Soil N_2O and CH_4 Emissions From Fodder Maize Production With and Without Riparian Buffer Strips of Differing Vegetation

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Abstract

Purpose: Nitrous oxide (N_2O) and methane (CH_4) are some of the most important greenhouse gases of the 21st century. Vegetated riparian buffers are primarily implemented for their water quality functions in agroecosystems and their location in the agricultural landscape allows them to intercept and process pollutants from immediately adjacent agricultural land. They recycle increase soil carbon (C), intercept nitrogen (N)-rich runoff from adjacent croplands, and are seasonally anoxic, promoting processes producing environmentally harmful gases including N_2O and CH_4. Against this context, the study quantified these atmospheric losses between a cropland and vegetated riparian buffers that serve it.

Methods: We used the static chamber to measure N_2O and CH_4 emissions simultaneously with soil. Gas measurements were done simulataneously with soil and environmental variables for a 6-month period in a replicated plot-scale facility comprising of maize cropping served by three vegetated riparian buffers, namely: (i) a novel grass riparian buffer; (ii) a willow riparian buffer, and; (iii) a woodland riparian buffer. These buffered treatments were compared with a no-buffer control.

Results: The no-buffer control generated the largest cumulative N_2O emissions of 18 929 g ha^{-1} (95% confidence intervals: 524.1 - 63 643) whilst the maize crop upslope generated the largest cumulative CH_4 emissions of 5 050 ± 875 g ha^{-1}. Soil N_2O and CH_4-based global warming potential (GWP) were lower in the willow (1223.5 ± 362.0 and 134.7 ± 74.0 kg CO_2-eq. ha^{-1} year^{-1}, respectively) and woodland (1771.3 ± 800.5 and 3.4 ± 35.9 kg CO_2-eq. ha^{-1} year^{-1}, respectively) riparian buffers..

Conclusions: Our results suggest that maize production in general, and situations where such cropping is not undertaken in tandem with a riparian buffer strip, result in atmospheric CH_4 and N_2O concerns.

1.0 Introduction

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

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

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

2.0 Materials And Methods

2.1 Experimental site

The replicated plots used in this experiment are located at Rothamsted Research, North Wyke, Devon, United Kingdom (50°46´ 10´´N, 3° 54´05´´E). The area is situated at an altitude of 177 m above sea level, has a 37-year (from 1982 to 2018) mean annual precipitation (MAP) of 1033 mm (with the majority of rainfall received between October and November of each year) and mean annual temperature (MAT) of 10.1°C (Orr et al., 2016). The experimental area has a slope of 8° and is on soils of the Hallsworth series (Clayden and Hollis, 1985), or a dystric gleysol (FAO, 2006), with a stony clay loam topsoil comprising of 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. 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), thereby making replicated experimental work using hydrologically-isolated plots feasible.

2.2 Experimental design and treatments

2.2.1 Experimental set-up

The experiment was laid out as three blocks of four plots corresponding to four treatments each (Fig. 1). Each plot consisted of the main maize crop area with one measurement chamber and either a control (no-buffer) with a single chamber or a buffer area (sown with one of three different vegetation types) that had two chambers (upper and lower). The three buffered treatments comprised grass, willow, and woodland. Each of the four 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 maize cropped area (area 'a' in Fig. 1) being 34 m in length (340 m^2) and the downslope buffer strip being 12 m (120 m^2) (areas 'b' and 'c' in Fig. 1, see description below). 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. The cropped upslope area was previously managed as a silage crop, with a permanent pasture dominated by ryegrass (*Lolium perenne* L.), Yorkshire fog (*Holcus lanatus* L.) and creeping bentgrass (*Agrostis stolonifera* L.) planted in 2016 which was ripped and ploughed on the 14th of May 2019 in preparation to plant maize and the riparian buffer areas remained untouched. Maize (*Zea mays* L.) was planted on the 17th of May 2019 for the experiment reported herein. Slurry and inorganic fertilizer were applied at times and rates summarised in Table 1.

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

Date	Application	N-input (kg ha^{-1})	P-input (kg ha^{-1})	K-input (kg ha^{-1})
14 May 2019	Cattle slurry	20.8	12	46
17 May 2019	Inorganic fertilizer	100†	85$^{¥}$	205‡
Nutrient sources: Nitrogen; †Nitram (Ammonium nitrate), Phosphorus; $^{¥}$ triple superphosphate (P_2O_5), Potassium‡ muriate of potash (K_2O)				

2.2.2 Treatments description

1. No-Buffer control: plots with no-buffer strip at the base of the hydrologically-isolated slope. The area of land described as a no-buffer control was always managed in exactly the same way as what is described for the areas used for the maize crop.
2. Grass Buffer: Novel grass buffer (*Festulolium loliaceum* cv. Prior) - The novel grass was planted at the end of 2016 at a seeding rate of 5 kg ha^{-1}. a recommended seeding rate for the species 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.
3. Woodland Buffer: Deciduous woodland - Six species, namely Pedunculate oak (*Quercus robur* L.), hazel (*Corylus avellana* L.), Hornbeam (*Carpinus betulus* L.), Small-leaved lime (*Tilia cordata* Mill.), Sweet chestnut (*Castanea sativa* Mill.) and Wych elm (*Ulmus glabra* Huds.) were planted in the woodland buffer strips. Five individual plants (each 40 cm in height and bare rooted) of each species

were planted 1.6 m apart in rows 2-m apart in December 2016 in the 10 x 10 m area, with 1.5 m tall protection tubes used to remove risk of browsing by wild herbivores (e.g., deer). Planting was done at a density of 3000 plants ha^{-1}; a recommended planting density for the Devon area. The woodland species were chosen for their ability to respond well to coppicing (where the wood is cut to near ground level and the tree sends out new shoots to form a stool the next growing season). The choice was also based on financial incentives for planting woodland along buffer zones and, as well as it's potential for water quality improvement (Sydes and Grime, 1981). This choice also fitted with the local agri-environment payment scheme available at the time (Countryside Stewardship) for a riparian buffer zone, so it would be something that farmers with watercourses would be able to receive a payment for, in terms of getting money to plant the trees in their riparian areas. During the current experiment, the 3-year old woodland trees were 1.6 m tall and had never been cut since planting in 2016.

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

Each of the three buffer strip areas were sprayed with glyphosate herbicide to remove pre-existing grassland vegetation to enable better establishment of the planted deep rooting grass (*Festulolium loliaceum* cv. Prior), willow and woodland trees. The deep rooting grass buffer strips were also rotavated prior to seed being broadcast. Each of the buffer strips was comprised of two parts – the lower slope area comprised a 2-m strip of natural grass (area ‘c’), with the upslope area comprising a 10-m strip of treated and planted vegetation (area ‘b’). Area ‘c’ is the requirement for cross-compliance in England whereby farmers with watercourses must adhere to GAEC (Good Agricultural and Environmental Condition) rule 1; establishment of buffer strips along watercourses (DEFRA, 2019). The 10 m x 10 m area (10-m width) is the GAEC recommended N fertilizer application limit away from surface waters.

