostino, R., 2017. Goodness-of-fit-techniques. Routledge.

Davis, M.P., Groh T.A., Jaynes D.B., Parkin T.B., Isenhart T.M., 2019. Nitrous oxide emissions from saturated riparian buffers: Are we trading a water quality problem for an air quality problem? *Journal Environmental Quality*, 48:261-269.

DEFRA, 2019. The guide to cross compliance in England 2019, in: FaRA Department for Environment (Ed.), United Kingdom.

Del Grosso, S., Parton W., Mosier A., Ojima D., Kulmala A., Phongpan S., 2000. General model for N_2O and N_2 gas emissions from soils due to dentrification. *Global Biogeochemical Cycles*, 14:1045-1060.

Dlamini, J., Chadwick D., Hawkins J., Martinez J., Scholefield D., Ma Y., Cárdenas L., 2020. Evaluating the potential of different carbon sources to promote denitrification. *Journal of Agricultural Sciences*, 158:194-205.

Fisher, K., Jacinthe P., Vidon P., Liu X., Baker M., 2014. Nitrous oxide emission from cropland and adjacent riparian buffers in contrasting hydrogeomorphic settings. *Journal of Environmental Quality*, 43:338-348.

Groffman, P.M., Axelrod E.A., Lemunyon J.L., Sullivan W.M., 1991. Denitrification in grass and forest vegetated filter strips. *Journal of Environmental Quality*, 20:671-674.

Groffman, P.M., Crawford M.K., 2003. Denitrification potential in urban riparian zones. *Journal of Environmental Quality*, 32:1144-1149.

Groffman, P.M., Gold A., Kellog D., Addy K., 2002. Mechanisms, rates and assessment of N_2O in groundwater, riparian zones and rivers, Non-CO_2 Greenhouse Gases: Scientific Understanding, Control Options and Policy

Aspects. Proceedings of the Third International Symposium, Maastricht, The Netherlands. pp. 159-166.

Groffman, P.M., Gold A.J., Jacinthe P.-A., 1998. Nitrous oxide production in riparian zones and groundwater. *Nutrient Cycling in Agroecosystems*, 52:179-186.

Groh, T.A., Davis M.P., Isenhart T.M., Jaynes D.B., Parkin T.B., 2019. In situ denitrification in saturated riparian buffers. *Journal of Environmental Quality*, 48:376-384.

Groh, T.A., Gentry L.E., David M.B., 2015. Nitrogen removal and greenhouse gas emissions from constructed wetlands receiving tile drainage water. *Journal of Environmental Quality*, 44:1001-1010.

Gundersen, P., Laurén A., Finér L., Ring E., Koivusalo H., Sætersdal M., Weslien J.-O., Sigurdsson B.D., Högbom L., Laine J., 2010. Environmental services provided from riparian forests in the Nordic countries. *Ambio*, 39:555-566.

Hamonts, K., Balaine N., Moltchanova E., Beare M., Thomas S., Wakelin S.A., O'Callaghan M., Condron L.M., Clough T.J., 2013. Influence of soil bulk density and matric potential on microbial dynamics, inorganic N transformations, N_2O and N_2 fluxes following urea deposition. *Soil Biology & Biochemistry*, 65:1-11.

Harrison-Kirk, T., Beare M., Meenken E., Condron L., 2013. Soil organic matter and texture affect responses to dry/wet cycles: Effects on carbon dioxide and nitrous oxide emissions. *Soil Biology & Biochemistry*, 57:43-55.

Højberg, O., Binnerup S.J., Sørensen J., 1996. Potential rates of ammonium oxidation, nitrite oxidation, nitrate reduction and denitrification in the young barley rhizosphere. *Soil Biology & Biochemistry*, 28:47-54.

Homyak, P.M., Kamiyama M., Sickman J.O., Schimel J.P., 2017. Acidity and organic matter promote abiotic nitric oxide production in drying soils. *Global Change Biology*, 23:1735-1747.

Iqbal, J., Parkin T.B., Helmers M.J., Zhou X., Castellano M.J., 2015. Denitrification and nitrous oxide emissions in annual croplands, perennial grass buffers, and restored perennial grasslands. *Soil Science Society of America Journal*, 79:239-250.

