

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 transitional 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 Isenhardt, 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, N₂O, N₂ and CO₂ 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, N₂O and N₂ 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 CO₂ 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-m² and each riparian buffer strip: 100-m²) 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% H₂O 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).

$$\%SM = 100 * \frac{W_w - D_w}{D_w} \quad (Eq. 9.1)$$

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: O₂ (80:20) at a flow rate of 30 ml min^{-1} for 14 hours, in order to facilitate N₂ 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, O₂ was kept at atmospheric levels in the gas mixture (20%).

In order to promote potential denitrification, KNO₃ 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., $1583.6 \text{ mg kg}^{-1}$ 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. CO₂ and N₂O 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 N₂ 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 NH₄⁺-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 $\text{NH}_4^+\text{-N}$ [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™ 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, $\text{NH}_4^+\text{-N}$, 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 ($62.5 \pm 1.3 \text{ mg kg}^{-1}$ dry soil) compared to all the three riparian buffer treatments. Even after incubation, the soil TON remained higher ($p = 0.0001$) in the cropland ($156.7 \pm 2.2 \text{ mg kg}^{-1}$ 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 $>60 \text{ mg N kg}^{-1}$ 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 ($27.1 \pm 0.58 \text{ mg kg}^{-1}$ dry soil), compared to the three riparian buffer treatments (ranging between 93.6 ± 7.2 and $106.4 \pm 1.6 \text{ mg N kg}^{-1}$ 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 ($14.6 \pm 0.32 \text{ mg N kg}^{-1}$ 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)	$4.7 \pm 0.04^\dagger \text{ d}^\ddagger$	$5.0 \pm 0.02 \text{ b}$	$4.9 \pm 0.02 \text{ c}$	$5.1 \pm 0.01 \text{ a}$
BD (g cm^{-3})	$1.3 \pm 0.0 \text{ a}$	$1.0 \pm 0.0 \text{ c}$	$1.2 \pm 0.0 \text{ b}$	$1.2 \pm 0.0 \text{ b}$
TON (mg kg^{-1} dry soil)	$62.5 \pm 1.3 \text{ a}$	$4.5 \pm 0.22 \text{ b}$	$4.6 \pm 1.30 \text{ b}$	$5.5 \pm 0.78 \text{ b}$
$\text{NH}_4^+\text{-N}$ (mg kg^{-1} dry soil)	$27.1 \pm 0.58 \text{ a}$	$3.1 \pm 0.07 \text{ b}$	$4.1 \pm 0.23 \text{ b}$	$3.6 \pm 0.24 \text{ b}$
OM (% w/w)	$10.1 \pm 0.09 \text{ c}$	$11.4 \pm 0.32 \text{ b}$	$12.8 \pm 0.04 \text{ a}$	$12.7 \pm 0.04 \text{ a}$
%WFPS (%)	$85.0 \pm 0.0 \text{ a}$	$85.0 \pm 0.0 \text{ a}$	$85.0 \pm 0.0 \text{ a}$	$85.0 \pm 0.0 \text{ a}$
After Incubation				
pH water (1:2.5)	$4.6 \pm 0.01 \text{ c}$	$4.9 \pm 0.03 \text{ b}$	$4.9 \pm 0.01 \text{ b}$	$5.0 \pm 0.02 \text{ a}$
BD (g cm^{-3})	$1.3 \pm 0.0 \text{ a}$	$1.0 \pm 0.0 \text{ c}$	$1.2 \pm 0.0 \text{ b}$	$1.2 \pm 0.0 \text{ b}$
TON (mg kg^{-1} dry soil)	$156.7 \pm 2.2 \text{ a}$	$93.6 \pm 7.2 \text{ c}$	$103.5 \pm 2.30 \text{ b}$	$106.4 \pm 1.6 \text{ b}$
$\text{NH}_4^+\text{-N}$ (mg kg^{-1} dry soil)	$13.5 \pm 0.28 \text{ b}$	$5.7 \pm 0.08 \text{ d}$	$14.6 \pm 0.32 \text{ a}$	$6.7 \pm 0.29 \text{ c}$
OM (% w/w)	$10.1 \pm 0.17 \text{ c}$	$11.7 \pm 0.17 \text{ b}$	$12.8 \pm 0.06 \text{ a}$	$12.4 \pm 0.07 \text{ a}$
%WFPS (%)	$82.3 \pm 0.61 \text{ a}$	$82.8 \pm 1.21 \text{ a}$	$83.7 \pm 0.68 \text{ a}$	$81.4 \pm 0.71 \text{ a}$

