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Riparian buffer strips influence nitrogen losses as nitrous oxide and leached N from upslope permanent pasture

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ABSTRACT

Riparian buffer strips can have a significant role in reducing nitrogen (N) transfers from agricultural land to freshwater primarily via denitrification and plant uptake processes, but an unintended trade-off can be elevated nitrous oxide (N_2O) production rates. Against this context, our 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) grass riparian buffer with novel deep-rooting species, (ii) willow (young trees at establishment phase) riparian buffer, and (iii) deciduous woodland (also young trees at establishment phase) riparian buffer. The experimental control was ryegrass pasture with no buffer strip. N_2O emissions were measured at the same time as total oxidized N in run-off, and soil and environmental characteristics in the riparian buffer strips and upslope pasture between 2018 and 2019. 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 compared to the remainder of the treatments. Our results also showed that the grass riparian buffer strip is a sink of N_2O equivalent to − 2310.2 g N_2O-N ha^{-1} day^{-1} (95% confidence interval:−535.5 to 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 (N-FWMC) of 0.041 ± 0.022 and 0.031 ± 0.015 mg N L^{-1}, when compared to the other treatments. Our 9-month experiment therefore, shows that riparian buffer strips with novel deep-rooting grass can therefore potentially address emissions to both water and air. The results imply that over a shorter timeline similar to the current study, the grass riparian buffer strip can potentially address N emission to both air and water, particularly when serving a permanent pasture in similar settings as the current experiment.

1. Introduction

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 European Member States in 2000 to ensure that waterbodies achieve 'good ecological status'. According to Scheure and Naus (2010), for some waterbodies, the installation of riparian buffer strips is essential to help achieve such status. Vegetated riparian buffer strips between agricultural fields receiving enhanced nutrient inputs and rivers and streams may include a variety of vegetation types including single species or a combination of shrubs, trees, grasses, and forbs (Schultz et al., 2004). Riparian buffer strips are commonly seen as practical interventions for soil and water resource conservation in agroecosystems (Lowrance et al., 2002).

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Numerous studies have advocated riparian buffer strips as practical tools to control NPS pollution effectively (Hubbard et al., 2004; Lowrance et al., 1984; Mitsch et al., 2001; Sabater et al., 2003).

Inclusion of riparian buffer strips into agroecosystems has been shown to improve carbon (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 to upslope agricultural land (Gundersen et al., 2010; Jaynes and Isenhart, 2014; Schultz et al., 2000).

Agricultural soils are an important source of nitrous oxide (N_2O), which is a potent greenhouse gas (GHG) with a global warming potential 298 times that of carbon dioxide (CO_2) over a 100-year timescale in the troposphere (IPCC, 2007). Some of the major soil and environmental factors driving the N_2O producing processes of denitrification and nitrification include the quantity and quality of labile C, hydrological status, organic N availability and oxygen (O_2) concentration (Firestone, 1982; Groffman et al., 1998; Dlamini et al., 2020). 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 major source of nitrate (NO_3^-) in rivers and estuaries (Howarth et al., 2012; Schultz et al., 2000; Zhang et al., 2014) and so 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 a major 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 upslope 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 (O_3) depleting substance of the 21st century in the stratosphere (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, 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, we hypothesised that riparian buffer strips are a source of N_2O emissions due to the movement of fertiliser 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 agricultural land; (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 agricultural land, and; (c) identify if a particular riparian buffer strip vegetation provides greater reductions in N transfers from agricultural land as leached N and N_2O emissions.

2. Materials and methods

2.1. 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%, 47.7% and 36.6% of sand, clay and silt, respectively (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). Some soil parameters at the commencement of the current experiment in June 2018, are shown in Table 1. This experiment forms part of a project investigating the environmental and economic efficiency of different types of vegetated buffer strips. The treatments were established in 2016 (Dlamini et al., 2021).

2.2. Experimental design and treatments

The experiment (Fig. 1) was laid out as three blocks of four plots. Each plot consisted of a main crop area and either a control (no buffer) area or a buffer area (sown with one of three riparian buffer vegetation covers). The four treatments comprised of three different types of riparian buffer strip vegetation (grass, willow and woodland riparian buffers) and a no-buffer control. Each of these treatments was replicated three times, making a total of twelve plots (Fig. 1). Each plot was 46 m in length and 10 m wide; the main upslope pasture (area 'a' in Fig. 1) being 34 m in length (340 m^2) and the buffer strip being 12 m (120 m^2) (areas 'b' and 'c' in Fig. 1, see description below). Plots with buffer vegetation also had area "b" planted with one of the three different riparian vegetation types and measured 10 m x 10 m, as well as area "c" - an untouched strip of existing vegetation measuring 2 m x 10 m (Dlamini et al., 2021).

To hydrologically isolate each plot, a plastic-lined and gravel-filled trench was installed to a depth of 1.40 m to avoid the lateral flow of water and associated pollutants including nutrients. 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.) (Dlamini et al., 2021). Nitrogen (N; as NH_4^+-N; Nitram), phosphorus (P; as P_2O_5,; triple

Table 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
Bulk density (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 Carbon (%)	4.3 ± 0.9	4.3 ± 1.1	4.2 ± 1.0	4.5 ± 0.9	4.6 ± 0.6	0.3
Total Nitrogen (%)	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