2.3 Field measurements and laboratory analyses

2.3.1 GHG measurements

Field sampling and analyses

Soil N_2O and CH_4 fluxes were measured using the static chamber technique (Chadwick et al., 2014; De Klein and Harvey, 2012). The polyvinyl chloride (PVC) chambers were square frames with lids (40 cm width x 40 cm length x 25 cm height) with an internal base area of 0.16 m^2. Thirty-three chamber collars were inserted to a depth of 5 cm below the soil surface using a steel base, and installation points were marked using a hand-held global positioning system (GPS; Trimble, California, USA) so that they could be moved into the same positions after periodic removal for agronomic activities (e.g., tillage). In the willow and woodland riparian buffers, maize cropped areas, and no-buffer control, chambers were installed in-between two crop rows, while in the grass riparian buffers, chambers were installed in pre-determined positions (Fig. 1). More specifically, the chambers were positioned as follows: (i) in area 'a' there was one chamber on the top of the plot (subsequently referred to as 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 two chambers, one on the top and one on the bottom of the buffer strip (subsequently referred to as area "b" top and bottom chambers, respectively). Gas sampling was conducted periodically from May to October 2019, between 10:00 and 13:00, using 60-mL syringes and pre-evacuated 22-ml vials fitted with butyl rubber septa. At each sampling occasion, samples were collected at four-time intervals (0, 20, 40, and 60 minutes) from three chambers to account for the non-linear increase in gas concentration with deployment time (Grandy et al., 2006; Kaiser et al., 1996). The remaining chambers were sampled terminally at 40 minutes after closure (Chadwick et al., 2014). Additionally, ten ambient gas samples were collected adjacent to the experimental area: five at the start and another five at the end of each sampling event. N_2O and CH_4, concentrations were measured using a Perkin Elmer Clarus 500 gas chromatograph (Perkin Elmer Instruments, Beaconsfield, UK) fitted with an electron capture detector (ECD) and a flame ionization detector (FID) for N_2O and CH_4, respectively, after applying a 5-standard calibration.

Gas flux determination and GWP calculations

As suggested by Conen and Smith (2000), soil N_2O and CH_4 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. Daily N_2O, and CH_4 fluxes were computed using the Livingston and Hutchinson (1995) model. Cumulative N_2O and CH_4 fluxes were estimated by calculating the area under the gas flux curve after linear interpolation between sampling points (Mosier et al., 1996). The GWP of CH_4 and N_2O are 28 and 298 times, respectively, that of CO_2 (IPCC, 2014). Therefore, GWP was estimated by multiplying total CH_4 and N_2O fluxes by 28, and 298, respectively (Del Grosso et al., 2008).

2.3.2 Soil analyses and meteorological variables

Soil pH [within-lab precision (RSD): 0.015] was measured using water (1:2.5) (Jenway pH meter, Staffordshire, UK), and soil organic matter (OM) was determined using the loss-on-ignition (LOI) technique (Wilke, 2005). Composite soil samples (0–10 cm), made up of four random sub-samples, were collected monthly within 1-m of each chamber using a soil corer with a semi-cylindrical gouge auger (2–3 cm diameter) (Poulton et al., 2018). Total oxidized N [comprised of nitrite (NO_2^-) and nitrate (NO_3^-) N, the former considered to be negligible] and ammonium N (NH_4^+) [within-lab precision (RSD%): 7.2%] 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™ analyzer (Thermo Fisher Scientific, Finland). 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 used to convert the gravimetric moisture determined during each of the gas sampling events into percent soil water-filled pore spaces (WFPS). Average daily precipitation was calculated from data measured at hourly intervals by an automatic weather station courtesy of the Environment Change Network (ECN) at Rowden, North Wyke (Lane, 1997; Rennie et al., 2020).

2.4 Data processing and statistical analysis

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

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

3.0 Results

3.1 Meteorological and soil characteristics

3.1.1 Rainfall patterns

Figure 2 shows the total monthly rainfall during the experimental period. The total rainfall for the whole experimental period was 492.2 mm, and the highest rainfall event of 118.2 mm fell in October 2019.

Before the highest rainfall in October, the second-highest rainfall events of 96.6 and 96.2 mm were recorded in June and September 2019, respectively.

3.1.2 Soil variables

Table 2 presents the average soil data during the experimental period. Soil pH ranged from 5.1 ± 0.17 and 5.5 ± 0.17, with the highest pH of 5.5 ± 0.17 (willow riparian buffer), which was however, not significantly (*LSD = 0.29*) different to the grass or woodland riparian buffers. The largest soil BD of 1.2 ± 0.05 g cm^{-3} was recorded in the no-buffer control, which was not significantly different from the upslope maize and the different vegetated riparian buffers (*LSD = 0.19*). Soil OM ranged from 9.0 ± 3.2 to 17.8 ± 2.3%, with the largest %OM of 17.8 ± 2.3% recorded in the willow riparian buffer, which was, however, not significantly (*LSD = 8.6*) different to the woodland riparian buffer (15.98 ± 2.3%).

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

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

3.1.3 Soil mineral N-dynamics

Figure 3 shows soil mineral N dynamics during the experimental period. At the commencement of the experiment, NH_4^+-N was < 17 mg kg^{-1} dry soil in all of the treatments, with the largest of 16.7 ± 3.5 mg kg^{-1} dry soil observed in the upslope maize. However, after the second sampling event, which had been preceded by two fertilizer application events (Table 1), NH_4^+-N increased by almost 3-fold in the no-buffer control and upslope maize treatments but remained relatively low in the vegetated riparian buffers. Despite the high NH_4^+-N values in the no-buffer control and upslope maize crop areas after fertilization, values dropped to < 30 mg kg^{-1} dry soil after the fourth sampling event and remained low until the end of the experimental period. The average NH_4^+-N for the whole experimental period ranged from 6.4 ± 2.78 to 27.4 ± 2.8 mg kg^{-1} dry soil, with the largest value of 27.4 ± 2.8 mg kg^{-1} dry soil obtained from the upslope maize crop areas, which was however, not significantly (*LSD = 7.8*) different to the no-buffer control. It was, however, significantly different (*LSD = 7.8*) to the vegetated riparian buffers (Table 2).

Total oxidized N was < 30 mg kg^{-1} dry soil in all of the treatments at the commencement of the experiment (Fig. 3). However, after the second sampling event, TON increased 4-fold in the upslope maize and no-buffer control but remained low in the riparian buffers. Despite a drop to ~ 35 mg kg^{-1} dry soil in all of the upslope maize and no-buffer control areas during the fifth sampling event, the upslope maize emerged with the highest TON of ~ 81 mg kg^{-1} dry soil during the sixth sampling event. However, these values dropped gradually up until the end of the experiment. Average TON for the whole experimental period ranged from 4.99 ± 3.0 to 55.7 ± 1.7 mg kg^{-1} dry soil, with the highest value of 55.7 ± 1.7 mg kg^{-1} dry soil obtained from the upslope maize. This was significantly different (*LSD = 10.0*) to all other treatments, except for the no-buffer control (Table 2).

3.1.4 %WFPS

Soil WFPS trends during the experimental period are shown in Fig. 4 (A), and Table 2 shows the average %WFPS for the whole season. The highest %WFPS was observed during the fifth sampling event, with the overall highest estimate observed in the woodland riparian buffer treatment. The woodland riparian buffer maintained higher %WFPS values than the remainder of the treatments during the experiment. The average %WFPS for the whole experimental period ranged from 81.7 ± 9.9 to 102.9 ± 7.2%, with the highest value recorded in the willow riparian buffer, which was however not significantly (*LSD = 18.6*) different to the woodland riparian buffer treatment, or any of the other treatments.

