RESEARCH ARTICLE

Soil methane (CH_4) fluxes in cropland with permanent pasture and riparian buffer strips with different vegetation[#]

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Abstract

Background: Methane (CH_4) has a global warming potential (GWP) 28 times that of carbon dioxide (CO_2) over a 100-year horizon. Riparian buffers strips are widely implemented for their water quality protection functions along agricultural land, but conditions prevailing within them may increase the production of radiative greenhouse gases (GHGs), including CH_4. However, a few information is available regarding the dynamics of unintended emissions of soil CH_4 in these commonplace features of agroecosystems and how the dynamics compare with those for agricultural land.

Aims: To understand the dynamics of soil CH_4 fluxes from a permanent upslope pasture and contiguous riparian buffer strips with different (grass, willow, and woodland) vegetation as well controls with no buffer vegetation, an experiment was carried out using the static chamber technique on a replicated plot-scale facility.

Methods: Gas fluxes were measured periodically with soil and environmental variables between June 2018 and February 2019 at North Wyke, UK.

Results: Soils under all treatments were sinks of soil CH_4 with the willow riparian buffer (-2555 ± 318.7 g CH_4 ha^{-1}) having the lowest soil CH_4 flux followed by the grass riparian buffer (-2532 ± 318.7 g CH_4 ha^{-1}), woodland riparian buffer (-2318.0 ± 246.4 g CH_4 ha^{-1}), no-buffer control (-1938.0 ± 374.4 g CH_4 ha^{-1}), and last, the upslope pasture (-1328.0 ± 89.0 g CH_4 ha^{-1}), which had a higher flux.

Conclusions: The three vegetated riparian buffers were more substantial soil CH_4 sinks, suggesting that they may help reduce soil CH_4 fluxes into the atmosphere in similar agroecosystems.

KEYWORDS
agricultural land, methane consumption, methane production, water quality functions

1 | INTRODUCTION

Since the start of the Industrial Revolution, human activities have resulted in an increase in atmospheric methane (CH_4) concentrations compared with the preindustrial values (700 ppb in 1750 to 1782 ppb in 2006) (Borrel et al., 2011), with a majority of CH_4 fluxes to the atmosphere originating in soils (Ghosh et al., 2015). Generally, CH_4 is emitted in smaller quantities than carbon dioxide (CO_2), but, over 100

years, 1 kg of CH_4 has a global warming potential (GWP) 28 times than that of CO_2 (IPCC, 2014).

Soils have often been documented as sources and sinks of CH_4 (Cameron et al., 2021; Ghosh et al., 2015). In anaerobic soil conditions, CH_4 is formed through the breakdown of organic compounds at a very low redox potential (Smith et al., 2018). Therefore, large CH_4 fluxes are typical in environments where anoxic fermentation is favored (Conrad, 2020; Philippot et al., 2009). On the other hand, well-drained, aerobic

soils have been identified as significant atmospheric CH_4 sinks due to CH_4 oxidation by methanotrophic bacteria into methanol (CH_3OH) for energy as well as into CO_2 in the presence of molecular oxygen (O_2) (Papen et al., 2001; Sadasivam & Reddy, 2014). This suggests that a net CH_4 flux from soils is a result of the balance between methanotrophy (microbial consumption) and methanogenesis (microbial production under anaerobic conditions) (Conrad, 2009; Dutaur & Verchot, 2007). In soils where oxidation exceeds production, methanotrophy tends to be a dominant process resulting in soil CH_4 consumption (Reddy et al., 2014). CH_4 consumption may be reduced by cultivation and ammonium nitrogen (NH_4^+-N) fertilizer application in cultivated soils, while permanent forest and grassland soils are well documented as active CH_4 sinks (Ball et al., 2002; Merino et al., 2004; Tate et al., 2007). Methane-oxidizing bacteria are generally inhibited by NH_4^+-N fertilizer leading to reduced CH_4 oxidation and, thus, resulting in larger CH_4 fluxes from fertilized and cultivated soils (Alam & Jia, 2012; Finn et al., 2020). In contrast, soils under permanent vegetation have improved aeration, which increases soil CH_4 oxidation and subsequently lowers soil CH_4 fluxes (Butterbach-Bahl & Papen, 2002; Veloso et al., 2019).

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

To investigate the CH_4 fluxes from permanent upslope pasture and riparian buffer strips with different vegetation, we used a replicated large plot experiment established in 2016 for water quality purposes in the UK. The objective of this study was to compare CH_4 fluxes in cropland planted with a permanent upslope pasture and downslope riparian buffer strips with different vegetation introduced to serve water quality functions. We hypothesized that high soil CH_4 fluxes would be generated by the directly fertilized upslope permanent pasture and no-buffer control, whereas low soil CH_4 fluxes would result from nonfertilized grass, willow, and woodland riparian buffers.

2 | MATERIALS AND METHODS

2.1 | Site description

The experimental site is located at Rothamsted Research, North Wyke, Devon, UK (50°46′10″N, 3° 54′05 ″E) (Figure 1). The site is at an altitude of 177 m asl, has a 37-year (from 1982 to 2018) mean annual precipitation of 1033 mm and mean annual temperature of 10.1°C (Orr et al., 2016). The slope is 8° and soils belong to the Hallsworth series (Clayden & Hollis, 1985), 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 & Garwood, 1991), overlying a mottled stony clay, derived from Carboniferous Culm rocks. Below the topsoil layer, the subsoil is impermeable to water, resulting in seasonal waterlogging; most excess water moves by either surface or subsurface lateral flow (Orr et al., 2016) thereby making replicated experimental work using hydrologically-isolated plots feasible.

