



Research article

Biochar mitigates methane emissions from organic mulching in urban soils: Evidence from a long-term mesocosm experiment

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ABSTRACT

Methane (CH₄), a potent greenhouse gas (GHG) with high global warming potential, significantly contributes to urban GHG emissions. Organic mulching, commonly practiced in urban forestry, may promote CH₄ emissions via anaerobic decomposition; yet its impact on the urban carbon budget has largely been unexamined. Biochar has shown promise in mitigating CH₄ emissions in agricultural soils, but its effectiveness in urban mulched systems remains unknown. This study employed a mesocosm experiment to investigate the effects of organic mulches (woodchips and bark) and biochar amendments (50 t/ha), applied either on the surface (top-dressed) or incorporated (mixed), on fluxes of CH₄, CO₂, and H₂O. Fluxes were measured using an off-axis integrated cavity output spectroscopy analyzer. Results indicate that mulched soils emitted CH₄ at 1.0–1.5 nmol m⁻²s⁻¹, whereas biochar amendments promoted CH₄ uptake, in the case of both woodchips (−1.65 ± 1.03 nmol m⁻²s⁻¹) and bark mulch (−0.49 ± 0.16 nmol m⁻²s⁻¹) by the second year. Mixed treatments showed greater CH₄ uptake; for instance, incorporating biochar into bark mulch led to a mean CH₄ uptake (−2.02 ± 1.02 nmol m⁻²s⁻¹), nearly fivefold greater than controls. While mulch additions reduced water loss and increased soil organic carbon—factors contributing to CH₄ emissions—biochar amendments increased CO₂ emissions by 26.7%–121.1%. Biochar-mediated CH₄ uptake correlated with substrate pH, bulk density, and C:N ratio, suggesting enhanced microbial activity and increased CO₂ release. Overall, findings indicate that biochar, combined with organic mulching, can serve as an effective GHG mitigation strategy, informing climate-smart soil management in urban landscapes.

1. Introduction

Methane (CH₄) is a potent greenhouse gas with a global warming potential significantly higher than carbon dioxide (CO₂), making its emission a critical environmental concern (Saunois et al., 2020, 2024). In urban environments, CH₄ emissions are ubiquitous and originate from biogenic sources like landfills, wetlands, wastewater treatment facilities (Carranza et al., 2018; Mostafavi Pak et al., 2021) and abiogenic sources such as natural gas leaks (Ars et al., 2020). Although less studied, urban soils can be net CH₄ sources due to anoxic conditions from compaction, construction, and other anthropogenic activities (Kulachkova and Kovalenko, 2021; Xue et al., 2023).

Urban soils often suffer from compaction, low organic matter, and contamination due to activities like construction and traffic, leading to poor drainage and reduced plant growth (Edmondson et al., 2011; Pouyat et al., 2020). To mitigate these issues, organic mulches such as woodchips and bark are commonly used in urban landscaping

(Chalker-Scott, 2007; Iqbal et al., 2020), offering benefits like water conservation, weed suppression, improved soil structure, and overall aesthetic value of urban landscapes. However, adding organic mulch to soils may inadvertently create anaerobic conditions conducive to methanogenesis, potentially transforming these soils into CH₄ sources.

Biogenic CH₄ production is driven by methanogenic archaea during anaerobic decomposition, while CH₄ oxidation is facilitated by methanotrophic bacteria (Möbius and Craft, 2021). Net CH₄ flux depends on the balance between these processes, influenced by microbial abundance and activity of methanogenic archaea in deeper anaerobic layers as well as methanotrophic bacteria in the uppermost oxic layers (Le Mer and Roger, 2001). Since these microorganisms are ubiquitous in soil (Angel et al., 2012; Shukla et al., 2013), CH₄ flux is mainly driven by soil physical and chemical properties such as temperature, moisture, bulk density, pH, salinity, organic matter, and carbon-to-nitrogen (C:N) ratio (Le Mer and Roger, 2001; Van den Pol-van Dasselaar et al., 1999).