3.3 Treatment effects on explanatory variables

Table 3 shows that soil OM differed between sampling areas; upslope and downslope chambers ($P < 0.05$), but there was no evidence of any other differences between treatments. Soil OM in the vegetated riparian buffer strips was different from the upslope maize but not to the no-buffer control, which was not different from the upslope maize. Soil NH_4^+-N also differed between areas, but there was no evidence of any other differences between treatments. The NH_4^+-N in the vegetated riparian buffer strips was different from the upslope maize and no-buffer control, and the upslope maize and no-buffer control were not different from each other. Soil pH was different between areas, and there was an interaction between treatments and the upper and lower buffer areas. The pH in the vegetated riparian buffer strips was different from the upslope maize and no-buffer control; but they were not different to each other. Soil pH was different in the upper and lower areas of the willow and woodland riparian buffer strips but not in the grass riparian buffer strips. TON was different between areas, but there was no evidence of any other treatment differences. All three riparian buffer vegetation types were different, and there was no evidence of any treatment differences for BD or WFPS (Table 2).

Table 3
P-values for tests from LMMs on each of the measured soil variables.

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

3.4 Gas emissions

3.4.1 Gas fluxes

Nitrous oxide

Nitrous oxide fluxes measured during each sampling event are shown in Fig. 4 (B). The commencement of the experiment was marked by relatively low fluxes in all of the treatments. These low fluxes were immediately followed by the highest peak in all the treatments, observed instantly after fertilizer application, with the maximum mean flux of 721.1 ± 464.3 g N_2O ha^{-1} day^{-1} observed in the upslope maize. There was also a smaller peak of up to 204 ± 5.7 g N_2O ha^{-1} day^{-1} observed in the upslope maize at around the 1st of August 2019. After that, fluxes remained < 10 g N_2O ha^{-1} day^{-1} in all the treatments, with the upslope maize and no-buffer control maintaining predominantly higher fluxes until the end of the experiment.

Methane

Daily CH_4 fluxes, which were mostly positive and sometimes negative, are illustrated in Fig. 4 (C). Similar to N_2O fluxes, the commencement of the experiment was marked by low CH_4 fluxes, which increased up to ~ 40 g CH_4 ha^{-1} day^{-1} (in the upslope maize and no-buffer control) immediately after fertilizer application. After these peaks, CH_4 fluxes remained low and mostly negative in all the treatments until the end of the experiment.

3.4.2 Cumulative gas emissions

Nitrous oxide

There was no evidence of significant treatment differences in N_2O emissions between the upslope maize, no-buffer control and the three vegetated riparian buffers ($p = 0.67$) (Fig. 5A). Cumulative N_2O emissions had a descending order: no-buffer control; 18 929 g ha^{-1} (95% confidence intervals: 524.1–63 643 g ha^{-1}) > upslope maize; 6 523 g ha^{-1} (95% CI: 550.7–19 060) > woodland riparian buffer; 2 641 g ha^{-1} (95%

CI: -267.9-14 195 g ha^{-1}), willow riparian buffer; 2 324 g ha^{-1} (95% CI: -382.1-13 448) > grass buffer 375 g ha^{-1} (95% CI: -2 340.6–7 592 g ha^{-1}).

Methane

The upslope maize and the no-buffer control (not significantly different from each other) emitted significantly higher cumulative soil CH_4 fluxes than the three vegetated riparian buffers (p = 0.02) (Fig. 5B). Cumulative soil CH_4 fluxes were in the descending order: upslope maize: 5050 ± 875 g ha^{-1} > no-buffer control: 4740 ± 1411g ha^{-1} > grass riparian buffer: 3289 ± 1135 g ha^{-1} > willow riparian buffer: 2597 ± 1135 g ha^{-1} > wood riparian buffer: -102 ± 1135 g ha^{-1}.

Global warming potential

Soil N_2O-based GWP ranged from 1223.5 ± 362.0 (willow riparian buffer) to 10 225.1 ± 4735.7 (no buffer control) kg CO_2-Eq. ha^{-1} year^{-1} (Table 7). A significantly the highest GWP found from the no-buffer control, which was, however not significantly different from the upslope maize. On the other hand, soil CH_4-based GWP ranged from 3.4 ± 35.9 (woodland riparian buffer) to 282.9 ± 33.4 (no buffer control) kg CO_2-Eq. ha^{-1} year^{-1}. Despite the large GWP found in the no buffer control, it was not significantly different to the other treatments, but to the woodland riparian buffer. (Table 7).

Table 7
Land-use effects on global warming potential (GWP)

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

Relationships between gas emissions and measured soil variables

Table 4 and Fig. 6 show that none of the measured soil variables had a significant relationship with cumulative N_2O, but a slight relationship with TON (r = 0.32; $p = 0.065$). N_2O emissions were shown to increase with an increase in soil BD, NH_4^+-N, TON, and %WFPS and to decrease with an increase in pH and OM (Fig. 7).

Table 4
P-values for the slope of the fitted line of the model for N_2O and measured soil variables.

Variable	Intercept	Standard error intercept	Slope	Standard error slope	*P-value*
BD	-172.6	142.1	201.9	119.98	0.126
pH	122.9	191.9	-10.56	36.194	0.786
NH_4	38.29	23.48	1.58	1.1513	0.18
TON	33.97	18.18	1.068	0.555	0.065
WFPS	44.16	69.45	0.2518	0.75597	0.742
OM	69.7	29.76	-0.2556	2.05029	0.902

Table 5 and Fig. 8 show that pH (r = -0.44; *p* = 0.042), TON (r = 0.44; *p* = 0.005), and NH_4^+-N (r = 0.33; *p* = 0.056) had significant relationships with cumulative CH_4 emissions. Soil CH_4 emissions increased with increased BD, NH_4^+-N, and TON and decreased with an increase in pH, %WFPS, and OM (Fig. 9).

Table 5
P-values for the slope of the fitted line of the model for CH_4 and measured soil variables.

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

4.0 Discussion

4.1 Gas emissions

4.2.1 Soil and environmental controls of gas fluxes

Nitrous oxide

The largest peak N_2O flux observed in the upslope maize coincided largest %WFPS in the treatment and followed N fertilizer application events in the upslope maize and no buffer control (Fig. 4A and B). N_2O fluxes following N fertilizer application are known to increase with increasing soil water content; most rapidly above 70% WFPS, wherein denitrification is a dominant process (Abbasi and Adams, 2000; Dobbie et al., 1999; Granli and Bockman, 1994; Skiba and Ball, 2002). As one of the major drivers of N_2O production, soil moisture directly affects N_2O production and consumption through its influence on the N-substrate availability, soil aeration and metabolic activity of N_2O-producing microorganisms; all controlling the capacity of soil to produce N_2O (Di et al., 2014; Khalil and Baggs, 2005; Simona et al., 2004). Fertilizer N increases soil mineral N availability; a substrate for dominant N_2O microbial producing reactions; nitrification and denitrification (Butterbach-Bahl et al., 2013; Dobbie et al., 1999). Thus, the higher fluxes were expected after fertilizer N application in the no-buffer control and the upslope maize of the current study, similar to other studies; particularly Halvorson et al. (2008) and Van Groenigen et al. (2004), who reported that soil N_2O emissions increased linearly with increasing fertilizer N. This was further attested to by an increase in N_2O emissions with every increase in soil TON and NH_4^+-N (Fig. 7). This was also in agreement with previous work, particularly Mosier (1994), Mosier et al. (1996), and Barton and Schipper (2001). Notably, the woodland and willow riparian buffers had the highest %WFPS but were characterised by lower N_2O emissions during the peak flux. On top of the low N substrate due to the fact that the riparian buffers were not fertilized, this could have been due to reduced diffusion in the high soil moisture causing a further reduction of N_2O to N_2 (Balaine et al., 2013; Hamonts et al., 2013). On the other hand, the no-buffer control and upslope maize had larger fluxes; which further highlights the interactive role of soil moisture and mineral N in enhanced N_2O production (Klemedtsson et al., 1988). The no buffer control emitted 15.6% while the upslope maize 5.4%, which means that of the total fertilizer N added, 21% was lost as N_2O in the 6 month experimental period. We however, did not use stable isotopes to ascertain this.