[†] Mean \pm 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 ($12.8 \pm 0.04\%$) and the woodland ($12.7 \pm 0.04\%$) 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 $10.1 \pm 0.17\%$ and $12.8 \pm 0.06\%$) 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 $85.0 \pm 0.0\%$ %WFPS before incubation, whilst post-incubation, they were at 82.3 ± 0.61 , 82.8 ± 1.21 , 83.7 ± 0.68 , and $81.4 \pm 0.71\%$ 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 N₂O fluxes increased immediately after amendment application; in almost a similar pattern to the NO fluxes (Figure 9.1). N₂O 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 N₂ 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 N₂ fluxes above $2.4 \pm 1.8 \text{ mg N m}^{-2} \text{ hr}^{-1}$ 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 $2.3 \pm 1 \text{ mg N m}^{-2} \text{ hr}^{-1}$ in, and the willow riparian buffer treatment had fluxes not exceeding $0.5 \pm 0.1 \text{ mg N m}^{-2} \text{ hr}^{-1}$, 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 $430 \pm 17 \text{ mg C m}^{-2} \text{ hr}^{-1}$ 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 $\sim 100 \pm 11 \text{ mg C m}^{-2} \text{ hr}^{-1}$ and the cropland with fluxes of $\sim 50 \pm 5 \text{ mg C m}^{-2} \text{ hr}^{-1}$ from 72-hours after amendment application until the end of the experiment.