In urban soils, these factors are strongly influenced by land use and

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management practices. Urban soils often have low organic matter and high alkalinity due to leaf litter removal and construction materials (Pouyat et al., 2020). Compaction from human activities reduces pore space and water infiltration, limiting plant growth (Epron et al., 2016). While mulch improves soil conditions in most respects, excess water retention and added organic matter may promote methanogenesis, as seen in wetland restoration (Scott et al., 2022).

In addition to CH₄, soil CO₂ and water vapor (H₂O) fluxes are crucial in soil respiration and evapotranspiration, affecting GHG emissions and water dynamics in urban ecosystems. Soil CO₂ efflux, resulting from microbial and root respiration, indicates microbial activity and soil health (Raich and Schlesinger, 1992; Bond-Lamberty and Thomson, 2010). Mulching can alter CO₂ emissions by affecting soil temperature, moisture, and microbial activity (Lal, 2004; Sánchez-Monedero et al., 2004) and influences H₂O fluxes by reducing evaporative loss (Cook et al., 2006; Li et al., 2020). Understanding the interplay among CH₄, CO₂, and H₂O fluxes is essential for assessing the impact of mulching on urban soil greenhouse gas dynamics and water conservation.

Soil temperature, moisture, and bulk density critically influence CH₄ emissions and consumption. Higher temperatures stimulate microbial activity, increasing methane oxidation and CO₂ production (Van den Pol-van Dasselaar et al., 1999). Optimal moisture supports gas diffusion, promoting methane uptake and influencing H₂O fluxes via evapotranspiration. Excess moisture limits oxygen, reducing methane oxidation and potentially increasing CH₄ emissions (Luo et al., 2013). Soil bulk density affects pore space; compaction limits gas movement, impacting CH₄ flux – as commonly observed in managed forests (Epron et al., 2016; Vantellingen and Thomas, 2021a).

Organic mulches like woodchips and bark stabilize soil temperatures and provide consistent conditions for microbial activities (Chalker-Scott, 2007; Iqbal et al., 2020). They enhance moisture retention by reducing evaporation and promoting infiltration, influencing H₂O fluxes and water availability. However, excess moisture can create saturated, anaerobic conditions that is expected to suppress CH₄ oxidation and promote methanogenesis. While mulches can lower bulk density and increase porosity, water saturation may impede gas exchange. Thus, although mulches may enhance methane uptake under optimal conditions, they may also foster CH₄ emissions under excessive moisture and anaerobic conditions.

Urban soils often have increased alkalinity due to road dust, cement dissolution, and leaf litter removal (Pouyat et al., 2020; Zhang et al., 2023). The optimal pH for methane production is ~7.5 (Vongvichiankul et al., 2017); elevated pH can shift soils from methane sinks to sources (Liu et al., 2008). Urban soils may also have increased salinity from winter salt application, inhibiting methanogens and reducing methane production. However, the high-water retention in mulch may dilute soil salinity, offsetting its inhibitory effect on methanogenesis.

High organic matter generally enhances microbial communities that facilitate methane oxidation (Lee et al., 2023; Zhang et al., 2016), but under hypoxic conditions, it may stimulate methanogenesis. In managed temperate forests, for instance, very high methane emissions have been observed in areas with high organic matter accumulation, such as log landings and skid trails (Vantellingen and Thomas, 2021b). The C:N ratio is critical; an optimal range of ~20:1 to 30:1 promotes methanogenesis, while deviations can inhibit it (Tg et al., 2022). Organic mulch amendments could alter methane dynamics by modifying the substrate's C:N ratio, though effects in urban soils are largely unexplored.

Wood mulches consist of small pieces from urban forestry waste, while bark mulch is derived from tree bark and lasts longer due to higher lignin content (R Chandrasekaran et al., 2012). Wood chips and bark differ in physical and chemical properties (which also varies with species and woody tissue type), influencing their decomposition and impact on soil. Bark usually has less than 50% holocellulose and 20–30% lignin (Huang and Yan, 2014). The chemical composition of both wood chips and bark changes considerably by species as they decompose (Rowell, 1984). In Toronto, a ring of organic mulch, usually 10 cm deep and

1.5–2 m in diameter, is applied around newly planted trees, tapering to ground level near the trunk (City of Toronto, 2024). This practice, coupled with high soil moisture, may lead to appreciable methane emissions, yet it has received little attention.