Methane

The overall positive CH_4 emissions from all treatments are most likely the result of the high %WFPS experienced during most of the experimental period. The upper values (~ 5 kg CH_4 ha^{-1}) are similar to those reported by Groh et al. (2015). A number of field investigations have identified soil water content as one of the critical controls of CH_4 production and consumption in soils from different ecosystems (Khalil and Baggs, 2005; Kim et al., 2010; Wu et al., 2010). Similarly, in our study, the peak CH_4 fluxes followed immediately after the highest %WFPS (Fig. 4C). High soil moisture contents are documented drivers of CH_4 production and emissions in soils; as a group of strictly anaerobic bacteria biologically produce a majority of CH_4 in reduced environments (Ehhalt et al., 2001; Ehhalt and Schmidt, 1978; Yang and Chang, 1998). Soil moisture directly affects the production of soil CH_4 through its influence on C-substrate availability, soil aeration, and metabolic activity of CH_4 producing microorganisms; all affecting the capacity of soil to produce or consume CH_4 (Khalil and Baggs, 2005; Simona et al., 2004). Further, the role of soil moisture in CH_4 production and subsequent emissions was attested to by the low (sometimes negative) CH_4 fluxes we observed; coinciding with low soil %WFPS at the end of August (Fig. 4); similar to (Luo et al., 2013). The latter work observed that soil moisture affected soil CH_4 consumption through its effect on substrate availability and redistribution, soil aeration, and the metabolic activity of microorganisms.

4.1.2 Gas emissions in upslope maize and downslope riparian buffer strips

Nitrous oxide

For a riparian buffer to be considered an atmospheric concern, it must emit more N_2O than the cropland it serves (Fisher et al., 2014). In the current study, the no-buffer control proved to be an atmospheric concern, since it generated the highest N_2O emissions compared to the upslope maize and the three vegetated riparian buffers (Fig. 5A). The maximum cumulative emissions of 20 kg N_2O (~ 12 kg N ha^{-1}) are similar to Kim et al. (2009) (2-year study) and Groh et al. (2015) (1-year study), who observed 24 and 14.8 kg N_2O ha^{-1}, respectively, in maize in a Humid Continental climate. The high N_2O emissions observed in the no-buffer control could have been due to applied fertilizer N (particularly readily available inorganic N); which increased mineral N availability for the N_2O-producing nitrification and denitrification processes, similar to the responses reported by other authors; particularly Dobbie et al. (1999) and (Butterbach-Bahl et al., 2013). In fact, the high N_2O emissions in the no-buffer control shows a downward movement of the fertilizer applied N with rainwater. This was further attested to by the high mineral N (TON and NH_4^+) in the no-buffer control compared to the remainder of the treatments (Table 2) and an increase in N_2O emissions with every increase in mineral N (Fig. 8). The fact that the vegetated riparian buffers had low N_2O emissions shows that they served their purpose of intercepting and processing N to N_2 through denitrification induced by their high soil moisture (Groffman et al., 1991; Knowles, 1982) before it was delivered off-site. Interestingly, the riparian buffers had ideal condition to promote full denitrification, reducing N to N_2, especially at the high moisture and in the case of willow and woodland the high organic matter and potentially available C which explains their low N_2O compared to the upslope pasture and no buffer control. The low N_2O emissions in the vegetated riparian buffers could also be a result of the fact that the riparian buffer strips were not directly fertilized; further highlighting the role of fertilizer N in increasing mineral N availability for N_2O producing processes; similar to Davis et al. (2019), Hefting et al. (2003) and Iqbal et al. (2015). The second-highest N_2O emissions observed in the upslope maize could have also been due to the N fertilizer applied.

Methane

The fact that the upslope maize and no-buffer control treatments exhibited high CH_4 emissions may have been a result of NH_4^+-N based fertilizer N applied in the two treatments, since NH_4^+-N has been shown to inhibit CH_4 oxidation (Hütsch, 1998; Kravchenko et al., 2002; Tlustos et al., 1998); which often results in a net increase in CH_4 emitted from soil (Bronson and Mosier, 1994). This inhibition is thought to be either a general salt effect (Gulledge and Schimel, 1998), a competition between ammonia (NH_3) and CH_4 for methane monooxygenase enzymes (Bédard and Knowles, 1989), or non-competitive inhibition by hydroxylamine (NH_2OH) or nitrite (NO_2^-) produced during NH_3 oxidation (King and Schnell, 1994). To further emphasize the role of mineral N in inhibiting CH_4 oxidation, the three vegetated and unfertilized riparian buffers had significantly lower CH_4 emissions than the upslope maize and the no-buffer control (Fig. 5).

4.1.3 Global warming potentials

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

4.2 Implications of the findings

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

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

4.3 Limitations of the study

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

5.0 Conclusions

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

Declarations

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Figures

Figure 1

A schematic diagram of the replicated experimental plots and their location at NorthWyke, United Kingdom.