Jaynes, D.B., Isenhart T.M., 2014. Reconnecting tile drainage to riparian buffer hydrology for enhanced nitrate removal. *Journal of Environmental Quality*, 43:631-638.

Khalil, K., Mary B., Renault P., 2004. Nitrous oxide production by nitrification and denitrification in soil aggregates as affected by O_2 concentration. *Soil Biology & Biochemistry*, 36:687-699.

Li, X., Sørensen P., Olesen J.E., Petersen S.O., 2016. Evidence for denitrification as main source of N_2O emission from residue-amended soil. *Soil Biology & Biochemistry*, 92:153-160.

Liu, C., Wang K., Meng S., Zheng X., Zhou Z., Han S., Chen D., Yang Z., 2011. Effects of irrigation, fertilization and crop straw management on nitrous oxide and nitric oxide emissions from a wheat–maize rotation field in northern China. *Agriculture, Ecosystems, & Environment*, 140:226-233.

Loick, N., Dixon E., Abalos D., Vallejo A., Matthews P., McGeough K., Watson C., Baggs E.M., Cardenas L.M., 2017. “Hot spots” of N and C impact nitric oxide, nitrous oxide and nitrogen gas emissions from a UK grassland soil. *Geoderma*, 305:336-345.

Loick, N., Dixon E.R., Abalos D., Vallejo A., Matthews G.P., McGeough K.L., Well R., Watson C.J., Laughlin R.J., Cardenas L.M., 2016. Denitrification as a source of nitric oxide emissions from incubated soil cores from a UK grassland soil. *Soil Biology & Biochemistry*, 95:1-7.

Lowrance, R., 1992. Groundwater nitrate and denitrification in a coastal plain riparian forest. *Journal of Environmental Quality*, 21:401-405.

Medinets, S., Skiba U., Rennenberg H., Butterbach-Bahl K., 2015. A review of soil NO transformation: Associated processes and possible physiological significance on organisms. *Soil Biology & Biochemistr*y, 80:92-117.

Meijide, A., Cardenas L., Bol R., Bergstermann A., Goulding K., Well R., Vallejo A., Scholefield D., 2010. Dual isotope and isotopomer measurements for the understanding of N_2O production and consumption during denitrification in an arable soil. *European Journal of Soil Science*, 61:364-374.

Morley, N., Baggs E., 2010. Carbon and oxygen controls on N_2O and N_2 production during nitrate reduction. *Soil Biology & Biochemistry*, 42:1864-1871.

Naiman, R.J., Decamps H., McClain M.E., 2010. Riparia: ecology, conservation, and management of streamside communities Elsevier Academic Press, Carlifornia.

Natural England, N., 2013. Entry Level Stewardship–Environmental Stewardship Handbook, DEFRA, UK.

Obia, A., Cornelissen G., Mulder J., Dörsch P., 2015. Effect of soil pH increase by biochar on NO, N_2O and N_2 production during denitrification in acid soils. *PloS One*, 10.

Olsthoorn, C.S., Fong N.P., 1998. The anthropogenic nitrogen cycle in the Netherlands. *Nutrient Cycling in Agroecosystems*, 52:269-276.

Paudel, B.R., Udawatta R.P., Anderson S.H., 2011. Agroforestry and grass buffer effects on soil quality parameters for grazed pasture and row-crop systems. *Applied Soil Ecology*, 48:125-132.

Pinay, G., Roques L., Fabre A., 1993. Spatial and temporal patterns of denitrification in a riparian forest. *Journal of Applied Ecology*, 30: 581-591.

Poulton, P., Johnston J., Macdonald A., White R., Powlson D., 2018. Major limitations to achieving “4 per 1000” increases in soil organic carbon stock in temperate regions: Evidence from long-term experiments at Rothamsted Research, United Kingdom. *Global Change Biology*, 24:2563-2584.

Robertson, G.P., Groffman P., 2007. Nitrogen Transformations, In: EA Paul (Ed.), Soil Microbiology, Ecology and Biochemistry, Elsevier, Amsterdam. pp. 341-364.