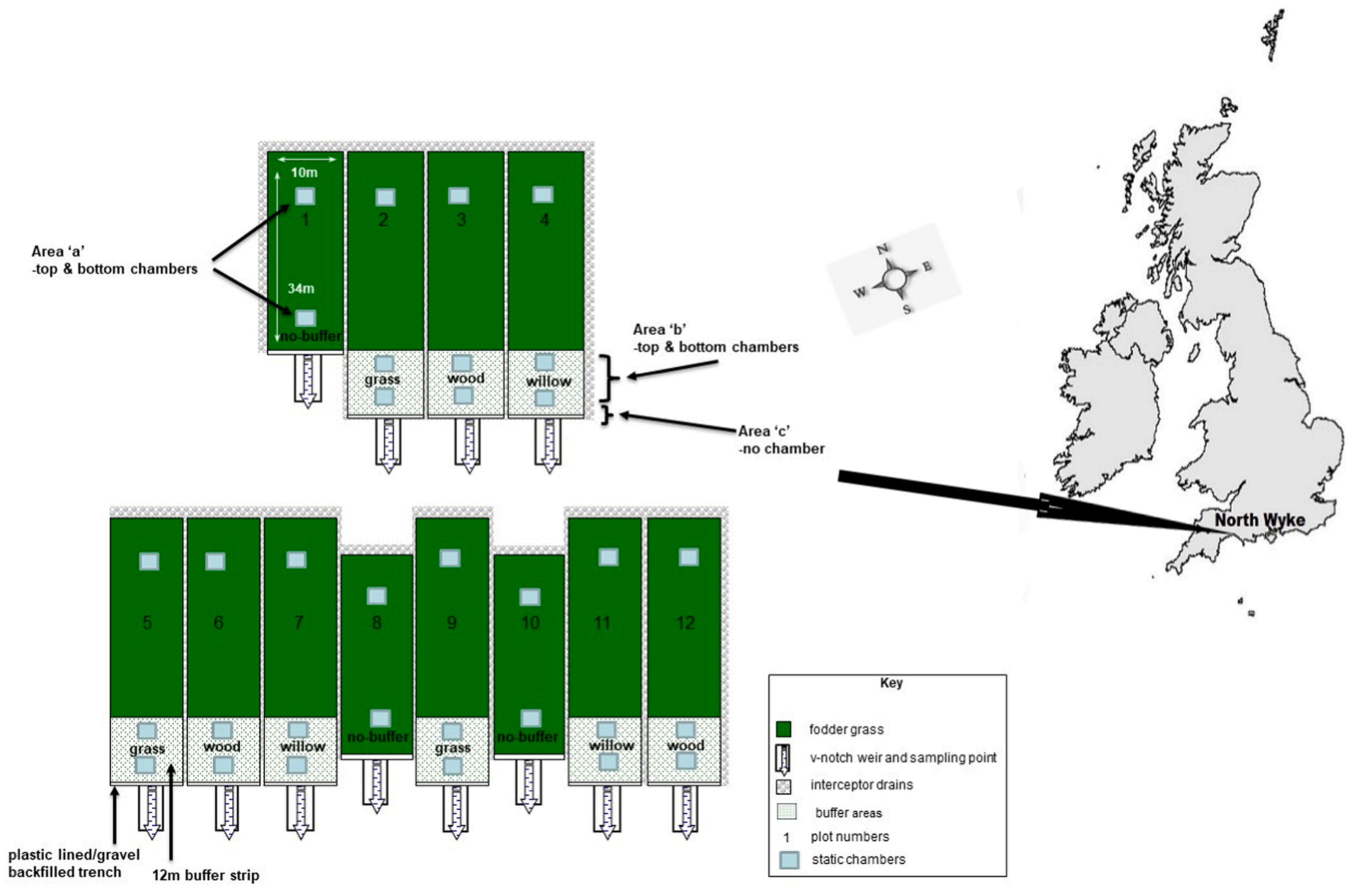

Fig. 1. Schematic of the replicated plot, treatment and chamber layout as well as their location at NorthWyke, United Kingdom.

supersphosphate) 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 permanent upslope pasture or grassland vegetation at rates of 80, 50, and 15 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, with no fertilization occurring in the riparian buffer strip areas. The experimental treatments comprised the following:

i) No-buffer strip controls: plots without the 12 m x 10 m buffer strips. The area of land described as a no-buffer control was always managed precisely as what is described for the permanent upslope pasture.
ii) Grass buffer strips: Novel grass buffer strips (*Festulolium loliaceum* cv. Prior) - The novel grass was planted in areas 'b' at the end of 2016 at a seeding rate of 5 kg ha^{-1}; a recommended seeding rate for the species in 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) Willow buffer strips: 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 to flush into the ground in May 2016 at a population of 200 plants per 10 m x 10 m area; a recommended planting density for willow plants in the Devon area. The willow cultivars were chosen from the National Willow Collection based at Rothamsted Research, Harpenden site, based on their suitability to grow in the wet clay-rich soils of the Devon site. They were also chosen based on their high capacity for pollutant uptake and their wide use for soil bioremediation (Aronsson and Perttu, 2001). During the current experiment, the 3-year old willow trees were about 3-m tall with branches and with stem diameter of about 2.5 cm, and their canopy almost completely covered the ground with little or no grass groundcover, and the trees had never been cut since planting in 2016.
iv) Woodland buffer strips: 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 strip areas. 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 × 10 m riparian buffer area, with 1.5 m tall protection tubes used to remove the 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 based on their ability to respond well to coppicing. The choice was also based on financial incentives for planting woodland along riparian buffer zones and, as well as its 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 financial incentive to plant these trees in their riparian buffer areas. The 3-year old woodland trees were 1.6 m tall with branch

canopy not fully covering the ground, hence some grass groundcover growing in between plants and rows and during the current experiment the trees and had never been cut since planting in 2016.

Area ‘c′ is the requirement for cross-compliance in England whereby it is mandatory for farmers with watercourses to adhere to GAEC (Good Agricultural and Environmental Condition) rule 1; establishment of buffer strips along watercourses (DEFRA, 2019). All of the areas within the 10 m x 10 m (10-m length is a GAEC recommended N fertilizer application limit 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 seed was sown as described above, whilst the willow and woodland riparian buffers had the trees planted within the swathe of dead grass.

2.2.1. Sampling design

Each plot consisted of a 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 chambers situated at a similar position on the slope to where the buffer strip chambers were, but they were still part of the fertilized crop area.

2.3. Field measurements

2.3.1. N_2O field measurement and laboratory analysis

i) Field sampling and laboratory analysis

N_2O 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. 33 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 silage cutting events. 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 (Fig. 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 March 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 min) from three chambers to account for the non-linear increase in gas concentration with deployment time and to assess adequately the quality of the calculated flux (Grandy et al., 2006; Kaiser et al., 1996). The remaining chambers were sampled terminally at 40 min 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. N_2O concentrations were measured using a Perkin Elmer Clarus 500 gas chromatograph (Perkin Elmer Instruments, Beaconsfield, UK) fitted with an electron capture detector (ECD) after applying a 5-standard calibration.

i) N_2O flux determination

As suggested by Conen and Smith (2000), soil N_2O 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. N_2O fluxes were computed using the Livingston and Hutchinson (1995) model:

$$Fn = \frac{\delta C_n}{\delta_t} \quad x\frac{V}{A} \quad x\frac{M_n}{V_{mol}} \tag{1}$$

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 N_2O; A is the base area of the chamber, and; V_{mol} is the volume of one mole of the N_2O at 20 °C (0.024 m^3).

ii) N_2O calculations

Cumulative N_2O emissions were estimated by calculating the area under the gas flux curve after linear interpolation between sampling points (Mosier et al., 1996).