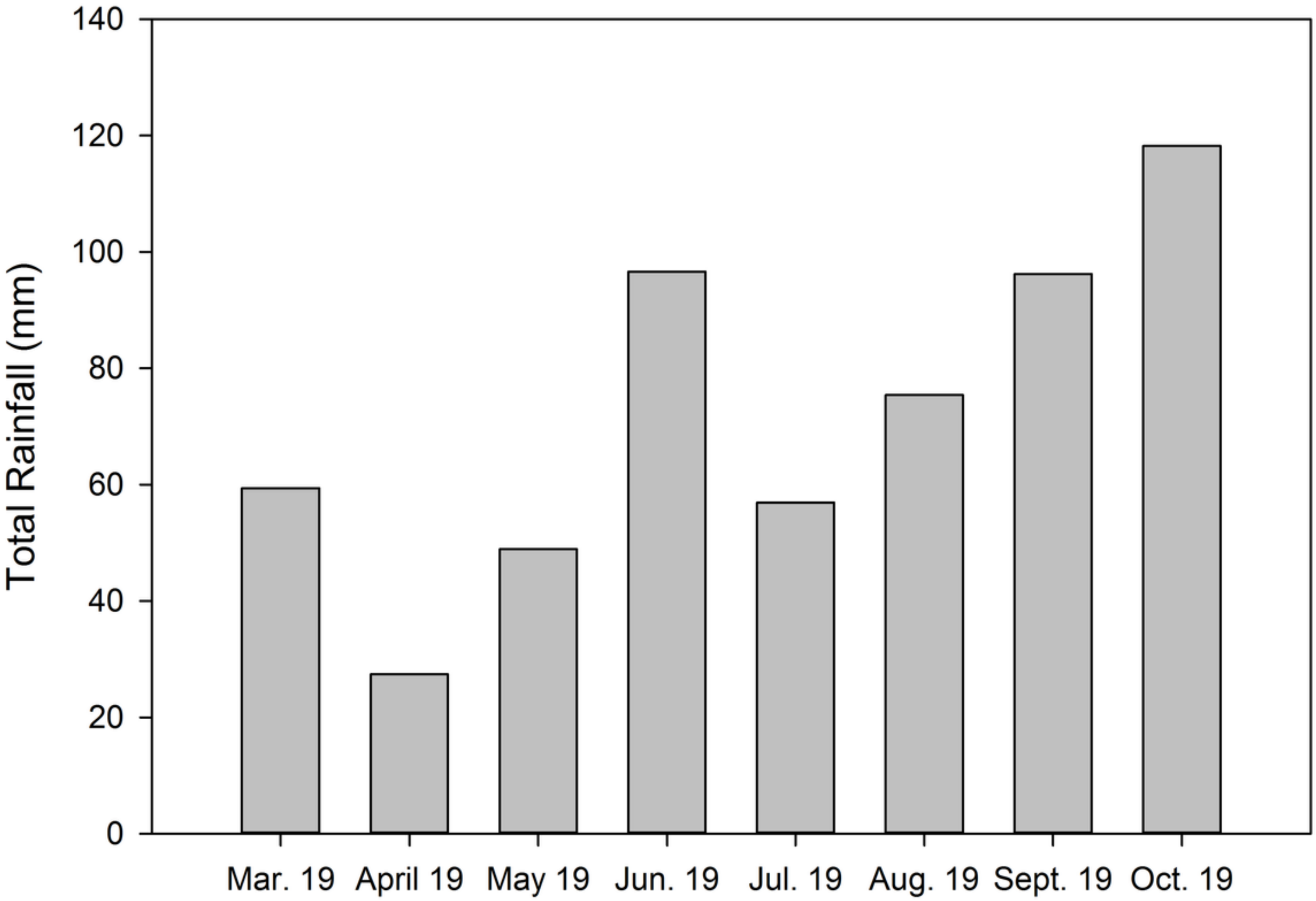

Figure 2

Total monthly rainfall during the experimental period.

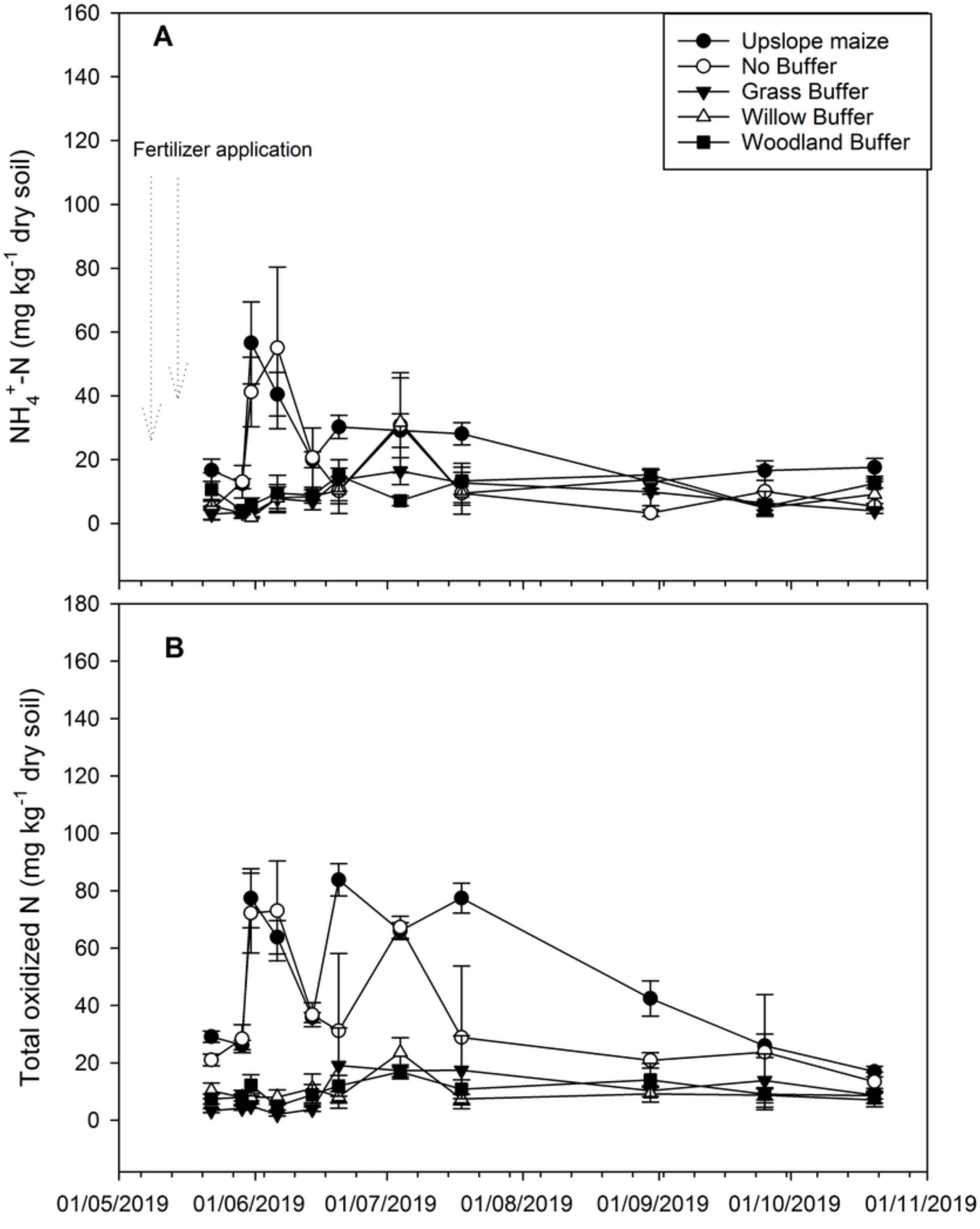

Figure 3

Soil NH4+ and TON in the upslope maize and downslope riparian buffers during the experimental period.