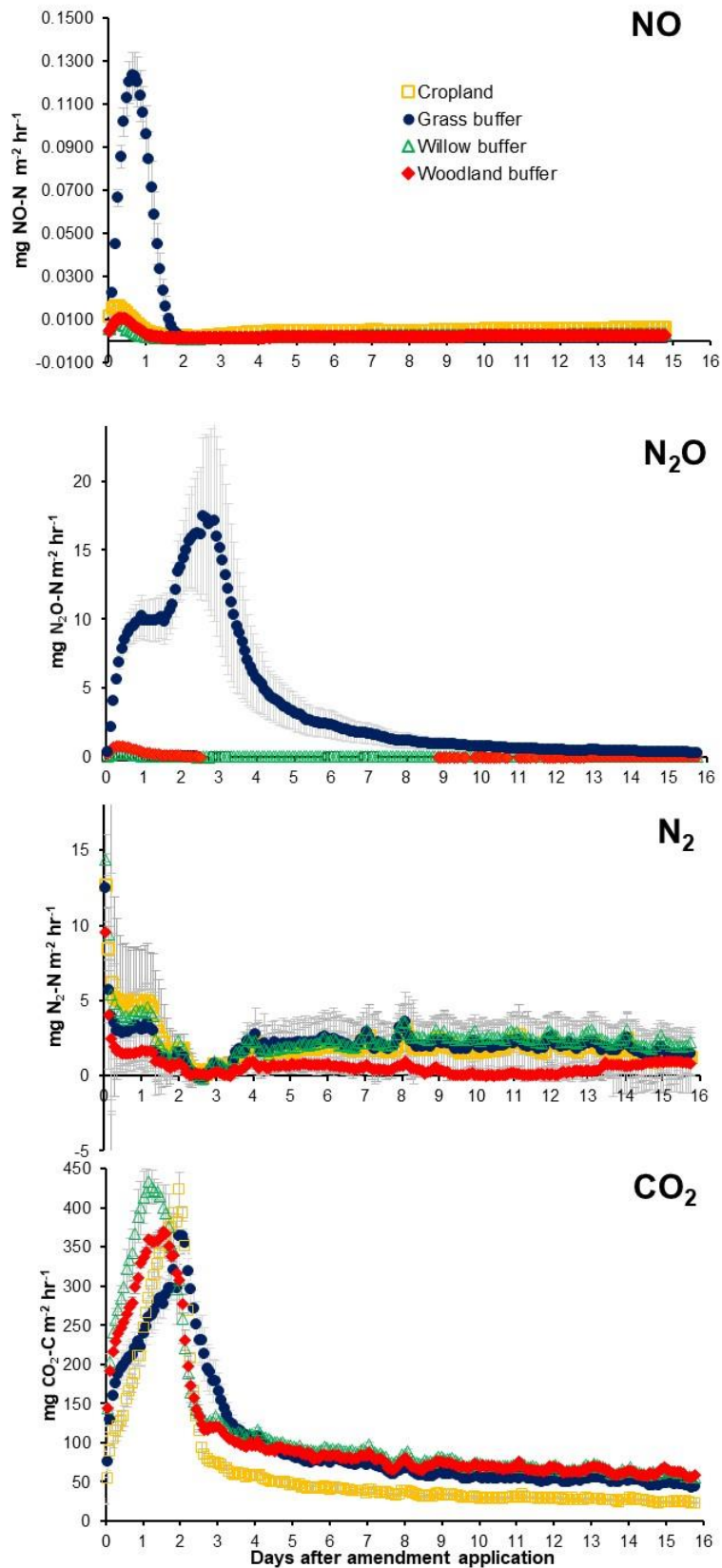


Figure 9. 1: Gaseous emissions during the experimental period. Error bars are standard errors of treatment mean ($n=3$).

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, N₂O, N₂ and CO₂ for each treatment.

Gas	Treatment			
	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 ₂ O (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 N₂O 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), 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 N₂O 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 N₂O 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 N₂ ranged from 113.6 ± 47.1 to $698.1 \pm$

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 ($p = 0.0001$) CO₂ emissions compared to the cropland, and the grass, and woodland riparian buffer treatments (Table 9.2). Cumulative CO₂ emissions were significantly correlated with NH₄⁺-N ($r = 0.98$; $p = 0.0$) after incubation (Figure 9.2).