2.3.2. Soil mineral N

Composite soil samples (0–10 cm), made up of four random subsamples, were collected monthly within 1-metre from each chamber using a soil corer, with a semi-cylindrical gouge auger (2–3 cm diameter) (Poulton et al., 2018). Total oxidized N [comprised of nitrite (NO_2^-) and nitrate (NO_3^-) N [within-lab precision (RSD%): 7.2%], the former considered to be negligible] and ammonium N (NH_4^+) (Jumppanen et al., 2014) were quantified by extracting field-moist 20 g soil samples using 2 M KCl; 1:5 soil: extractant ratio, and analysis performed using an Aquakem™ analyser (Thermo Fisher Scientific, Finland).

2.3.3. 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 (BD) 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 water filled pore-spaces (WFPS).

2.3.4. Soil temperature

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

2.3.5. 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).

2.3.6. 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 auto samplers (ENVIROTECH, UK) installed at 1.4 m below the soil surface (Fig. 2) in collection pits. Water samples were collected during storm events and analysed for total oxidized nitrogen (TON) using photometric analysis. Flow-weighted mean N concentrations (N-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).

2.4. Statistical analysis

Linear mixed models (LMMs) were used to determine whether any of

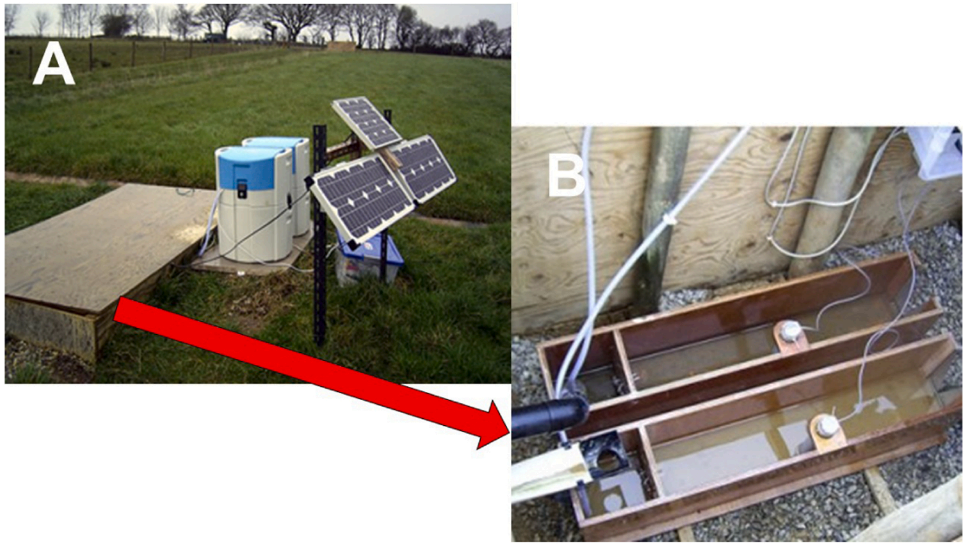

Fig. 2. The automated SampSys samplers installed at the end of each replicated plot (A), and the weirs for measuring run-off (B).

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) is *block/plot/chamber*. The fixed structure (accounting for treatment effects) is a*rea /(treatment crop * buffer area),* where *area* is a comparison of the upslope pasture, no-buffer-control and 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) in order to meet the homogeneity of variance assumption of the analysis. In each of the models, the random structure of the models (accounting for the structure of the experiment) is *block/plot/chamber* and the fixed structure (accounting for treatments effects) is 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 made using SigmaPlot (Systat Software Inc., CA, USA).

3. Results

3.1. Meteorological data and environmental soil conditions

The total rainfall during the experimental period was 204.7 mm. The highest daily rainfall event (27.3 mm) was recorded at the end of September 2018. Prior to 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.