Russow, R., Stange C., Neue H.-U., 2009. Role of nitrite and nitric oxide in the processes of nitrification and denitrification in soil: results from ^{15}N tracer experiments. *Soil Biology & Biochemistry*, 41:785-795.

Scheer, C., Wassmann R., Kienzler K., Ibragimov N., Eschanov R., 2008. Nitrous oxide emissions from fertilized, irrigated cotton (*Gossypium hirsutum* L.) in the Aral Sea Basin, Uzbekistan: Influence of nitrogen applications and irrigation practices. *Soil Biology & Biochemistry*, 40:290-301.

Schmid, M., Fuhrer J., Neftel A., 2001. Nitrous oxide concentrations in the soil of a mown grassland: comparison of model results with soil profile measurements. *Water, Air & Soil Pollution: Focus*, 1:437-446.

Schultz, R., Colletti J., Isenhart T., Marquez C., Simpkins W., Ball C., Schultz O., 2000. Riparian forest buffer practices, In: WRaRF HE Garrett (Ed.), North American Agroforestry: an Integrated Science and Practice. Eds. , America Society of Agronomy, Madison, Wisconsin. pp. 189-281.

Searle, P.L., 1984. The Berthelot or indophenol reaction and its use in the analytical chemistry of nitrogen. A review. *Analyst*, 109:549-568.

Seobi, T., Anderson S., Udawatta R., Gantzer C., 2005. Influence of grass and agroforestry buffer strips on soil hydraulic properties for an Albaqualf. *Soil Science Society of America Journal*, 69:893-901.

Silverthorn, T.K., Richardson J.S., 2021. Forest Management Impacts on Greenhouse Gas Fluxes from Riparian Soils Along Headwater Streams. *Ecosystems*, 24: 1810–1822.

Skiba, U., Ball B., 2002. The effect of soil texture and soil drainage on emissions of nitric oxide and nitrous oxide. *Soil Use & Management*, 18:56-60.

Skiba, U., Fowler D., Smith K., 1997. Nitric oxide emissions from agricultural soils in temperate and tropical climates: sources, controls and mitigation options. *Nutrient Cycling in Agroecosystems*, 48:139-153.

Smith, K., Ball T., Conen F., Dobbie K., Massheder J., Rey A., 2018. Exchange of greenhouse gases between soil and atmosphere: interactions of soil physical factors and biological processes. *European Journal of Soil Science*, 69:10-20.

Smith, K.A., Ball T., Conen F., Dobbie K., Massheder J., Rey A., 2003. Exchange of greenhouse gases between soil and atmosphere: interactions of soil physical factors and biological processes. *European Journal of Soil Science*, 54:779-791.

Steele, K., Saunders W., Wilson A., 1980. Transformation of ammonium and nitrate fertilisers in two soils of low and high nitrification activity. *New Zealand Journal of Agricultural Research*, 23:305-312.

Stehfest, E., Bouwman L., 2006. N_2O and NO emission from agricultural fields and soils under natural vegetation: summarizing available measurement data and modeling of global annual emissions. *Nutrient Cycling in Agroecosystems*, 74:207-228.

Stevens, R.J., Laughlin R.J., Burns L., Arah J., Hood R., 1997. Measuring the contributions of nitrification and denitrification to the flux of nitrous oxide from soil. *Soil Biology & Biochemistry*, 29:139-151.

Stüven, R., Vollmer M., Bock E., 1992. The impact of organic matter on nitric oxide formation by Nitrosomonas europaea. *Archives of Microbiology*, 158:439-443.

Tiedje, J.M., 1988. Ecology of denitrification and dissimilatory nitrate reduction to ammonium, In: A Zehnder (Ed.), Environmental Microbiology of Anaerobes, John Wiley and Sons, New York. pp. 179-244.

Udawatta, R.P., Kremer R.J., Garrett H.E., Anderson S.H., 2009. Soil enzyme activities and physical properties in a watershed managed under agroforestry and row-crop systems. *Agriculture, Ecosystems, & Environment*, 131:98-104.

Valkama, E., Usva K., Saarinen M., Uusi-Kämppä J., 2019. A meta-analysis on nitrogen retention by buffer zones. *Journal of Environmental Quality*, 48:270-279.