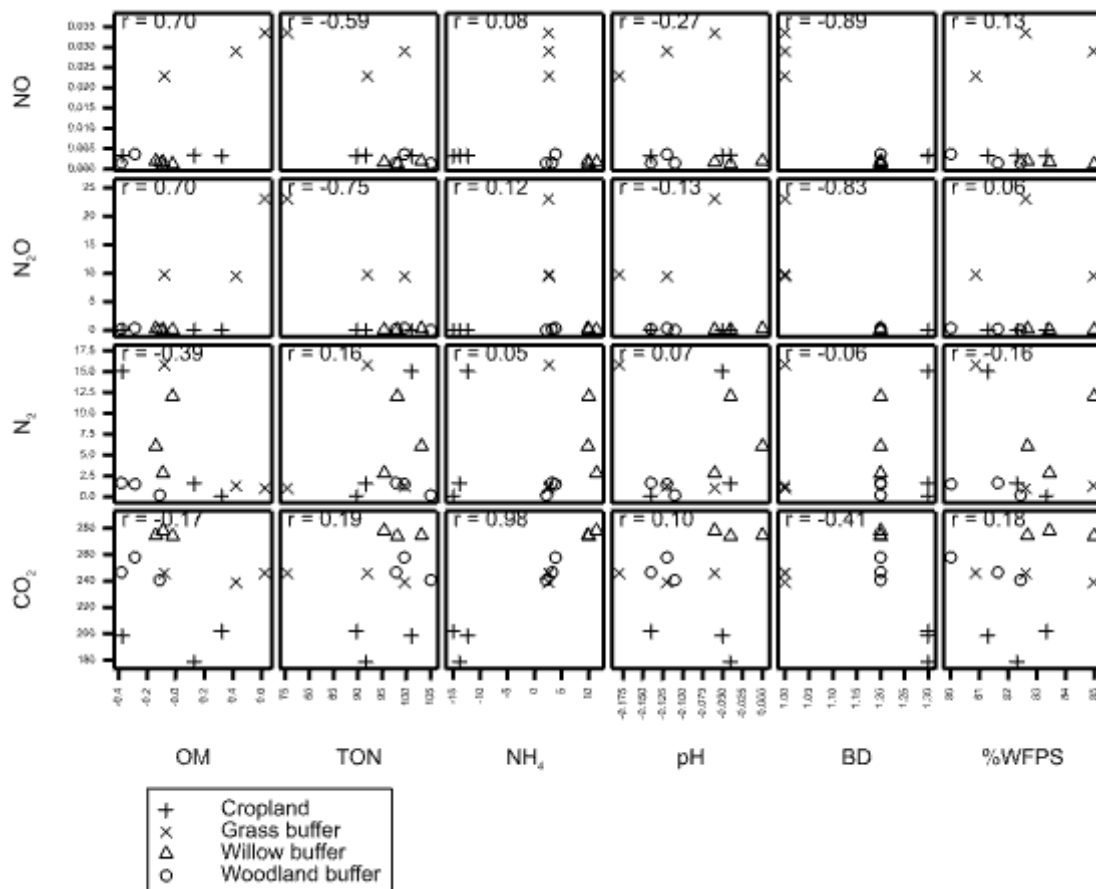


Figure 9. 2: Pearson correlation coefficients between cumulative gas emissions and soil parameters after incubation for all the treatments.

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 $\text{NH}_4^+\text{-N}$ 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 $\text{NH}_4^+\text{-N}$ 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 N₂O flux; but this was not confirmed in the current study.

Soil BD is widely recognized as one of the major drivers of soil N₂O emissions, since low BD is known to facilitate N₂O 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 N₂O 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 N₂O and BD in the current experiment (Figure 9.2). A high soil BD is known to increase the chances of N₂O being reduced to N₂ (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 N₂O emissions decreased with increasing soil BD since it reduces soil gas diffusivity. The current study further shows a significant correlation between N₂O emissions and OM ($P = 0.012$) after incubation (Figure 9.2), in agreement with Harrison-Kirk *et al.* (2013), who reported that higher N₂O emissions were associated with higher soil OM. Despite the significant correlation observed between N₂O and OM in the current study (Figure 9.3), the grass riparian buffer treatment which had significantly higher N₂O emissions had relatively lower OM. Thus, it is evident that low BD was a major driver of N₂O 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 N₂O 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 N₂O peak observed could have been that, initially there was a small contribution to N₂O from nitrification, followed by a larger pulse of N₂O from denitrification; an N₂O 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 NO₃⁻ to reproduce and multiply within the first two days of the experiment.

9.4.2.3 Nitrogen gas

The high N₂ fluxes in all treatments immediately after the amendment application were most likely due to the release of N₂ dissolved in the amendment into the vessels, which was being flushed-out during the first 60-hours, and decreasing N₂ concentrations to background levels, before an actual N₂ peak commenced. Although the current study did not use a ¹⁵N labelled amendment to confirm the source of the N₂, 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 N₂ in the amendment gets flushed-out within 2.5-3 days after incubation. After flushing the amendment dissolved N₂ (48 hours), the willow riparian maintained relatively larger N₂ fluxes compared to the remainder of the treatments, which could mean that its relatively high soil BD could have facilitated complete denitrification to N₂ (Aulakh *et al.*, 1992; Firestone, 1982). Nonetheless, high N₂ 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 N₂O molecule cannot readily diffuse from a site of production into an oxygenated pore, it has a good chance of being reduced into N₂ 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 N₂ 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 N₂ is the final product of denitrification and the wet soil conditions (85% WFPS in the current study) favoured N₂ production through denitrification. The N₂O: (N₂ + N₂O) 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 N₂ (Ciarlo *et al.*, 2008).

9.4.2.4 Carbon dioxide

The initial increase in CO₂ 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 CO₂ fluxes and emissions indicate microbial respiration and activity. The large CO₂ 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 substance to the soil. This then explains the peak CO₂ fluxes immediately 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 assumed 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 N₂O emissions from the grass riparian buffer, and larger N₂ and CO₂ 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 N₂O 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 N₂O production in similar agroecosystems with prevailing high soil moisture.

9.5 Conclusion

The study hypothesized that high NO, N₂O and N₂ 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 CO₂ 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 N₂O were produced in the grass riparian buffer treatment and high N₂ and CO₂ 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, N₂O, N₂ and CO₂ emissions as a result of certain soil properties affected by various land management practices. Further, future research combining molecular tools with isotopic analyses may be useful to expand the findings of the current study.

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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.