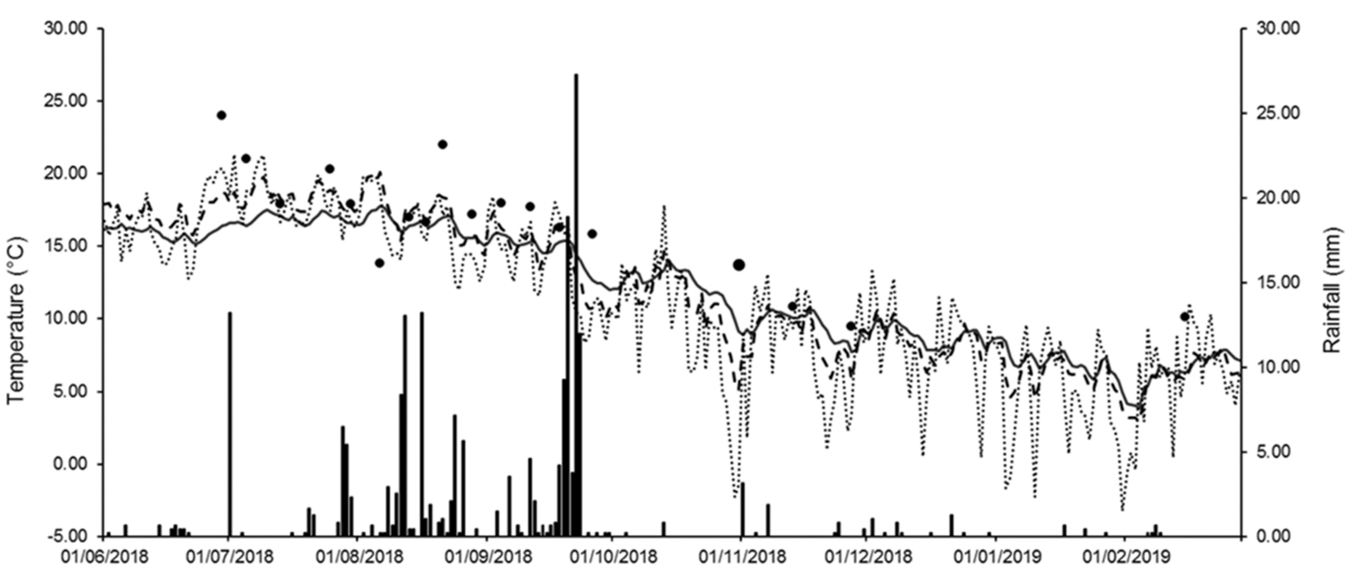

Fig. 3. Average daily rainfall, air temperature, and soil temperature at 10 cm, 30 cm and the soil surface during the experimental period. The dots (•) represent an average soil surface temperature ($n = 3$) measured during each gas sampling event.

Daily average air temperature ranged from − 3.2–21.4 °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 (Fig. 3).

3.2. 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 experimental period (Table 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 these 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, 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 concerntrations ranged between 0.021 ± 0.011 and 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. Similarly to the first storm, all the parameters were insignificant between treatments.

3.3. Soil mineral N dynamics

Fig. 4 shows the soil N concentrations determined during sampling days. Fig. 4 (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 biggest increase of about 10-fold was detected in the no-buffer control treatment, which showed between 5 and 18 times higher TON concentrations than the vegetated riparian buffer treatments. Following this, peak soil TON concentrations decreased to pre-fertilizer application levels for the grass, woodland and willow riparian buffer treatments, but stayed elevated for a longer period for the no-buffer control treatment and the upslope pasture which reached similar levels. As shown in Fig. 4 (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 buffer treatment at the sampling time immediately after fertilizer application.

3.4. %WFPS

Table 3 shows mean %WFPS for the whole experimental period and Fig. 5 shows %WFPS dynamics during the sampling occasions. The mean %WFPS ranged from 56.5 ± 5.1% to 69.1 ± 5.1%, with the grass buffer treatment having the lowest mean %WFPS. Fig. 5 shows that%WFPS had a similar temporal trend for all treatments. The biggest increase in % WFPS was observed after prolonged rainfall events during October 2018.

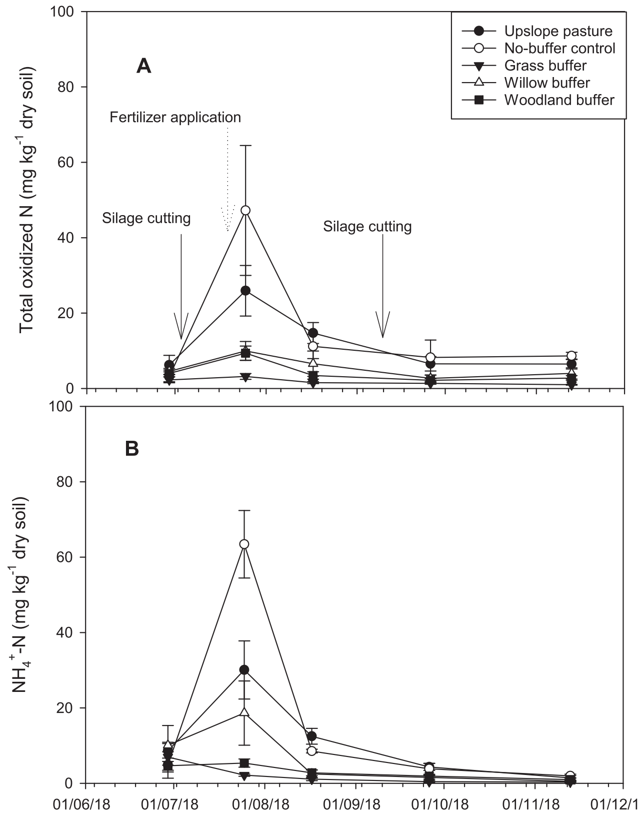

Fig. 4. Soil TON (A) and NH_4^+-N (B) dynamics for the upslope pasture and the downslope riparian buffers with different vegetation treatments during the experimental period; data points and error bars represent the treatment means (upslope pasture: $n = 12$, no-buffer control: $n = 3$, grass, woodland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

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

Parameter	Upslope pasture	No-Buffer control	Grass Buffer	Willow Buffer	Woodland Buffer	Max. LSD
Bulk Density (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

Table 2
Mean (± standard error) TON concentrations, total flow and flow weighted mean N concerntrations (N-FWMC) 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 November 2018	Total TON (mg)	15,391.9 ± 5431.1	11,076.9 ± 3849.1	18,653.7 ± 9404.8	12,343.5 ± 9613.1	192,395
	Total flow (L)	494,825 ± 22186	431,947 ± 23071	47,0371 ± 18893	497,484 ± 23569	303,482
	FWMC (mg N L^{-1})	0.031 ± 0.012	0.026 ± 0.0096	0.041 ± 0.022	0.024 ± 0.018	0.059
11 February 2019	Total TON (mg)	3370.1 ± 584.5	2621.5 ± 991.1	4581 ± 2476.6	3152.4 ± 1576.2	21,284
	Total flow (L)	132,152 ± 1884.1	113,176 ± 14451	147,964 ± 5631.3	148903 ± 7918	137,754
	FWMC (mg N L^{-1})	0.026 ± 0.0044	0.022 ± 0.0058	0.031 ± 0.015	0.021 ± 0.011	0.0251

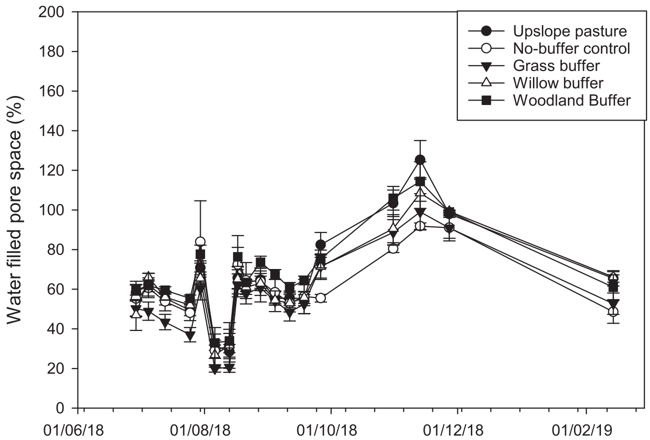

Fig. 5. Soil water filled pore space (SWFPS) within the upslope pasture and the downslope riparian buffers with different vegetation treatments. Data points and error bars represent the treatment means (upslope pasture: $n = 12$, no-buffer control: $n = 3$, grass, woodland and willow buffer: $n = 6$) and SE during each sampling day.