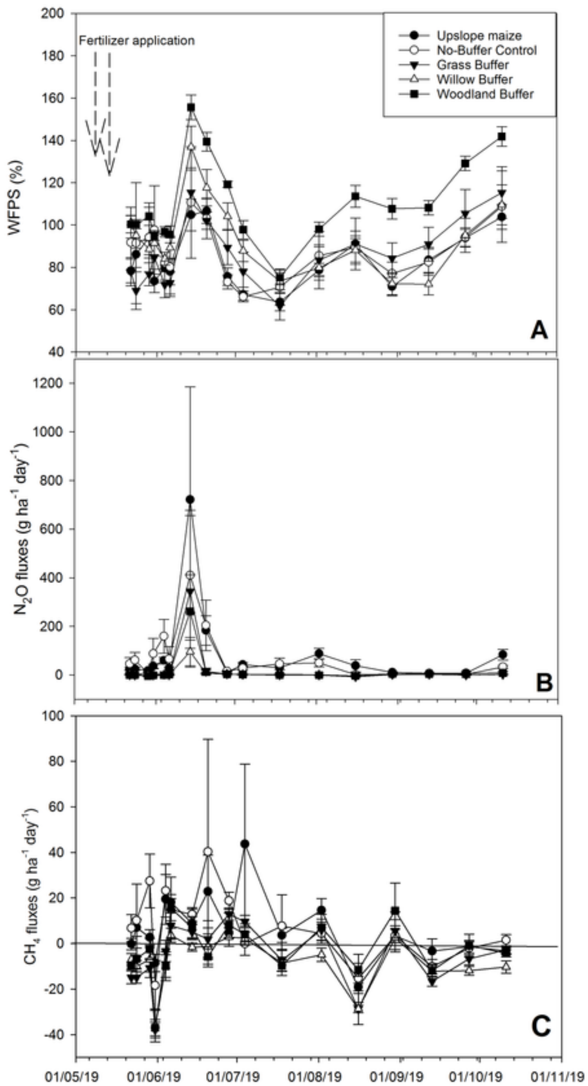

Figure 4

Daily (A) soil WFPS, and (B) N2O, and (C) CH4 fluxes in the upslope maize and downslope riparian buffers. Data points and error bars represent the treatment means (cropland: n = 12, no-buffer control: n = 3, grass, woodland and willow buffer: n = 6) and SE during each sampling day. The vertical line in CH4 marks 0 fluxes.

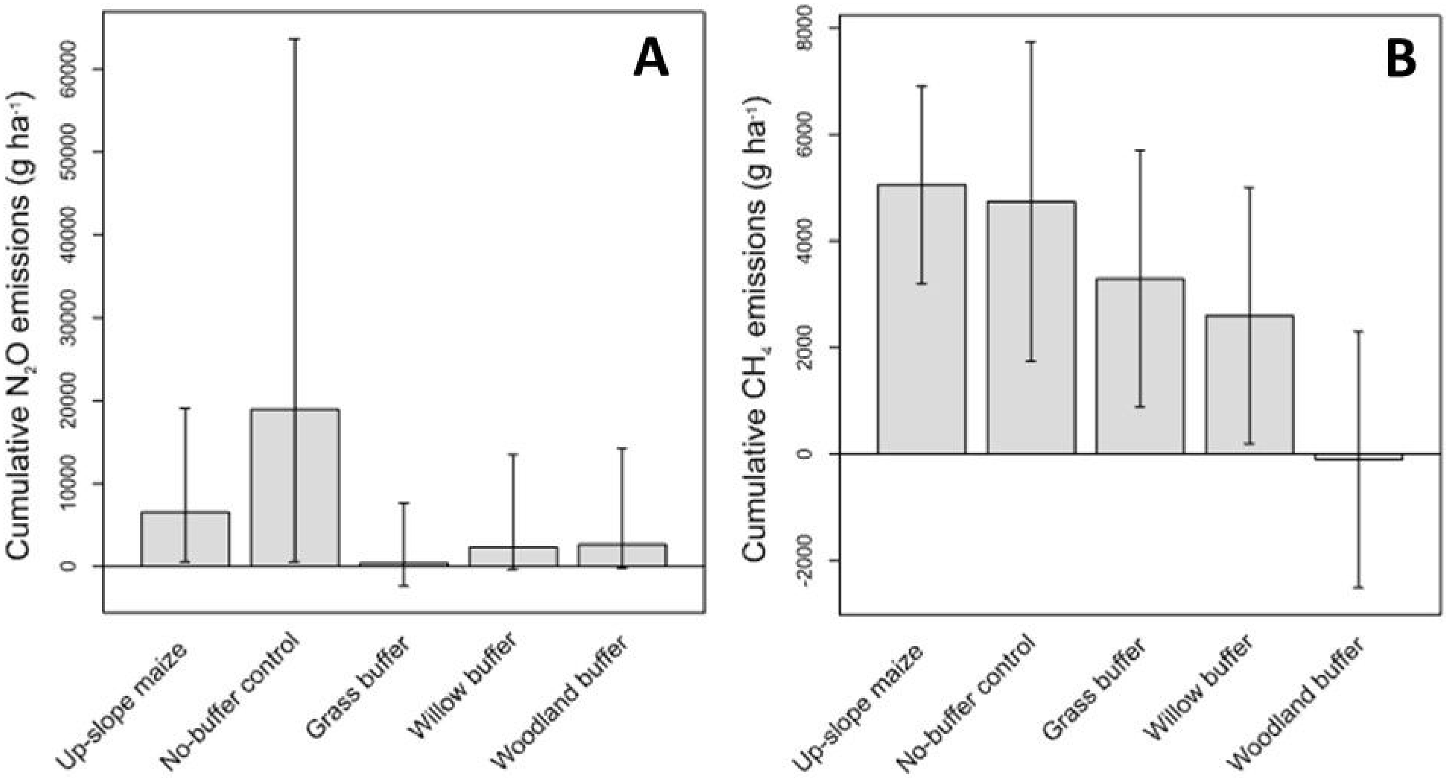

Figure 5

Cumulative (A) N2O and (B) CH4 emissions for the whole experimental period from the upslope maize and different downslope buffer vegetation. Error bars represent 95% confidence intervals (cropland: n = 12, no-buffer control: n = 3, grass, woodland and willow buffer: n = 6). Vertical lines are 95% confidence intervals.