2.2 | Experimental design and treatments

The experiment was laid out as three blocks of four plots, with four treatments replicated three times on the 12 plots (Figure 1). The four treatments comprised three different riparian buffer strip vegetation (grass, willow, and woodland riparian buffers) and a no-buffer control; each with a permanent upslope pasture (Figure 1). Each plot consisted of the main crop area and either a control (no buffer) area or a riparian buffer (sown with one of three riparian buffer vegetation covers) area. Each plot was 46 m in length and 10 m wide; the main upslope pasture (area "a" in Figure 1) being 34 m in length (340 m^2) and the riparian buffer strip being 12 m (120 m^2) (areas "b" and "c" in Figure 1, see description below). Areas "b" were planted with one of the three different riparian vegetation types (10 m × 10 m) and areas "c" were an untouched strip of existing vegetation measuring 2 m × 10 m.

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 (*Holcus lanatus* L.), and creeping bentgrass (*Agrostis stolonifera* L.). Nitrogen (N; as NH_4^+-N; Nitram), phosphorus (P; as P_2O_5; triple superphosphate), and potassium (K; as K_2O; muriate of potash) were previously split applied into three silage cutting events, with annual rates of 180 (split: 80, 50, 50), 140 (split: 100, 25, and 15), and 290 (split: 80, 100, and 80 and autumn: 30) kg ha^{-1}, respectively. During the current study, fertilizer was applied all at once in the upslope pasture at rates of 50, 15, and 80 kg ha^{-1} for N, P, and K, respectively, which were initially

FIGURE 1 Schematic representation of the plot, treatment, and chamber layout, as well as the location at North Wyke, UK

recommended by routine soil analysis. Fertilizers were only applied to the upslope pasture and no buffer control areas, with no fertilization occurring in the three vegetated riparian buffer strips. Further details for the treatments are described below:

1. No-buffer strip controls: plots without the 12 m × 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.

2. 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.

3. 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 × 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 & 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.

4. 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 & 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 during the current experiment and had never been cut since planting in 2016.

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). All of the areas within the 10 m × 10 m (10 m length is a GAEC recommended N fertilizer application distance away from surface waters) managed riparian buffer strips were sprayed with glyphosate to remove the existing vegetation in spring 2016. The grass riparian buffer strips were cultivated and seed sown as described above, whereas the willow and woodland buffer vegetation was planted within the swathe of dead grass.

2.2.1 | Sampling design

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

2.3 | Field measurements and laboratory analysis

2.3.1 | CH$_4$ measurements

Field sampling and laboratory analysis. Methane fluxes were measured using the static chamber technique (Chadwick et al., 2014; De Klein & Harvey, 2012). The polyvinyl chloride chambers were square frames with lids (40 cm width × 40 cm length × 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 (Trimble, CA, USA) so that they could be precisely replaced after removing them during silage cutting events. In the willow and woodland riparian

buffer strips, chambers were installed in-between two rows, whereas in the upslope permanent pasture, no-buffer strip control, and grass riparian buffer strips, chambers were installed in predetermined positions (Figure 1). More specifically, the chambers were positioned as follows: (1) in area "a," there was one chamber near the upslope margin of the plot (subsequently referred to as area "a" top chamber); in the no-buffer strip control plots, there was an additional chamber near the lower margin of the plot (called area "a" bottom chamber); (2) in area "b," there were two chambers, one near the upper and one near the lower margins of the buffer strip (subsequently referred to as area "b" upper and lower chambers, respectively). Gas sampling was conducted periodically from June 2018 to March 2019, between 10:00 and 13:00, using 60-mL syringes and preevacuated 22-mL vials fitted with butyl rubber septa. A gas sampling plan was developed at the beginning of the experiment with biweekly samplings after fertilizer application and less frequently (i.e., once or twice a month) afterward, making up 18 sampling events for the whole experimental period. On each sampling occasion, gas samples were collected at four time intervals (0, 20, 40, and 60 min) from three random chambers to account for the nonlinear increase in gas concentration with deployment time (or more specifically plateauing of gas concentration over time) and to adequately assess the quality of the calculated flux (i.e., evaluated by using the goodness of fit test and/or by visual inspection) and data that failed to meet the linearity standards was rejected (Collier et al., 2014; Grandy et al., 2006; Parkin & Venterea, 2010). The remaining chambers were sampled terminally at 40 min after closure (Chadwick et al., 2014). Additionally, 10 ambient gas samples were collected adjacent to the experimental area: five at the start and five at the end of each sampling event. CH$_4$ concentrations were measured using a Perkin Elmer Clarus 500 gas chromatograph (PerkinElmer Instruments, Beaconsfield, UK) fitted with a flame ionization detector after applying a five-standard calibration.