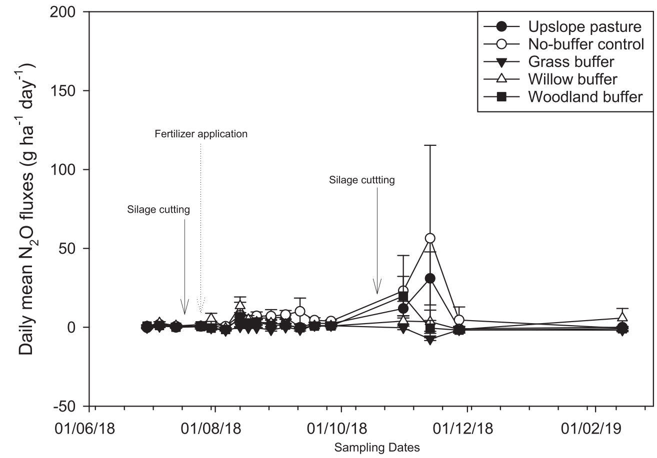

Fig. 6. Daily N_2O fluxes from the upslope pasture and the downslope riparian buffers with different vegetation treatments. Data points and error bars represent the treatment means (upslope pasture: $n = 12$, no-buffer control: $n = 3$, grass, woodland and willow buffer: $n = 6$) and SE during each sampling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

3.5. Treatment effects on soil explanatory variables

Table 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 the set of buffer treatments different to the no-buffer control treatment and upslope pasture; but the no-buffer control and upslope pasture were not significantly different to each other (LSD = 0.2725). All the buffer treatments were different to each other (LSD = 0.1223). There was no main effect difference between upper and lower chambers, but there was an interaction effect. The interaction effect indicated that the grass, willow and woodland riparian buffer treatments were only significantly different to each other in the upper chambers and only the willow riparian buffer treatment showed a difference between the upper and lower chambers (LSD = 0.3560) (Table 4). Significant differences in $\log_{10}$ TON between treatments were also observed. The average of the set of vegetated buffer treatments was different to the no-buffer control treatment and the upslope pasture; but no-buffer control and the upslope pasture were not significantly different to each other (LSD = 0.21). The willow and woodland riparian buffers were both significantly different to the grass buffer treatment, but not to each other (LSD =0.1943) (Table 4).

3.6. N_2O emissions

3.6.1. Daily fluxes

Fig. 6 shows N_2O fluxes measured on the respective sampling days. During most of the 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 buffer treatment. After the silage cut, N_2O emissions increased for all but the grass buffer treatment. Whilst the upslope pasture and no-buffer control treatment showed a further increase at the second sampling after the silage cut, the other treatments decreased again and remained around the same level as before the silage cut. The grass buffer showed the smallest fluxes, which frequently were found to be negative.

3.6.2. Total cumulative emissions

Total cumulative emissions followed the descending order: no-buffer control; 1193.2 g N_2O-N ha^{-1} (95% confidence interval: −129.2 to 3430) > upslope pasture; 717.7 g N_2O-N ha^{-1} (95% CI: 10.9–1713) > woodland riparian buffer; 306.3 g N_2O-N ha^{-1} (95% CI: −392.9 to 1583) > willow riparian buffer; 255.1 g N_2O-N ha^{-1} (95% CI: −413.8 to

Table 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

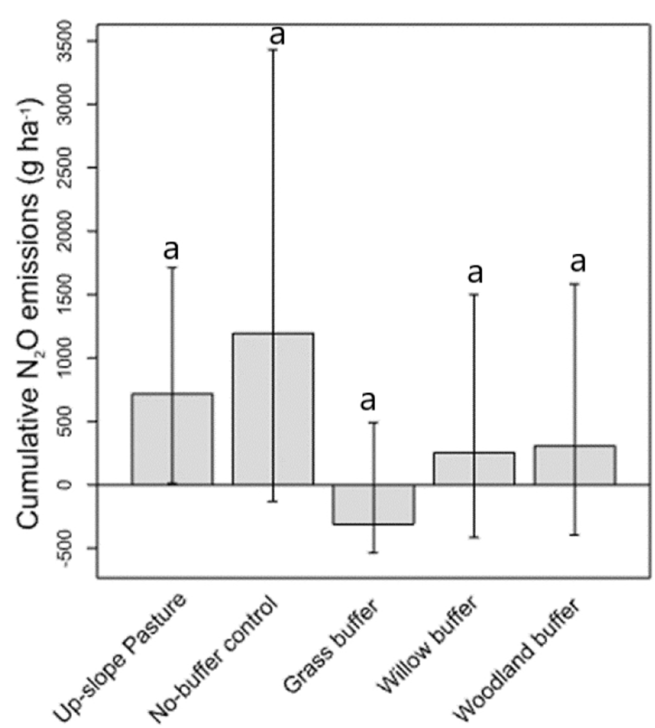

Fig. 7. Cumulative N_2O emissions for the whole experimental period from the upslope pasture and downslope riparian buffers with different vegetation treatments. The error bars represent upper 95% limit confidence intervals for the population values of the treatment means (upslope pasture: $n = 12$, no-buffer control: $n = 3$, grass, woodland and willow buffer: $n = 6$).

1501) > grass riparian buffer; − 310.2 g N_2O-N ha^{-1} (95% CI:−535.5 to 492) (Fig. 7). There was no evidence of any differences in N_2O emissions between the upslope pasture, no-buffer control and the three vegetated riparian buffers ($p = 0.110$). Also, there was no evidence of a difference amongst the three different vegetated riparian buffers ($p = 0.361$) as well as between the upper and lower parts of the riparian buffer areas ($p = 0.486$). There was also no evidence of difference of an interaction between the riparian buffer vegetation and the area within the riparian buffer vegetation (lower/upper) ($p = 0.831$).