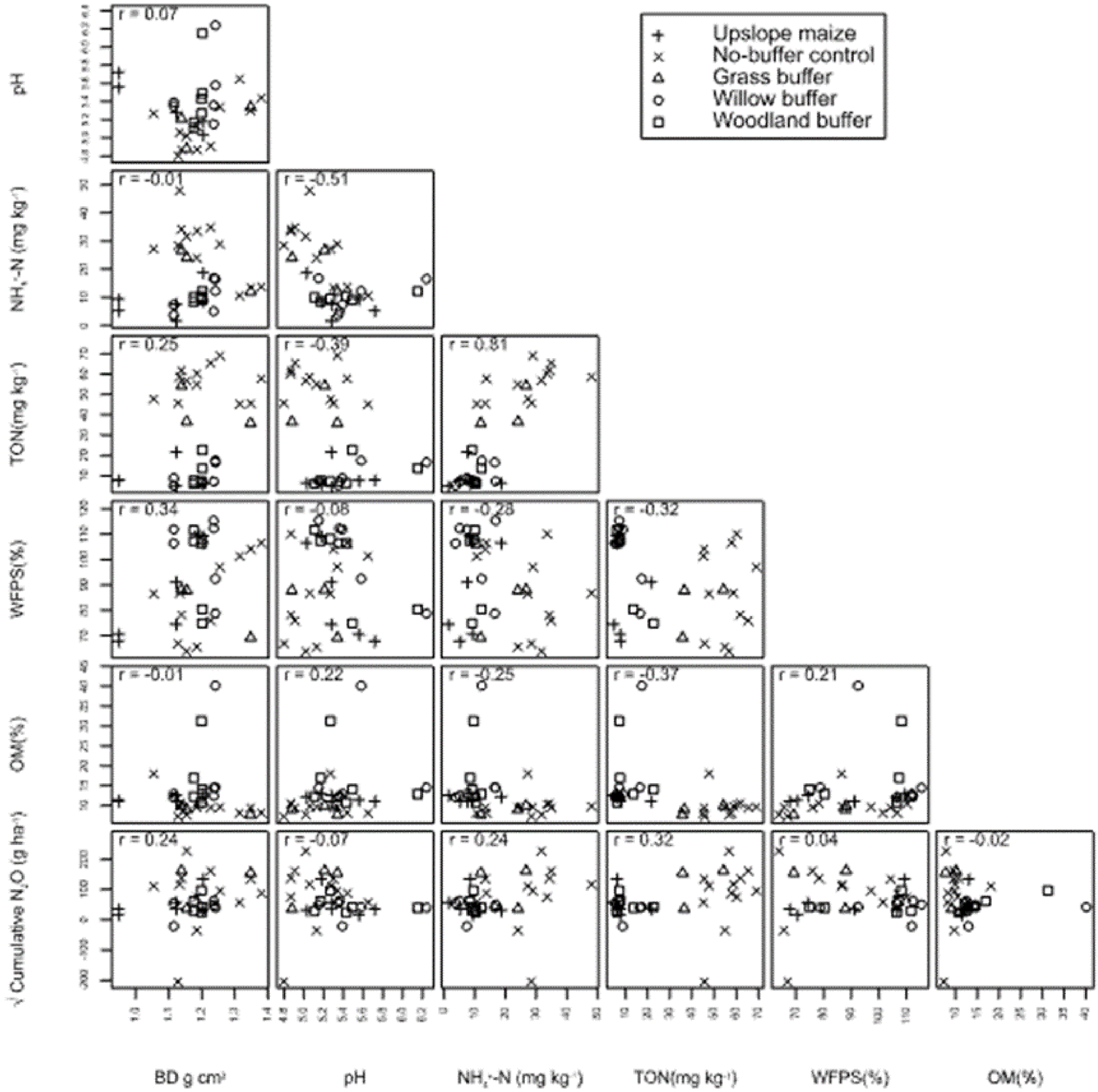

Figure 6

Scatterplot showing the relationships between the variables pH, soil NH4+-N, soil TON, water filled pore space (WFPS%), organic matter (OM), bulk density (BD) and cumulative N2O emissions for the upslope maize and the downslope riparian buffers with different vegetation treatments. r = Pearson's correlation coefficient.

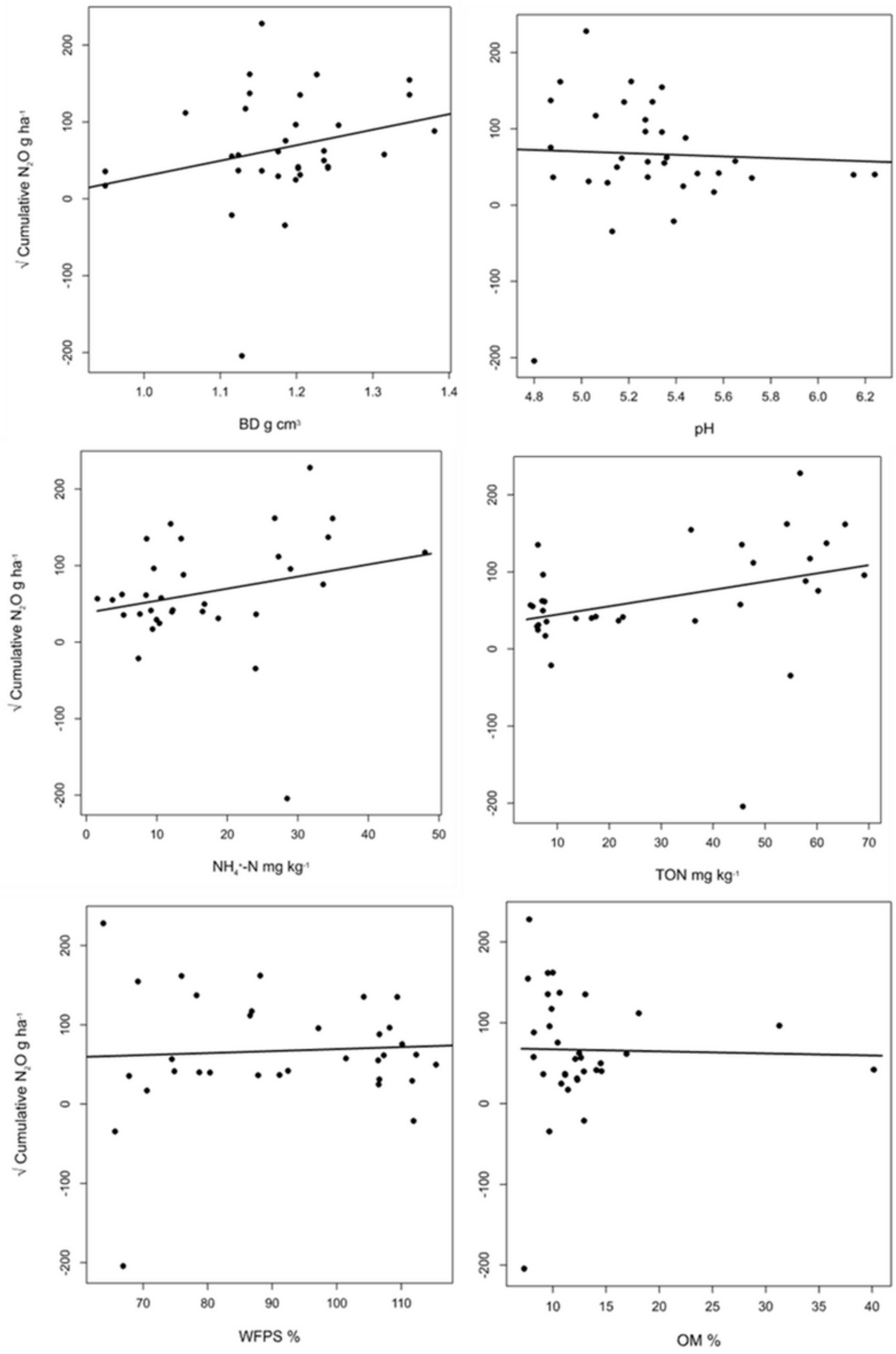

Figure 7

Relationships between cumulative N2O emissions and each of the explanatory soil variables.