Determination and calculation of CH$_4$ flux. As suggested by Conen and Smith (2000), soil 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 CH$_4$ fluxes were computed using the Livingston and Hutchinson (1995) model. Cumulative CH$_4$ fluxes 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 analysis and meteorological measurements

Soil pH [within-laboratory precision (RSD): 0.015] was measured in water (1:2.5 soil:water) (Jenway pH meter, Staffordshire, UK), and soil organic matter (OM) was determined using the loss on ignition technique (Wilke, 2005). Composite soil samples (0–10 cm); made up of four random subsamples, 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 [TON; comprised of nitrite (NO$_2^-$) and nitrate (NO$_3^-$) N, the former considered

to be negligible] and ammonium (NH_4^+-N) [within-laboratory 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^{TM} analyzer (Thermo Fisher Scientific, Finland). On every gas-sampling occasion, composite soil samples (0–10 cm) made of four random subsamples were collected within 1-m from each chamber using the soil corer described above 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) using the following equation:

$$WFPS = \frac{SWC}{1 - \frac{BD}{PD}} \times 100, \tag{1}$$

where WFPS is the water-filled pore spaces (%), SWC is the volumetric water content (vol. %), BD is the soil bulk density (g cm^{-3}), and PD is the soil particle density (2.65 g cm^{-3}) (Fichtner et al., 2019).

Average daily precipitation was acquired from data measured at hourly intervals by an automatic weather station courtesy of the Environmental Change Network (ECN) at Rowden, North Wyke (Lane, 1997; Rennie et al., 2020).

2.4 | Statistical analysis

The data were analyzed using linear mixed models (LMMs) in Genstat 20 (VSN International, Hemel Hempstead, UK). LMMs were used to determine whether cumulative soil CH_4 fluxes or any measured soil variables (BD, pH, NH_4^+, TON, WFPS, and OM) differed with treatment. NH_4^+ and TON were log_{10} transformed to satisfy the homogeneity of variance assumption of the analysis. The random structure of each model (accounting for the structure of the experiment) was *block/plot/chamber*. The fixed structure (accounting for treatment effects) was area/(treatment crop × buffer area). The structure gives the following four tests: (1) area tests for any difference between main crop versus control area versus buffer, (2) area × treatment × crop tests for differences between grass, willow, and woodland riparian buffers, (3) area × buffer area tests for the difference between upper and lower chambers within the different vegetated riparian buffers, and (4) area × treatment crop × buffer area tests for the interaction between riparian buffer type and distance, that is, whether the difference between the upper and lower area of the riparian buffers differs depending on the riparian buffer vegetation (or vice versa). LMMs were also used to assess the relationship between cumulative soil CH_4 fluxes and each measured variable.

Pearson's correlation coefficient (r) was used to indicate the strength of relationships between soil and environmental factors and cumulative soil CH_4 fluxes. This was tested more formally in the LMMs described above. If the LMMs indicated that treatment differences were present, the least significant differences (LSDs) were calculated to determine which specific pairs of treatments resulted in the signifi-
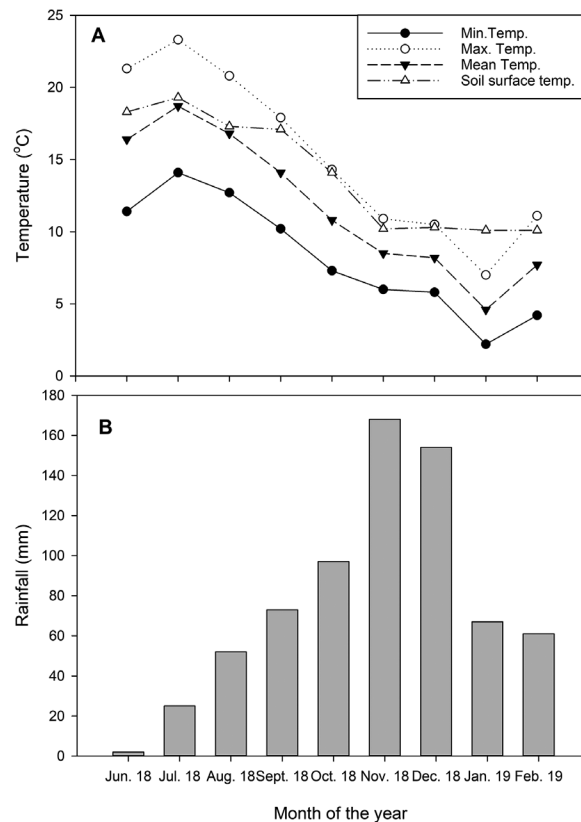

FIGURE 2 Monthly (A) minimum, maximum and soil surface temperatures, and (B) rainfall during the in the site during the experimental period

cant differences in cumulative soil CH_4 fluxes. All graphs were generated using SigmaPlot V14.5 (Systat Software Inc., CA, USA).

3 | RESULTS

3.1 | Meteorological and soil characteristics

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

Soil BD ranged from 1.09 ± 0.05 to 1.21 ± 0.07 g cm^{-3}, with the highest BD of 1.21 ± 0.07 g cm^{-3} occurring in the upslope pasture and the no-buffer strip control treatment. This was significantly different from the willow and woodland riparian buffer treatments, but not the riparian grass buffer strip (LSD = 0.14). Soil pH ranged from 5.4 ± 0.09 to 5.7 ± 0.24, and there was no evidence of significant difference