Despite the widespread use of organic mulches, their impact on CH₄, CO₂, and H₂O fluxes in urban soils is largely unstudied. Biochar—pyrolyzed organic material used as a soil amendment (Lehmann and Joseph, 2009)—has gained prominence recently in agriculture due to its multifaceted benefits. Recently, biochar has also been introduced into urban green infrastructure, where it has demonstrated positive effects on soil water retention, plant performance, and soil microbial activity (Huang and Yan, 2014; Liao et al., 2023). Biochar amendments have shown promising results in reducing CH₄ emissions from agricultural soil (Lee et al., 2023; Nan et al., 2021), suggesting potential for urban soil applications. Biochar has been found to reduce soil bulk density by 3–31% while increasing porosity (Blanco-Canqui, 2017; Liao et al., 2023). Its porous structure and large surface area promote soil aeration, potentially increasing oxygen levels. Additionally, biochar releases labile carbon much more slowly than organic mulches, which may favor methanotroph activity and increase methane consumption in urban soils, but its potential in urban mulched systems is unexplored.

In this study, we quantify the effects of organic mulches on biogenic CH₄ flux and biochar's role in modulating this flux. We investigate the effects of mulch and biochar on CO₂ and water vapor flux, as CO₂ flux is relevant as GHG emission, and one main intended function of wood mulch is to inhibit soil surface evaporation. Specifically, we use a mesocosm experiment to compare the effects of woodchips and bark mulch, in combination with biochar, on CH₄, CO₂ and H₂O flux from a representative urban soil under two application modes: surface (top-dressed) and incorporated (mixed). We hypothesize that (1) organic mulching will promote CH₄ emissions by creating substrate conditions conducive to methanogenesis; (2) biochar applications will reduce CH₄ emissions, potentially offsetting mulching effects; (3) the effects of biochar will be more pronounced in mixed treatments; (4) both mulch and biochar amendments will reduce CO₂ and water vapor fluxes from mulch-amended soils.

2. Methodology

A 16-month-long (June 2021 to October 2022) soil mesocosm experiment was designed and executed to examine comparative effects of biochar, substrates (control soil, woodchips, and bark mulches) and mode of their application on CH₄, CO₂ and H₂O fluxes. Experimental soil was collected from upper 15 cm surface soils at Downsview Park, Toronto. The reference soil for the site is a clayey silt till Luvisol, formed by glacial ice deposits. However, development in the area has transformed these sensitive soils into greyfields, characterized by human-mixed deposits and surface fill (De Sousa and Spiess, 2018). Such soils are classified as "transportic" in the World Reference Base for Soil Resources (Burghardt et al., 2015), or as Human-Altered or Human-Transported (HAHT) and Human-Altered Material (HAM) in the USDA system (Pouyat et al., 2020). The soil's relatively high bulk density is typical of disturbed urban and industrial areas (Pouyat et al., 2007).

A 25-cm high PVC pipe with 10 cm diameter was used as the treatment mesocosm. Each PVC unit was filled to 15 cm with the reference soil. Mulches used were commercially sourced. For both woodchips and bark mulch treatments, a 5-cm layer (particle size range: 0.42–50 mm) of cedar woodchips (from *Thuja occidentalis*) or bark (from *Pinus resinosa*) was applied on top of the soil, while, for biochar treatments, 36 g biochar was applied to each experimental unit, correspond to a dosage of 50 t/ha. This is in the upper range of optimum dosages for plant growth responses (Gale and Thomas, 2019). The biochar used in this experiment had a particle size ranging from 0.06 to 5 mm and was sourced from Titan Clean Energy Projects, Canada. The feedstock for this biochar was composed of a conifer mixture of *Pinus* spp., *Picea* spp., and *Abies* spp., pyrolyzed at 625 °C.