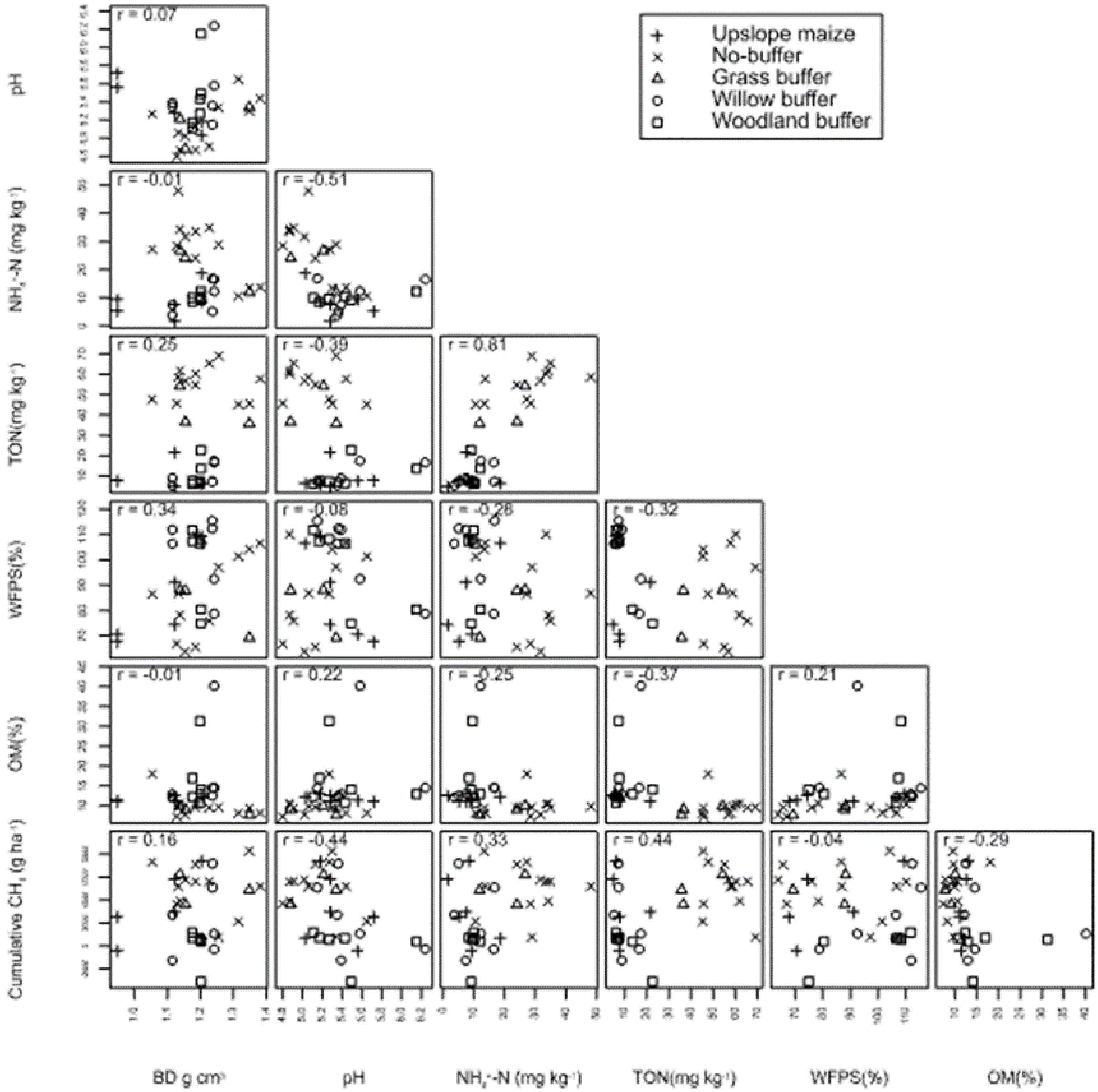

Figure 8

Scatterplot showing the relationships between the variables pH, soil NH4+-N, soil TON, water filled pore space (WFPS%), organic matter (OM), bulk density (BD) and cumulative CH4 emissions for the upslope maize and the downslope riparian buffers with different vegetation treatments. r = Pearson's correlation coefficient.

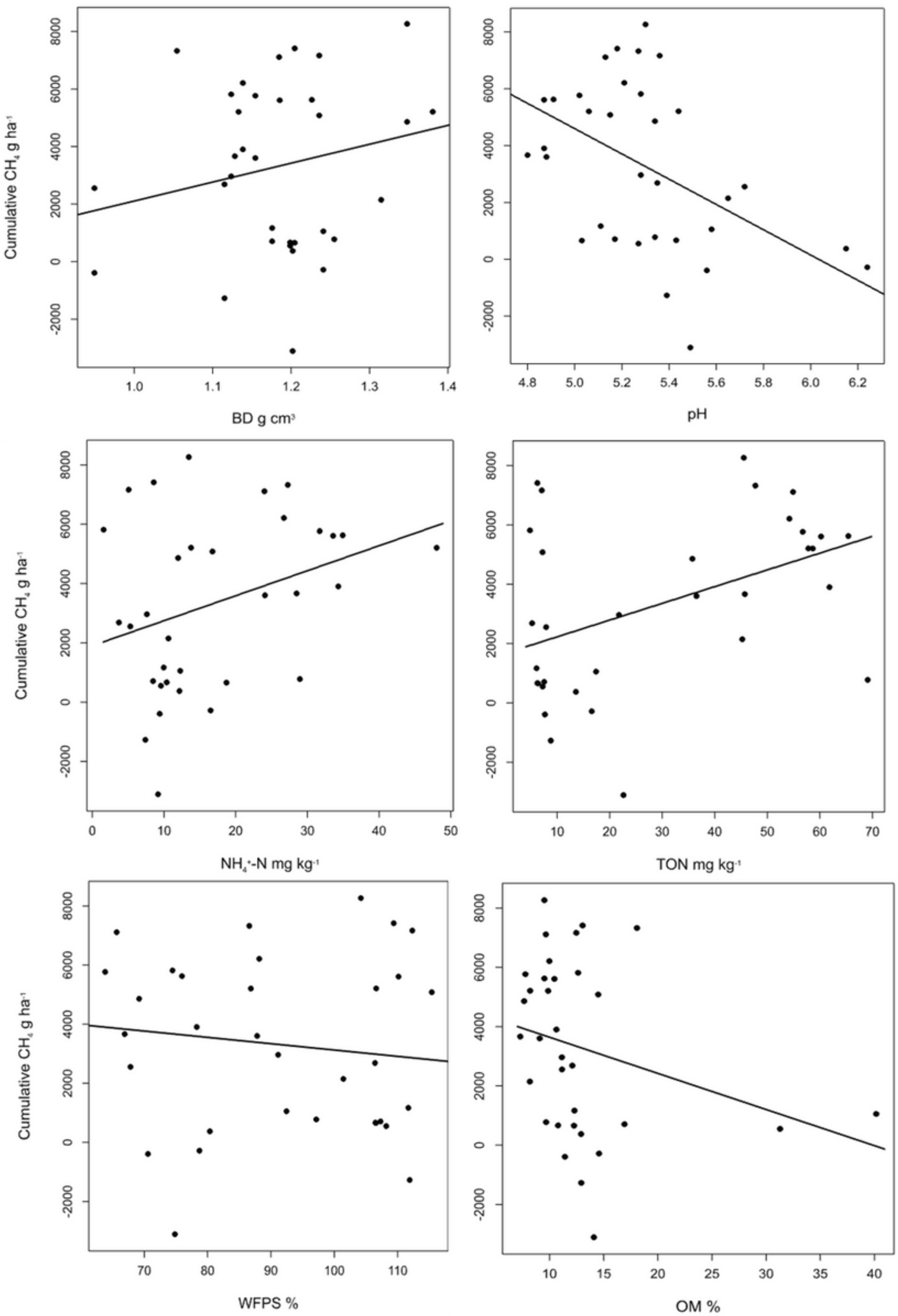

Figure 9

Relationships between cumulative CH4 emissions and each of the explanatory soil variables.