TABLE 1 Means (±standard error) of some soil physical and chemical properties of the upslope pasture and the downslope riparian buffer strips during the experimental period. Upslope pasture: $n = 12$, no-buffer control: $n = 3$, grass, willow, and woodland riparian buffer: $n = 6$

| Parameter	Upslope pasture	No-buffer control	Grass buffer	Willow buffer	Woodland buffer	Max. LSD
BD (g cm^{-3})	1.21 ± 0.028	1.21 ± 0.05	1.09 ± 0.041	1.20 ± 0.041	1.19 ± 0.041	0.14
pH	5.5 ± 0.16	5.5 ± 0.20	5.4 ± 0.17	5.5 ± 0.17	5.4 ± 0.17	0.38
OM (% w/w)	9.4 ± 0.29	12.9 ± 0.69	10.1 ± 0.53	13.9 ± 0.53	14.1 ± 0.53	1.92
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
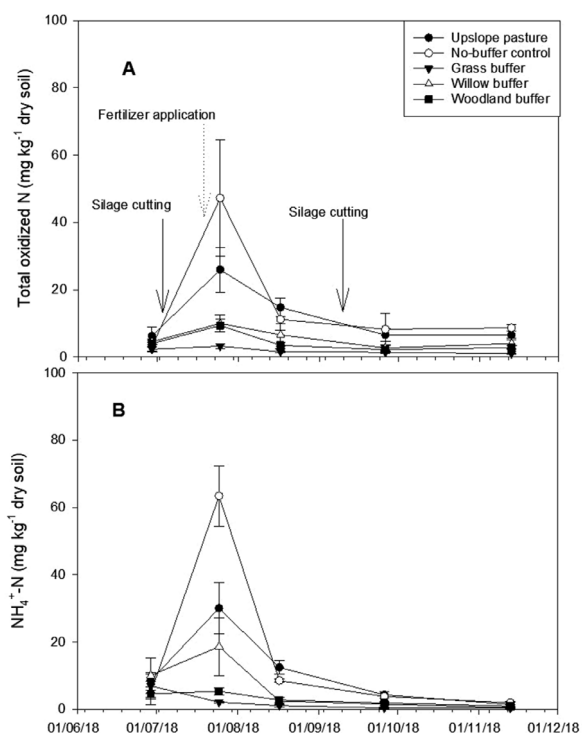
FIGURE 3 Soil TON (A) and NH$_4^+$-N (B) dynamics for the upslope pasture and the downslope riparian buffers with different vegetation treatments during the experimental period; data points and error bars represent the treatment means (upslope pasture: $n = 12$, no-buffer control: $n = 3$, grass, woodland, and willow riparian buffers: $n = 6$) and SE during each sampling event

first sampling event prior to the first silage cut and fertilizer application. During the first sampling day after fertilizer application, soil TON concentration increase was detected in all the treatments. The most considerable 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 prefertilizer application levels for the grass, woodland, and willow riparian buffer treatments. However, they stayed elevated for a more extended period for the no-buffer control treatment and the upslope pasture, which reached similar levels. As shown in Figure 3(B), the soil NH$_4^+$-N concentrations during the experimental period behaved the same way as soil TON, except that there was no increase in NH$_4^+$-N in the grass riparian buffer treatment at the sampling time immediately after fertilizer application.

3.3 | %WFPS

Soil WFPS started <70%, following the same trend throughout the experimental period. The largest %WFPS peak was observed at the end of November 2018, with the highest value observed from the upslope pasture during the peak (Figure 4A). Soil WFPS ranged from 56.6 ± 4.1% to 69.0 ± 2.6%, with the highest value measured in the woodland riparian buffer (69.0 ± 2.6%) treatment, which was only significantly different (LSD = 14.3) to the grass riparian buffer treatment (Table 1).

(LSD = 0.38) between any treatments. The highest concentration of soil OM occurred in the willow riparian buffer (14.1 ± 0.4%) treatment, which was not significantly different from the grass (13.1 ± 0.6%) or woodland (13.9 ± 0.4%) riparian buffer treatments but was significantly different to the no-buffer control (10.0 ± 0.7%) treatment and the upslope pasture (9.4 ± 0.3%) (LSD = 1.92) (Table 1).

3.2 | Soil mineral N dynamics

Figure 3 shows the soil N concentrations determined during specific sampling days. Figure 3(A) shows that soil TON concentrations during the sampling period were similar between all treatments during the

3.4 | Treatment effects on explanatory variables

Table 2 shows evidence of treatment differences in log$_{10}$NH$_4^+$, with the no-buffer control having significantly larger log$_{10}$NH$_4^+$ concentrations compared with the three differently vegetated riparian buffer strips (significantly different from each other), which was, however, not significantly different to the upslope pasture. There was no main effect significant difference between the upper and lower chambers within the different vegetated riparian buffer strips, but there was an interaction effect. This indicates that the riparian buffer vegetation treatments were only different in the upper chambers. The willow riparian buffer was the only treatment with significant differences between the upper and lower chambers. Similar to log$_{10}$NH$_4^+$, there
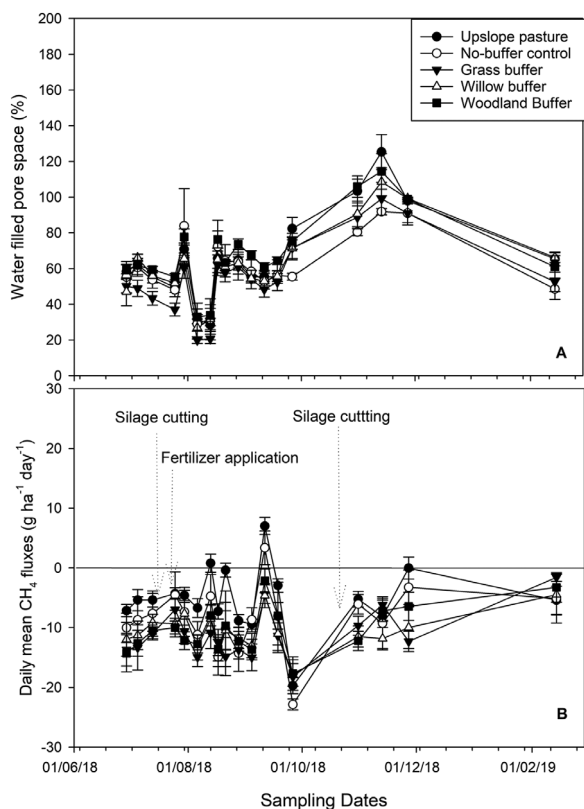
FIGURE 4 Daily (A) WFPS and (B) CH_4 fluxes from the upslope pasture and the downslope riparian buffers with different vegetation treatments. Data points and error bars represent the treatment means (upslope pasture: $n = 12$, no-buffer control: $n = 3$, grass, wood, and willow riparian buffers: $n = 6$) and SE during each sampling day. The line at zero flux (B) is included to indicate fluxes below zero