3.6.3. *Relationships between cumulative N_2O emissions and soil environmental variables*

Fig. 8 and Table 5 show that the cumulative N_2O emissions were significantly correlated with NH_4^+-N (r = 0.4; $p = 0.041$), soil TON (r = 0.41; 0.052), pH (r = 0.13; $p = 0.0786$), and %WFPS (r = 0.27; $p = 0.268$). Fig. 9 shows that the cumulative N_2O emissions increased with an increase in NH_4^+-N, soil TON, and %WFPS and decreased with an

Table 5
P-values for the slope of the fitted line of the model.

Variable	Intercept	Standard error intercept	Slope	Standard error 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

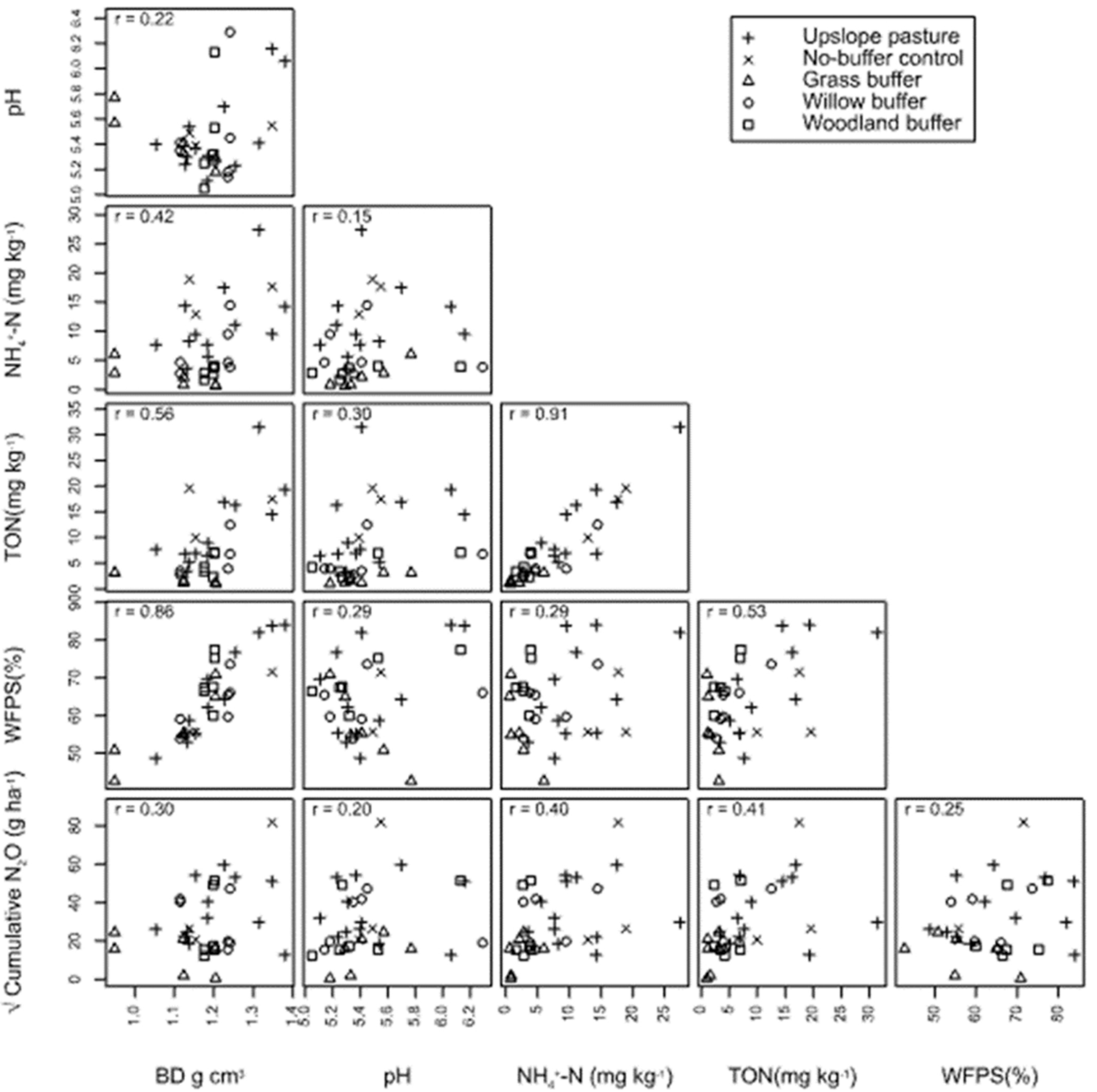

Fig. 8. Scatterplots showing the relationships between variables for the upslope pasture and the downslope riparian buffers with different vegetation treatments. r = Pearson's correlation coefficient.