The experimental set-up was installed in the Institute of Forestry and Conservation courtyard at the University of Toronto and maintained under natural weather conditions throughout the experimental period. Table S1 describes the elemental properties of reference substrates.

2.1. Experimental design

An augmented factorial design was utilized to examine the effects of organic mulching and biochar amendment on CH₄, CO₂ and H₂O fluxes from urban soil. Mulch and biochar treatments were applied in two different modes of application as (i) surface (top-dressed) and, (ii) incorporated (mixed) applications. Biochar treatments were (i) biochar present and, (ii) biochar absent. Substrate types were (i) soil only, (ii) soil + woodchips mulch and, (iii) soil + bark mulch. Surface application consisted of applying biochar and/or mulch in a layer while incorporate applications involved mixing the biochar and/or mulch with soil. All treatment combinations were replicated four times. The main part of the experiment thus consisted of a total of 12 treatments, with 48 experimental units in total.

This experiment was supplemented with another set of experimental PVC units to examine effects of biochar placement on CH₄, CO₂, and H₂O flux since the location of biochar placement with mulch could be of practical importance. For this part, two placement locations were considered including “biochar above” and “biochar below” the mulch (woodchips and bark mulch) with four replications similar to the main experiment. Thus, the full experiment consisted of a total of 16 treatments each with four replications, with 64 experimental units in total.

2.2. Data collection

The experimental set-up was maintained for 16-months (June 2021 to October 2022). Flux measurements for CH₄, CO₂ and H₂O were taken with an integrated off-axis output spectroscopy gas analysis system (UGGA: Los Gatos Research, San Jose, CA, USA) interfaced with a pressure equilibrated chamber (LI-8100A survey chamber, LICOR, Lincoln, Nebraska, USA). Measurements were made every 2–3 months from July 2021 until October 2022. During each measurement soil moisture content (MC) (%) and temperature (T) (°C) were also recorded from each experimental mesocosm. The substrate temperature and moisture content were measured at a depth of ~5 cm using a CS-SM2 soil moisture sensor (accuracy: ±2.5%) equipped with a temperature sensor (accuracy: ±0.5°C) (CredoSense Inc., Toronto, Canada).

During Summer 2022, soil samples were collected from each PVC unit using a stainless-steel sampler with a known volume, later used to quantify bulk density. Soil samples were collected from the top 10 cm after removing the coarse mulch and biochar layers which were not integrated with soil underneath. Soil samples were oven-dried at 105°C for 48h to determine the bulk density. Prior to pH and EC measurements, the solutions were shaken on an oscillating table at 60 RPM for 24 h. The pH and EC were determined in a 1:1 suspension of soil in deionized water at room temperature using a pH/mV Meter (IQ Scientific Instruments, USA) and an Orion Star A112 benchtop conductivity meter (Thermo Scientific, USA), respectively. In each case, triplicate measures were conducted. A subset of soil samples was ground to <0.5 mm for total C and N determination using a CN analyzer (628 Series, LECO Corporation, St. Joseph, MI, USA). Amount of total inorganic carbon (TIC) content was determined using a coulometer (UIC Model 5014 CO₂ Coulometer), which quantified TIC as CO₂ equivalent from acid treatment of the soil samples. Total organic carbon (TOC) was then determined by subtracting total inorganic carbon from total carbon.

2.3. Flux calculations

Output files from the LGR gas analyzer were post-processed using R version 4.3.2 (R Core Team, 2022) using an algorithm to estimate flux rates (dc/dt) of concentrations of CH₄, CO₂ and H₂O (Halim et al., 2022,

2024). First, a “dead band” of initial 30 s was eliminated from each measurement, which is affected by artifacts triggered by the closing of the chamber (Hoffmann et al., 2017; Halim et al., 2024). After this exclusion, we applied a straightforward algorithm using the Pearson correlation coefficient (r) between concentration and time, focusing specifically on CO₂ concentration data to identify the optimal time window (50–60 s) for flux calculations. The time window yielding the highest r value for CO₂ was selected for both CO₂ and CH₄ gases in subsequent flux calculations. We selected CO₂-based time window for CH₄ because CO₂ fluxes tend to exhibit less noise than CH₄, allowing potential leakage or pressure artifacts to be more easily detected from CO₂ data than from CH₄. Fig. S1 shows example slope calculation from the raw data stream following the algorithm described above.