TABLE 2 p Values for tests from LMMs on each soil variable

	BD	pH	$\log_{10} NH_4$	$\log_{10}$ TON	WFPS	OM
Area	0.33	0.78	<0.001	<0.001	0.55	<0.001
Area × treatment	0.14	0.85	0.001	<0.001	0.11	0.36
Area × buffer area	1	0.96	0.863	0.46	0.91	0.61
Area × treatment × buffer area	1	0.25	0.034	0.69	0.94	0.82

was evidence of treatment differences in $\log_{10}$ TON concentration, with the no-buffer control treatment having the highest $\log_{10}$ TON concentration compared to the differently vegetated riparian buffer strips, which was however not significantly different to the upslope pasture.

3.5 | Soil CH_4 fluxes

3.5.1 | Daily soil CH_4 fluxes

Daily CH_4 fluxes from all treatments during the study period were primarily negative; reflecting soil CH_4 consumption/uptake, except on
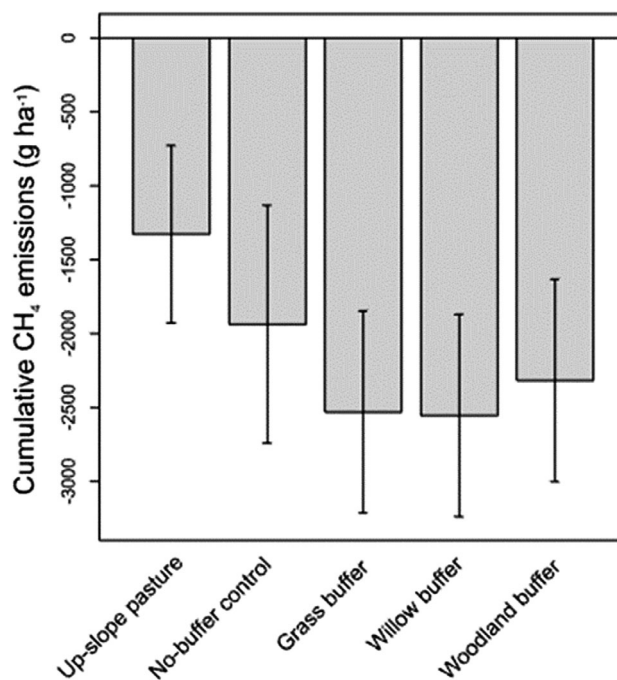

FIGURE 5 Cumulative CH_4 fluxes for the whole experimental period from the upslope pasture and downslope riparian buffers with different vegetation treatments. Error bars represent 95% confidence intervals (upslope pasture: $n = 12$, no-buffer control: $n = 3$, grass, wood and willow riparian buffers: $n = 6$)

three occasions in the upslope pasture and one occasion in the no-buffer strip control (Figure 4B). The most extensive daily soil CH_4 flux was 7.0 ± 1.4 g CH_4 ha^{-1} d^{-1} in the upslope pasture at the end of September 2018, followed by a flux decline in all treatments. The lowest daily soil CH_4 flux was -22.9 ± 0.9 g CH_4 ha^{-1} d^{-1} in the no-buffer strip control in early October 2018. The average daily soil CH_4 fluxes for all the treatments ranged from -5.1 ± 0.3 to -11.5 ± 0.9 g CH_4 ha^{-1} d^{-1} with the upslope pasture exhibiting a large mean daily soil CH_4 flux of -5.1 ± 0.3 g CH_4 ha^{-1} d^{-1}.