Wang, R., Willibald G., Feng Q., Zheng X., Liao T., Brüggemann N., Butterbach-Bahl K., 2011. Measurement of N_2, N_2O, NO, and CO_2 emissions from soil with the gas-flow-soil-core technique. *Environmental Science & Technology*, 45:6066-6072.

Watts, S.H., Seitzinger S.P., 2000. Denitrification rates in organic and mineral soils from riparian sites: a comparison of N_2 flux and acetylene inhibition methods. *Soil Biology & Biochemistry*, 32:1383-1392.

Weerasekara, C., Udawatta R.P., Jose S., Kremer R.J., Weerasekara C., 2016. Soil quality differences in a row-crop watershed with agroforestry and grass buffers. *Agroforestry Systems*, 90:829-838.

Welham, S.J., Gezan S.A., Clark S.J., Mead A., 2014. Statistical methods in biology: design and analysis of experiments and regression CRC Press.

Wilke, B.-M., 2005. Determination of chemical and physical soil properties, In: A Varma (Ed.), Monitoring and assessing soil bioremediation, Springer, Berlin Heidelberg. pp. 47-95.

Wollenhaupt, N., Wolkowski R., 1994. Grid soil sampling. *Better Crops*, 78:6-9.

Xia, Y., Zhang M., Tsang D.C., Geng N., Lu D., Zhu L., Igalavithana A.D., Dissanayake P.D., Rinklebe J., Yang X., 2020. Recent advances in control technologies for non-point source pollution with nitrogen and phosphorous from agricultural runoff: current practices and future prospects. *Applied Biological Chemistry*, 63:1-13.

Ye, R.W., Averill B.A., Tiedje J.M., 1994. Denitrification: production and consumption of nitric oxide. *Applied & Environmental Microbiology*, 60:1053.

Zhang, Y., Mu Y., Zhou Y., Tian D., Liu J., Zhang C., 2016. NO and N_2O emissions from agricultural fields in the North China Plain: origination and mitigation. *Science of the Total Environment*, 551:197-204.

CHAPTER 10.0

SYNTHESIS AND RECOMMENDATIONS

10.1 Synthesis

Vegetated riparian buffers are primarily introduced to agricultural lands for water quality functions. Their position in the landscape allows them to intercept and process NO_3^--rich sub-surface and surface runoff which would otherwise reach freshwater ecosystems. They are seasonally inundated from high water tables, recycle OM which increases soil C, and retain N intercepted from the upslope agricultural lands. The decomposition of N- and C-rich pollutants (organic and inorganic) and processes dominant within riparian buffer zones result in the production of gases such as NO, N_2O, N_2, CH_4, and CO_2.

Based on field results from this study, riparian buffers, which are primarily installed to improve water quality in permanent pasture and maize, emit less of the highly radiative greenhouse gases (i.e., N_2O and CH_4) than croplands and the no-buffer control. This finding is in agreement with the meta-analysis, which found that buffer strips from different vegetation emit approximately one-third of the total amount of N_2O recorded on adjacent croplands.

Although riparian buffers emitted significantly more CO_2 than the crop land they serve and the no-buffer control, this difference was insignificant when compared with the permanent pastures. Nonetheless, total CO_2-equivalent GHG emissions from riparian buffers were lower than those from croplands they serve and a no-buffer control. The study concludes that riparian buffers installed for water quality protection have an unintended benefit of reducing greenhouse gas emissions, despite being primarily designed to protect water quality.

10.2 Recommendations

Greenhouse gas emission is a function of the availability, abundance, and quality of substrates (organic matter and source of nitrogen) and abiotic factors (climatic and edaphic factors). The current study was conducted in a temperate region using riparian buffer vegetation adapted to the region. In light of this, it is recommended that:

1. A similar long-term study should be conducted in the tropics using indigenous riparian vegetation in order to reach conclusive recommendations.
2. A long-term study should be conducted in temperate regions in order to understand the role of buffer age in water quality functions and greenhouse gases emission dynamics.
3. In future riparian buffer studies (both in temperate and tropical regions), isotopic analysis should be conducted in order to understand how microbiology contributes to GHG emissions, which may inform mitigation measures.