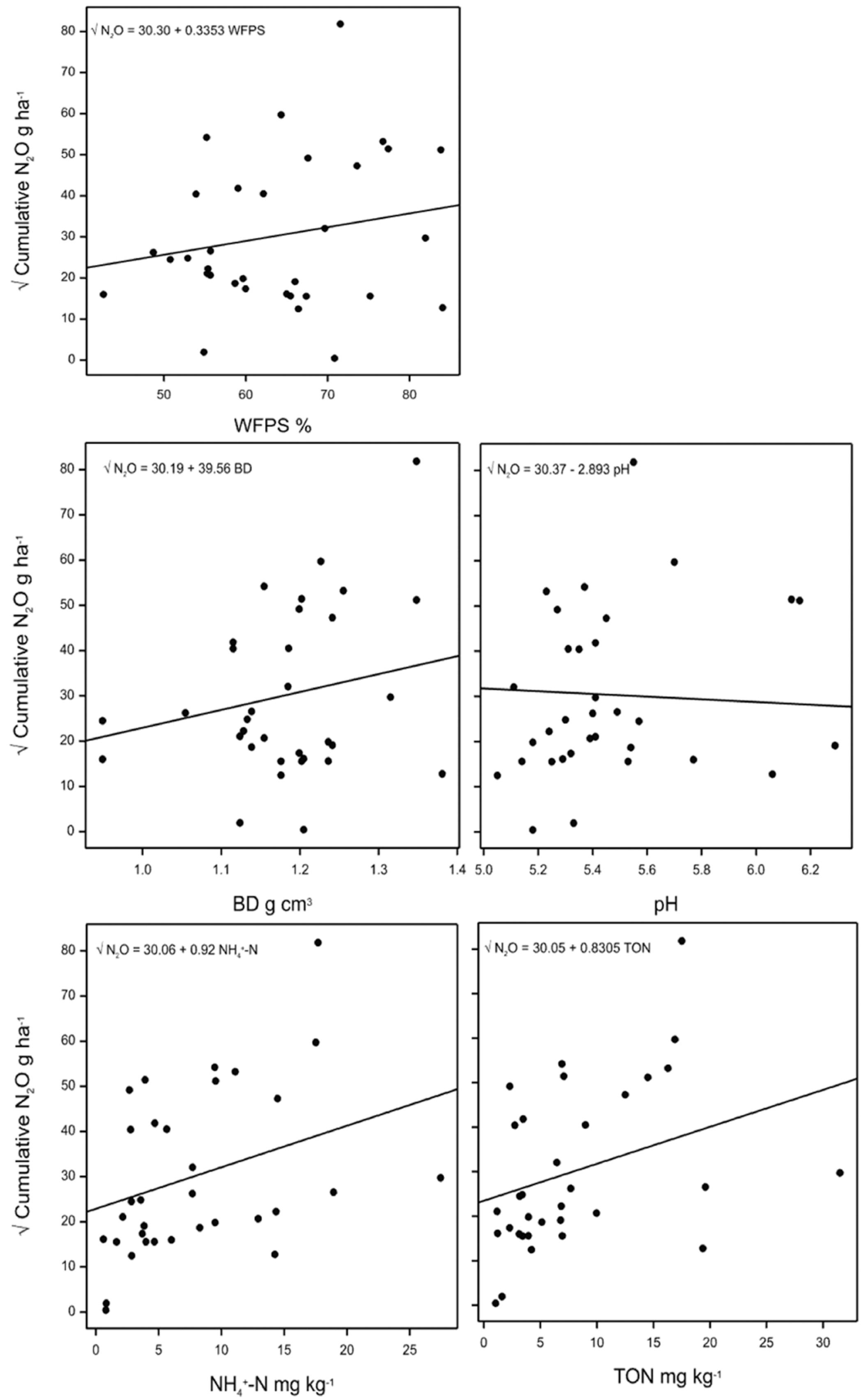

Fig. 9. Relationships between cumulative N_2O emissions versus each of the explanatory soil variables.

increase in soil pH.

4. Discussion

4.1. N_2O and soil environmental conditions

Our results 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 (Figs. 5 and 6). We observed that N_2O emissions increased with an increase in %WFPS (Fig. 9). Our findings here are consistent with previous work, including that by 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. We also observed a significant positive correlation between soil NH_4^+-N and N_2O emissions (Fig. 8) and, further, an increase in N_2O emissions with an increase in soil mineral and organic N (NH_4^+-N and TON) (Fig. 9), as reported by other authors including Perego et al. (2016) and Ngoc Tuong Hoang and Maeda (2018). High N_2O production rates are known to increase when both 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 treatment and the upslope pasture, the three vegetated riparian buffer treatments exhibited lower N_2O fluxes during this time period (Figs. 5 and 6). This can be explained as this period corresponded with lower mineral N within the three vegetated buffer treatments and higher mineral N in the no-buffer control treatment and the upslope pasture (Fig. 4). 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 treatment 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 the international literature (Fisher et al., 2014; Linn and Doran, 1984; Sehy et al., 2003).

In instances when there is no vegetation to facilitate plant N-uptake, high N_2O production rates may result (Kim et al., 2013; Snyder et al., 2009). This is as a result of abundant mineral N being available for microbial N_2O production processes; nitrification and denitrification, especially when other soil and environmental N_2O production factors are not limiting (Drury et al., 2014; Müller et al., 2004; Sehy et al., 2003). 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 treatment situated in the lower part of the plot (area 'a' bottom chamber) had higher N_2O emissions compared to 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 buffer treatments had relatively low mineral N compared to the no-buffer control treatment and the upslope pasture, yet all the treatments had a higher %WFPS in the majority of the experimental period (Figs. 4 and 5). The negative N_2O emissions in the grass riparian buffer treatment (Figs. 6 and 7) correspond to the lowest mineral N values from all treatments (Fig. 4). Riparian buffer vegetation usually retains higher soil moisture and of some riparian buffer vegetations (i.e. trees) have deeper rooting systems which may reduce sub-surface bulk density and increase organic matter compared to some upslope agricultural land (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 (mostly 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). We speculate 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 have not reached the soil surface but was reduced to N_2 through 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 treatment of the current experiment was therefore as a result of high %WFPS coupling with low mineral N as well as the impediment of N_2O diffusivity from subsurface layers.

Riparian locations 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). Our findings were in agreement with such work, since we observed 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.

4.2. N_2O emissions in the upslope pasture and downslope riparian buffers with different vegetation treatments

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 treatment may be a justifiable concern for air quality, when compared to the three vegetated buffer treatments. However, there is less alarm for the 3-year-old woodland and willow riparian buffers (which were at established phase), and there is no concern regarding the 3-year-old grass buffer (fully established); as it was an N_2O sink during the experiment (Fig. 7). 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 our study herein, we observed greater N_2O emissions from the upslope permanent pasture and no-buffer control treatment (both 3 years old), compared to the 3-year-old (establishment phase for willow and woodland) vegetated riparian buffers (Table 6 and Fig. 7). Similarly to our study, Kim et al. (2009b) 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 the adjacent maize field they served. Additionally, Groh et al. (2015) observed larger N_2O emissions in an upslope maize field compared to a 18-year-old downslope grass riparian buffer that serves it (Table 6). Our results and international literature suggest that agricultural land may sometimes emit more N_2O than neighboring downslope vegetated riparian buffers regardless of their age (Table 6).