3.5.2 | Cumulative soil CH_4 fluxes

Cumulative soil CH_4 fluxes followed the ascending order: willow riparian buffer (-2555 ± 318.7 g CH_4 ha^{-1}) < grass riparian buffer (-2532 ± 318.7 g CH_4 ha^{-1}) < woodland riparian buffer (-2318.0 ± 318.7 g CH_4 ha^{-1}) < no-buffer control (-1938.0 ± 279.7 g CH_4 ha^{-1}) < upslope pasture (-1328.0 ± 279.7 g CH_4 ha^{-1}) (Figure 5). The upslope pasture buffer had a significantly ($p = 0.0013$) large cumulative soil CH_4 flux compared with the remainder of the treatments, and the willow riparian buffer was the largest CH_4 sink (with the largest negative flux). Nevertheless, there were no differences in cumulative soil CH_4 fluxes between the upper and lower buffer strip areas ($p = 0.705$). Also, there was no interaction between the upslope pasture and the upper and lower riparian buffer strip areas.
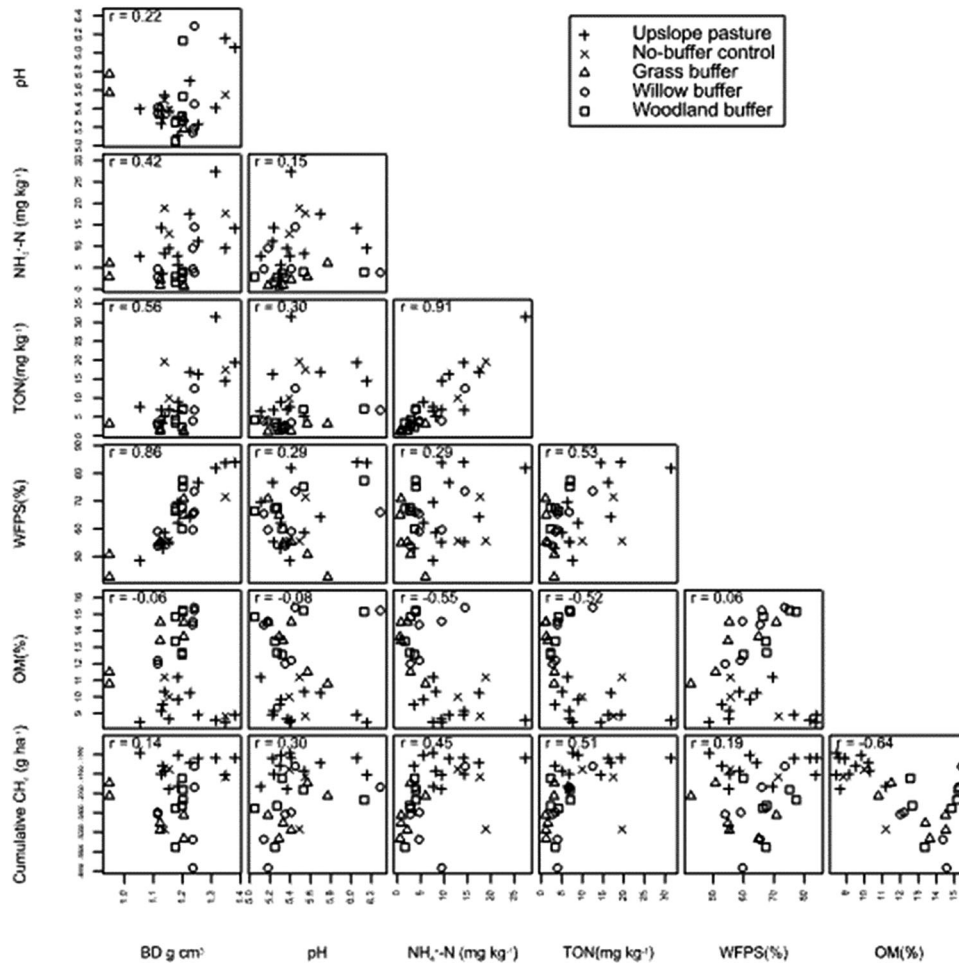
FIGURE 6 Scatterplot showing the relationships between the variables soil pH, NH$_4$$^+$-N, TON, WFPS, OM, BD, and cumulative CH$_4$ fluxes for the upslope pasture and the downslope riparian buffers with different vegetation treatments. r = Pearson's correlation coefficient

TABLE 3 p Values for the slope of the fitted line of the models

Variable	Intercept	Standard error intercept	Slope	Standard error slope	p value
BD	−2676	1673	568.5	1398.04	0.69
pH	−4010	2725	367.5	497.4	0.47
log$_{10}$ NH$_4$	−2677	277.6	919.7	277.8	0.002
log$_{10}$ TON	−2859	280.9	1151	301.9	<0.001
WFPS	−2245	908.8	3.8	13.7	0.79
OM	437.6	499.2	−207.9	37.9	<0.001

3.5.3 | Relationships between cumulative soil CH$_4$ fluxes and measured soil variables including treatment effects

There were significant relationships between cumulative soil CH$_4$ fluxes and NH$_4$$^+$ (r = 0.45; p = 0.0023), TON (r = 0.51; p = 0.001), and OM (r = 0.64; p = 0.001) (Figure 6 and Table 3). Cumulative soil CH$_4$ fluxes increased with an increase in soil BD, pH, NH$_4$$^+$, TON, and WFPS and decreased with an increase in OM (Figure 7).