To determine dc/dt for calculating CO₂ and CH₄ fluxes, we used either linear or non-linear regression (Hüppi et al., 2018) depending on the statistical properties of the concentration data. If the quadratic coefficient of the concentration data was not statistically significant ($p > 0.05$), we used linear regression to determine dc/dt and calculated the flux as (LI-COR, 2015):

$$F = \frac{10VP_0}{RS(T_0 + 273.15)} \frac{dc}{dt} \quad (1)$$

where F is the flux of water-corrected CH₄, CO₂ or H₂O, V is total volume (sum of chamber head-space volume and the volume inside the collar aboveground) (cm³), P_0 is the initial pressure (kPa), R is the Universal Gas Constant (0.83144598 m³ kPa·k⁻¹·mol⁻¹), S is the soil surface area (cm²), T_0 is the initial air temperature (°C), and dc/dt is the initial rate of change in the water-corrected CH₄, CO₂ or H₂O mole fraction. Throughout this paper, we expressed CH₄ fluxes as nmol·m⁻²·s⁻¹ and, CO₂ and H₂O fluxes as μmol·m⁻²·s⁻¹ and. If the quadratic coefficient was significant ($p < 0.05$), we chose the non-linear regression approach. We fitted the following empirical equation (Welles et al., 2001) to the data points of the selected time window:

$$C'_{(t)} = C'_x + (C'_0 - C'_x)e^{-a(t-t_0)} \quad (2)$$

where, $C'_{(t)}$ is the instantaneous water-corrected mole fractions for the gases, C'_0 is the value of $C'_{(t)}$ when the chamber just closed, C'_x is the asymptote parameter, a specifies the curvature of the fit, and t_0 is time (s) when the chamber closed. The parameters a , t_0 , C'_x , and C'_0 were estimated from the fitted nonlinear regression. Subsequently, using the following equation (Eq. (3)), which is derived from Eq. (2) (at $t = t_0$) was used to calculate the initial rate of change of the water-corrected CH₄, CO₂ and H₂O mole fraction (LI-COR, 2015):

$$\frac{dC}{dt} = a(C'_x - C'_0) \quad (3)$$

The value of dc/dt obtained from Eq. (3) was used in Eq. (1) to calculate the CH₄, CO₂ and H₂O flux. Overall, using the above algorithm, 18 % of the total CH₄ flux, 16 % of the total CO₂ flux, and 9% of H₂O flux were calculated using the nonlinear regression approach (primarily for high flux rates). The average of the three replicated flux measurements of each gas, taken at each collar per campaign, was used for further analyses.

2.4. Data analysis

Statistical analysis was performed to examine the effects of biochar and organic mulching (woodchips and bark mulch) on CH₄, CO₂, and H₂O fluxes, while also considering the mode of application (surface vs. incorporated) and seasonal variations in flux responses. To evaluate these effects, a linear mixed-effects model (LMM) was applied using the “lmer” function from the lme4 package in R (Bates et al., 2015). The fixed effects were selected based on the research hypotheses and included substrate type (control soil, woodchips, bark mulch), biochar

application, mode of application (surface vs. incorporated), and their interaction. Random effects were included to account for variability between experimental collars over time, addressing the potential heterogeneity in site conditions and temporal autocorrelation.

The significance of the fixed effects was evaluated using ANOVA through the “Anova” function from the “car” R package (Fox and Weisberg, 2019). To further explore significant interactions or main effects, we applied the Mann-Whitney *U* test for pairwise comparisons, particularly suited for cases where normality assumptions may not hold, as confirmed by prior testing (Shapiro-Wilk normality test). Given the multiple comparisons involved, the Benjamini-Hochberg False Discovery Rate (FDR) correction was applied ($\alpha = 0.05$) to control for the risk of false positives while maintaining statistical power.