Comparing a grass riparian buffer (age not specified) and an adjacent maize field, Hefting et al. (2003) reported emissions of 20 and 4 kg N_2O-N ha^{-1}, respectively, whilst respective emissions of 3.3 and 2.2 kg N_2O-N ha^{-1} were reported in a 19-year-old reforested riparian buffer and an adjacent maize field in another study (Kachenchart et al., 2012); similar to findings of our study (Table 6 and Fig. 7). This could be as a result of the N fertilizer applied in the upslope pasture, and this was also attested to by a significant correlation between mineral N and N_2O in the current study (Fig. 8). A study on 22-year-old forest and 19-year-old grass riparian buffers in Indiana reported N_2O emissions of 4.83 and

Table 6
N_2O emissions in croplands and their riparian buffers reported in some authors compared to the current study.

Crop Type	Riparian Buffer Vegetation Type	Riparian Buffer Age (years)	N_2O emissions (kg ha^{-1} $year^{-1}$)		Study
			Cropland	Riparian Buffer	
Maize			1.16		Baskerville et al. (2021)
	Grass	20		0.54	Baskerville et al. (2021)
	Trees	30–50		0.53	Baskerville et al. (2021)
	Trees	100–130		0.3	Baskerville et al. (2021)
	Trees	20–50		0.18	Baskerville et al. (2021)
Maize	Grass	†NS	6.8	9.3	Bradley et al. (2011)
Pasture	Trees	NS	1.7	1.6	Cuevas et al. (2020)
Maize	Trees	21	10	1.33	Davis et al. (2018)
Maize	Grass	16	12.1	1	Davis et al. (2018)
Maize	Trees	22	7.8	4.3	Fisher et al. (2014)
Maize	Grass	18	6.4	1.0	Fisher et al. (2014)
Maize	Grass	19	14.8	9.1	Groh et al. (2015)
Maize	Grass	NS	2.1	0.3	Hefting et al. (2003)
Maize	Grass	19	4.4	1.3	Iqbal et al. (2015)
Maize	Trees	19	2.2	3.3	Kachenchart et al. (2012)
Maize			3.6		Kim et al. (2009a, 2009b)
	Grass	7–17		6.3	Kim et al. (2009a, 2009b)
	Grass	7–17		4.2	Kim et al. (2009a, 2009b)
	Grass	7–17		4.1	Kim et al. (2009a, 2009b)
Maize			2.1		Mafa-Attoye et al. (2020)
	Trees	150		1.9	Mafa-Attoye et al. (2020)
	Trees	NS		3.3	Mafa-Attoye et al. (2020)
	Grass	NS		1.2	Mafa-Attoye et al. (2020)
Maize	Grass	9	3.5	0.08	Salehin et al. (2020)
Maize	Grass	NS	4	0.69	Vilain et al. (2010)
Maize	Trees	NS	2	1	Weller et al. (1984)
Pasture			0.72		This study
	No-buffer	3		1.2	This study
	Grass	3		-0.31	This study
	Trees	3		0.31	This study
	Trees	3		0.26	This study

†NS = not specified

1.03 kg N_2O-N ha^{-1}, respectively, compared to values ranging between 6.3 and 7.8 kg N_2O-N ha^{-1} in the adjacent maize fields (Fisher et al., 2014) (Table 6). Our findings, together with wider international literature, suggest that the intensity of N_2O emissions may vary between upslope utilized land and riparian buffers (both young and matured) and may be highly dependent on the buffer vegetation type (Fisher et al., 2014; Kim et al., 2009b).

4.3. N losses to water

Riparian buffer strips are fundamentally established to protect watercourses from pollutants emanating 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 buffer treatments, since it emitted the highest N-FWMC during both sampled storm events. Although the willow riparian buffer had a high N-FWMC during the both storms, theN-FWMC of the second storm was ~25% less than that of the first storm. We speculate that the majority of N applied with the fertilizer-N in the upslope pasture had been washed down with the first storm as there was no subsequent fertilization after the first storm. Our findings were therefore 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 N-FWMC of up to 7.6 mg N L^{-1}, whereas we observed a maximum of 0.041 mg N L^{-1}, despite that majority of our riparian buffer treatments being at an establishment phase. We speculate that with age, riparian buffer vegetation may become a secondary source since some N will be derived from litter mineralization, but we did not test this in the current study. Our study further shows 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 it consumed N_2O instead of emitting it like the other riparian buffer treatments.

4.4. Implications of our findings

Although our study was undertaken on a replicated experimental facility, the results have far-reaching implications for both research on non-point source pollution as well as for 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 that there was 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. Our experimental results, however, point to some concerns for the willow treatment during the establishment phase. This is because in the current experiment, this riparian buffer recorded the highest N-FWMC and emitted fairly large amounts of N_2O. Thus, the current results signal the need to consider some trade-offs for willow treatments during the establishment phase. Based on the results of the current study, farmers with permanent pasture in similar conditions 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.

4.5. Limitations of our findings

Since our experiment was undertaken using bounded replicate plots, there are inevitably some limitations in scaling up the findings. Our results are clearly most representative of the soils, climatic conditions, and management practices associated with the pasture and downslope riparian buffers in our study. 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 our new experimental evidence on business-as-usual emissions to both water and air in those parts of England. Our findings reported herein relate to the establishment phases only of the willow and woodland riparian treatments. 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.

5. Conclusions

Our experimental plot scale results imply that careful selection of riparian buffer vegetation is critical in order not to risk environmental disbenefits associated with N_2O emissions. Our results from a short study timeline showed that the grass riparian buffer was the best riparian buffer vegetation choice, particularly when serving a permanent pasture, since it was an N_2O sink but also reduced run-off N compared to the other riparian buffer vegetation. Additional studies with different upslope crops and varying soil/rainfall/slope conditions are required to if the grass riparian buffer vegetation is consistently the best riparian buffer treatment across different settings. Strategic longer-term studies are also required to explore the relative merits of the of using the novel grass species as a riparian buffer vegetation at its different maturity levels. Our results, clearly point out that the novel grass species may be a useful short-term consideration for permanent pasture for farmers in similar conditions finalizing the selection of mitigation measures for improving sustainability and minimizing unintended trade-offs within pastoral agroecosystems.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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