4 | DISCUSSIONS

4.1 | Soil CH$_4$ fluxes and measured soil variables

Results from this study show that daily incidences of soil CH$_4$ fluxes (Figure 2) were similar to other authors, particularly Dutaur and Verchot (2007) and Reay et al. (2007), who reported that soils could be both a source and sinks for soil CH$_4$ fluxes. Furthermore, our results show large daily soil CH$_4$ fluxes after N fertilizer application, coinciding with an increase in soil WFPS (Figures 4A,B). These results are in agreement with the findings reported by Tate et al. (2007), Wang et al. (2014), and Liu et al. (2017), who observed that NH$_4$$^+$- N fertilizer inhibits CH$_4$ oxidation to CO$_2$, thus reducing the soil CH$_4$ sink capability, explaining the observed extensive daily soil CH$_4$ fluxes after fertilizer application, particularly in the upslope pasture and no-buffer control. In the current experiment, likely, the inhibitory role of NH$_4$$^+$-N on CH$_4$ oxidation to CO$_2$ in the N-fertilized no buffer control and upslope pasture resulted in the exponential increase cumulative soil CH$_4$ fluxes associated with increases in soil mineral N (Figure 7) as well as a significant correlation between CH$_4$ and mineral N (Figure 6). The inhibitory effect of NH$_4$$^+$-N fertilizer addition on CH$_4$ oxidation could
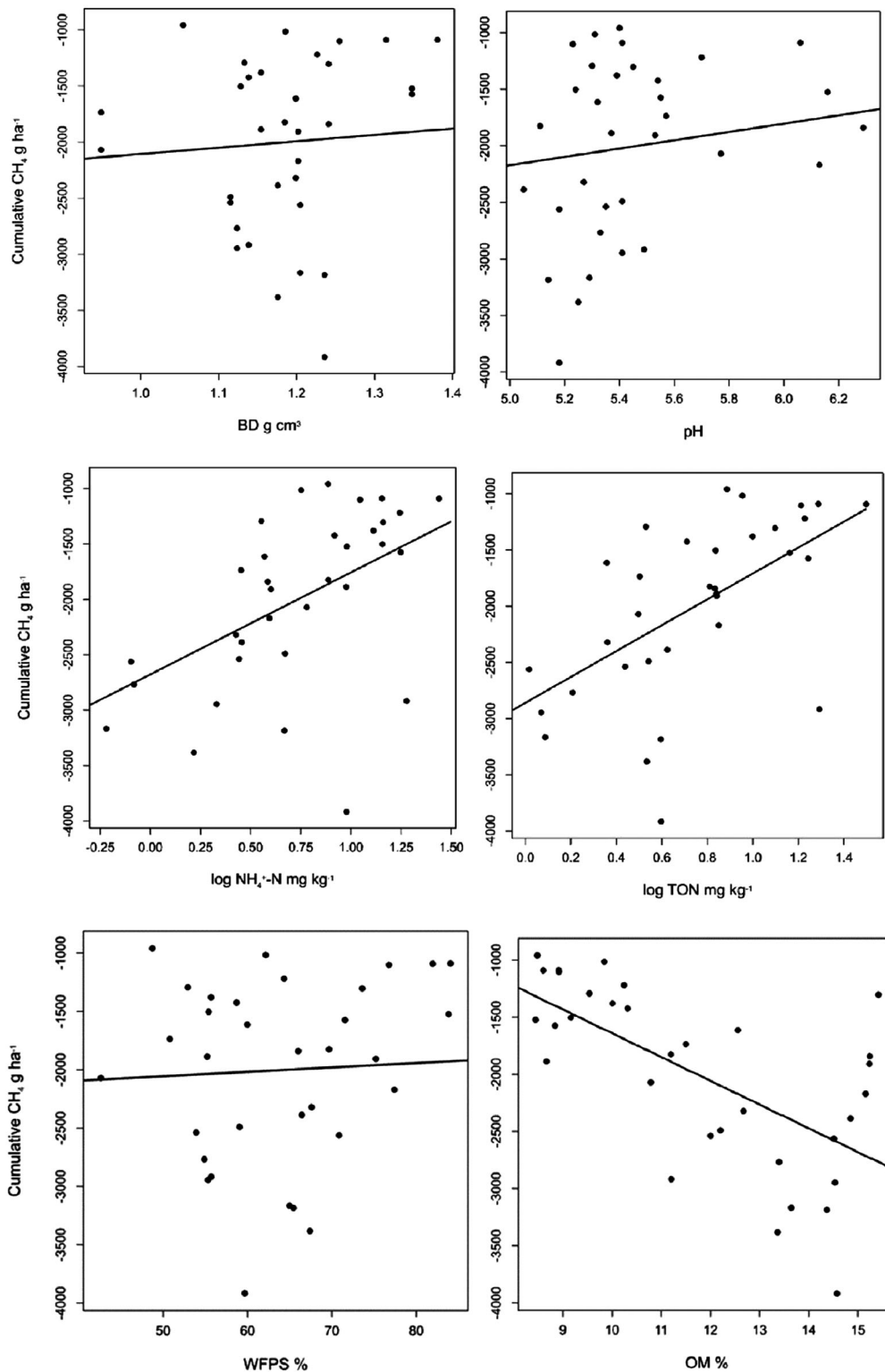
FIGURE 7 Relationships between cumulative soil CH$_4$ fluxes and each of the explanatory soil variables

be attributed to the fact that CH$_4$ monooxygenase of methanotrophs can oxidize a variety of substrates besides soil CH$_4$ (Bian et al., 2019; Wang et al., 2014). Thus, the majority of higher soil CH$_4$ fluxes by the upslope pasture and no-buffer control than in the vegetated

downslope riparian buffer strips during the experimental period (Figure 4B) could have resulted from the N fertilizer directly applied into the former treatments. On the contrary, the riparian buffers only received secondary N leached downslope from the upslope pasture

in conjunction with runoff, which might not have necessarily been in the form of NH_4^+-N, which is known to inhibit CH_4 oxidation. It could happen that the applied fertilizer N in upslope pasture and no-buffer control might have reduced the capacity of the treatments to consume CH_4, but we did not have any other way to confirm this in the current study.