To elucidate the potential causal relationships between substrate properties and CH₄ flux, we constructed two full mediation structural equation models (SEMs) using the ‘glmer’ and “piecewise-SEM” R packages (Danner et al., 2015; Gunzler et al., 2013), which allowed us to test the hypotheses regarding how substrate properties mediate the effect of treatment and mode of application on CH₄ fluxes. We constructed two models: the first comparing “mulch only (woodchips and bark mulch pooled)” with “biochar,” and the second comparing “mulch only” with “mulch + biochar.” The substrate properties used as predictor variables included CO₂ flux, pH, total organic carbon (TOC), moisture content (MC), bulk density (BD), carbon-to-nitrogen ratio (C:N), total inorganic carbon (TIC), and electric conductivity (EC). The SEMs were designed with the assumption that the categorical variables (treatment and mode of application) fully mediate the substrates properties, which, in turn, influenced CH₄. Additionally, an unmeasured variable was included as a latent variable to account for potential unknown factors influencing CH₄ flux, such as microbial community structure. Tests of directed separation were used to assess the statistical significance of the proposed pathways and evaluate whether additional non-hypothesized pathways should be included in the models.

Variance inflation factors (VIFs) were calculated for each predictor variable to assess multicollinearity, ensuring that VIFs remain below 5, indicating no strong multi-noncollinearity. Model fit was evaluated using the Comparative Fit Index (CFI). Standardized path coefficients were generated to quantify the relative contribution of each pathway to CH₄ flux, providing insight into dominant factors driving CH₄ emissions. Finally, we computed conditional pseudo-R² values for each model term, incorporating both fixed and random effects. These pseudo-R² values were used to quantify the amount of variance explained by each term, providing a comprehensive view of how treatment and substrate properties influenced CH₄ flux dynamics.

3. Results

3.1. Mulch and biochar effects on CH₄ flux

The mixed-effects model examined effects of biochar amendment, mode of application (surface vs. incorporated), substrates type (woodchips, bark mulch and control soil), and time expressed as CTE (cumulative temporal effect), on CH₄ flux. Significant effects were observed for substrate type ($\chi^2 = 9.54, p < 0.001$), biochar amendment ($\chi^2 = 54.67, p < 0.001$), and CTE ($\chi^2 = 36.89, p < 0.001$) on CH₄ flux. In addition, the interaction between biochar and CTE was significant ($\chi^2 = 35.75, p < 0.001$), indicating that biochar’s influence on CH₄ flux varied significantly among measurements (Table 1). In general, all substrate types (woodchips, bark mulch and control soil) in both surface and incorporated application showed CH₄ emissions initially, but by the second year all biochar addition treatments consistently exhibited CH₄ uptake compared to their 2021 counterparts, with apparent seasonal fluctuations (Fig. 1).

Initially, in the first year during summer and fall 2021, all treatments emitted CH₄ except control soil with biochar in summer 2021 (which showed no detectable net flux: $-0.070 \pm 0.080 \text{ nmol m}^{-2} \text{ s}^{-1}$) (Fig. 1a);

Table 1

Results from the generalized linear mixed effect model predicting CH₄, CO₂ and H₂O flux with application mode (surface vs. incorporated), substrate (control soil, woodchips and bark mulch) and biochar (present vs. absent) as fixed effects and cumulative temporal effects (season and year) as random effects.