Soil moisture content is well documented as a regulator of soil CH_4 fluxes (Le Mer & Roger, 2001; Natali et al., 2015; Veloso et al., 2019; Wang et al., 2017) since increased soil moisture impedes O_2 diffusivity, which reduces methanotrophic oxidation activities, thus allowing soil CH_4 fluxes (Konda et al., 2010; Smith et al., 2018; Wachiye et al., 2020). Similar to the previous studies, we observed that soil CH_4 fluxes increased with increasing soil WFPS (Figures 4A, 4B, and 7). Higher soil WFPS are attributed to soil structural alterations, including reduced macro-porosity, increasing anaerobicity, and reduced soil CH_4 fluxes (Butterbach-Bahl & Papen, 2002; Veloso et al., 2019). In the current study, the observed increases in cumulative soil CH_4 fluxes with increasing soil BD (Figure 7) are consistent with the previous work cited above.

Soil OM derived from plant litter is converted into soil organic C (an electron donor), which microbes further convert into CH_4 (Megonigal & Guenther, 2008); thus, it is expected that vegetation that produces a lot of OMs (i.e., leaves) that enters the soil will have higher CH_4 fluxes. On the contrary, in the current experiment, the willow riparian buffer treatment, which had the highest mean OM concentration, had the lowest cumulative soil CH_4 fluxes instead (Table 1, Figure 5). There was also a significant negative correlation between soil OM and cumulative soil CH_4 fluxes (Figure 4), as well as a decrease in cumulative soil CH_4 fluxes with an increase in soil OM (Figure 5). It is possible that the OM derived of the litter of the willow riparian buffer vegetation was of high quantity but low quality with regards to labile C content, similar to other authors, particularly Dlamini et al. (2020) and Surey et al. (2020). These authors observed that organic material containing highly labile C compounds is readily available for soil microbial degradation.

4.2 | Soil CH_4 fluxes in upslope pasture and downslope riparian buffer strips

The cumulative soil CH_4 fluxes in all treatments indicate that the soils under the riparian buffer strips with different vegetation as well as in the upslope pasture and no-buffer control acted as a sink for soil CH_4 fluxes. Similar findings were reported by McLain and Martens (2006), Kim et al. (2009), and Jacinthe (2015). The upslope pasture had the most considerable quantities of cumulative soil CH_4 fluxes than the other treatments, and the willow riparian buffer had the least fluxes. Despite this, the upslope pasture had lower cumulative soil CH_4 fluxes (-1.3 kg CH_4 ha^{-1}) compared with the values reported for maize (*Zea mays* L.; -0.8 kg CH_4 ha^{-1}) by Kim et al. (2009) in loamy soils in Iowa. Such comparisons highlight that repeated cultivation associated with annual crops (i.e., maize) as opposed to the less frequent cultivation associated with permanent pasture production (i.e., the upslope pasture in the current study) can further reduce the capability of soils

under maize production to reduce soil CH_4 fluxes (Ball et al., 2002; Tate et al., 2007).

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

The significant soil CH_4 fluxes in the upslope pasture, as well as the lower fluxes from the vegetated riparian buffers, agree with results reported by Merino et al. (2004) and Tate et al. (2007), among others, who reported that forest riparian soils are the most active sinks of soil CH_4 fluxes followed by grasslands and cultivated soils. The inhibitory effect of NH_4^+-N fertilizer addition to soils on CH_4 oxidation has been reported in soils under different agricultural uses (Liu et al., 2017; Wang et al., 2014). Thus, the significant soil CH_4 fluxes in the upslope pasture and no buffer control of the current study could have been a result of the applied NH_4^+-N fertilizer having increased the soil CH_4 fluxes, which is also in agreement with previous studies (Butterbach-Bahl & Papen, 2002; Le Mer & Roger, 2001).

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

Our study further suggests that as well as providing beneficial water-quality functions, grass, woodland, and willow riparian buffer strips serving a permanent pasture may be significant sinks for soil CH_4. The fact that these riparian buffer strips consume soil CH_4 in the current experiment suggests that these may simultaneously reduce water quality threats while not posing atmospheric pollution concerns through increased soil CH_4 fluxes, primarily when they serve permanent ungrazed pastures. Despite the current study being carried out on plots situated on a single soil type, climatic zone, and

agricultural system, the results reported supply a basis for exploring the application of different riparian buffer strips in areas with different soils and environmental settings.

5 | CONCLUSIONS

We hypothesized that the fertilized upslope pasture, as well as the no buffer control, would have high soil CH_4 fluxes than the nonfertilized grass, willow, and woodland riparian buffers. We accept this hypothesis because, as theorized, our results showed higher soil CH_4 fluxes in the upslope pasture and the no-buffer control and lower soil CH_4 fluxes resulted from the grass, willow, and woodland riparian buffers. Despite that our database has limitations, these results suggest that all the vegetation types for riparian buffer strips tested in this study may be helpful for soil CH_4 flux mitigation in similar agroecosystems and management practices. More generally, our results would be helpful to policymakers as well as scientists requiring to calibrate mechanistic models that explore mitigation measures for soil CH_4 fluxes in agroecosystems through the use of different riparian buffers.

DATA AVAILABILITY STATEMENT
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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