Greenhouse gas	Effects	Chisq (DF _{between} , DF _{within})	p-value	
CH ₄	Mode	1.75 (1, 427)	0.185	
	Substrate	9.54 (2, 427)	<0.001	
	Biochar	54.66 (1, 427)	<0.001	
	CTE	36.89 (4, 427)	<0.001	
	Mode × Substrate	4.69 (2, 427)	0.096	
	Mode × Biochar	0.15 (1, 427)	0.696	
	Substrate × Biochar	0.75 (2, 427)	0.685	
	Mode × CTE	4.71 (4, 427)	0.318	
	Substrate × CTE	3.18 (8, 427)	0.922	
	Biochar × CTE	35.74 (4, 427)	<0.001	
	CO ₂	Mode	69.08(1, 432)	<0.001
		Substrate	86.11 (2, 432)	<0.001
		Biochar	193.51 (1, 432)	<0.001
CTE		24.41 (4, 432)	<0.001	
Mode × Substrate		48.35 (2, 432)	<0.001	
Mode × Biochar		5.06 (1, 432)	0.024	
Substrate × Biochar		0.003 (2, 432)	0.998	
Mode × CTE		11.41 (4, 432)	0.022	
Substrate × CTE		19.10 (8, 432)	0.014	
Biochar × CTE		12.69 (4, 432)	0.014	
Mode × Substrate × Biochar		5.92 (2, 432)	0.051	
Mode × Substrate × CTE		30.36 (8, 432)	<0.001	
Substrate × Biochar × CTE		28.37 (8, 432)	<0.001	
H ₂ O	Mode	1.27 (1, 432)	0.250	
	Substrate	12.94 (2, 432)	<0.001	
	Biochar	0.07 (1, 432)	0.780	
	CTE	228.63 (4, 432)	<0.001	
	Mode × Substrate	5.94 (2, 432)	0.051	
	Mode × Biochar	6.44 (1, 432)	0.011	
	Substrate × Biochar	56.64 (2, 432)	<0.001	
	Mode × CTE	56.64 (4, 432)	<0.001	
	Substrate × CTE	27.43 (8, 432)	<0.001	
	Biochar × CTE	8.12 (4, 432)	0.087	
	Mode × Substrate × Biochar	11.75 (2, 432)	<0.001	
	Substrate × Biochar × CTE	17.92 (8, 432)	0.021	

Cumulative Temporal Effect (CTE) is the cumulative effect of season and year.

however, no significant differences were observed among treatments, as indicated by the post-hoc analysis ($p > 0.05$) (Fig. 1). In summer 2021, surface application of woodchip mulch without biochar showed high emissions for this measurement with a mean flux of $0.95 \pm 0.87 \text{ nmol m}^{-2} \text{ s}^{-1}$ (Fig. 1c). In fall of first year (2021), incorporated applications generally showed higher emissions compared to surface applications; for instance, surface-applied bark with biochar had a mean flux of $0.49 \pm 0.27 \text{ nmol m}^{-2} \text{ s}^{-1}$ (Fig. 1b), while the same treatment in a mixed application showed a slightly higher flux of $0.79 \pm 0.79 \text{ nmol m}^{-2} \text{ s}^{-1}$ (Fig. 1e).

Starting the second year, the spring of 2022 marked a significant shift in flux patterns, with all biochar addition treatments showing CH₄ uptake. In this measurement, the highest CH₄ emission was measured from surface-applied woodchips without biochar ($0.98 \pm 0.7 \text{ nmol m}^{-2} \text{ s}^{-1}$), while the corresponding treatment with biochar showed a mean uptake of $-0.14 \pm 0.3 \text{ nmol m}^{-2} \text{ s}^{-1}$ (Fig. 1c). A similar pattern was observed for surface-applied bark mulch with and without biochar (-0.49 ± 0.16 vs. $0.08 \pm 0.12 \text{ nmol m}^{-2} \text{ s}^{-1}$, respectively) (Fig. 1b). Conversely, in the spring 2022, incorporated applications of both woodchips and bark mulch showed CH₄ uptake, but with the rate of CH₄ uptake increased in the presence of biochar; in fact, the highest CH₄ uptake in this season was incorporated woodchip mulch with biochar ($-1.65 \pm 1.03 \text{ nmol m}^{-2} \text{ s}^{-1}$) (Fig. 1f). Control soil in spring 2022 was found to be near-zero CH₄ flux ($0.02 \pm 0.32 \text{ nmol m}^{-2} \text{ s}^{-1}$), while the corresponding biochar

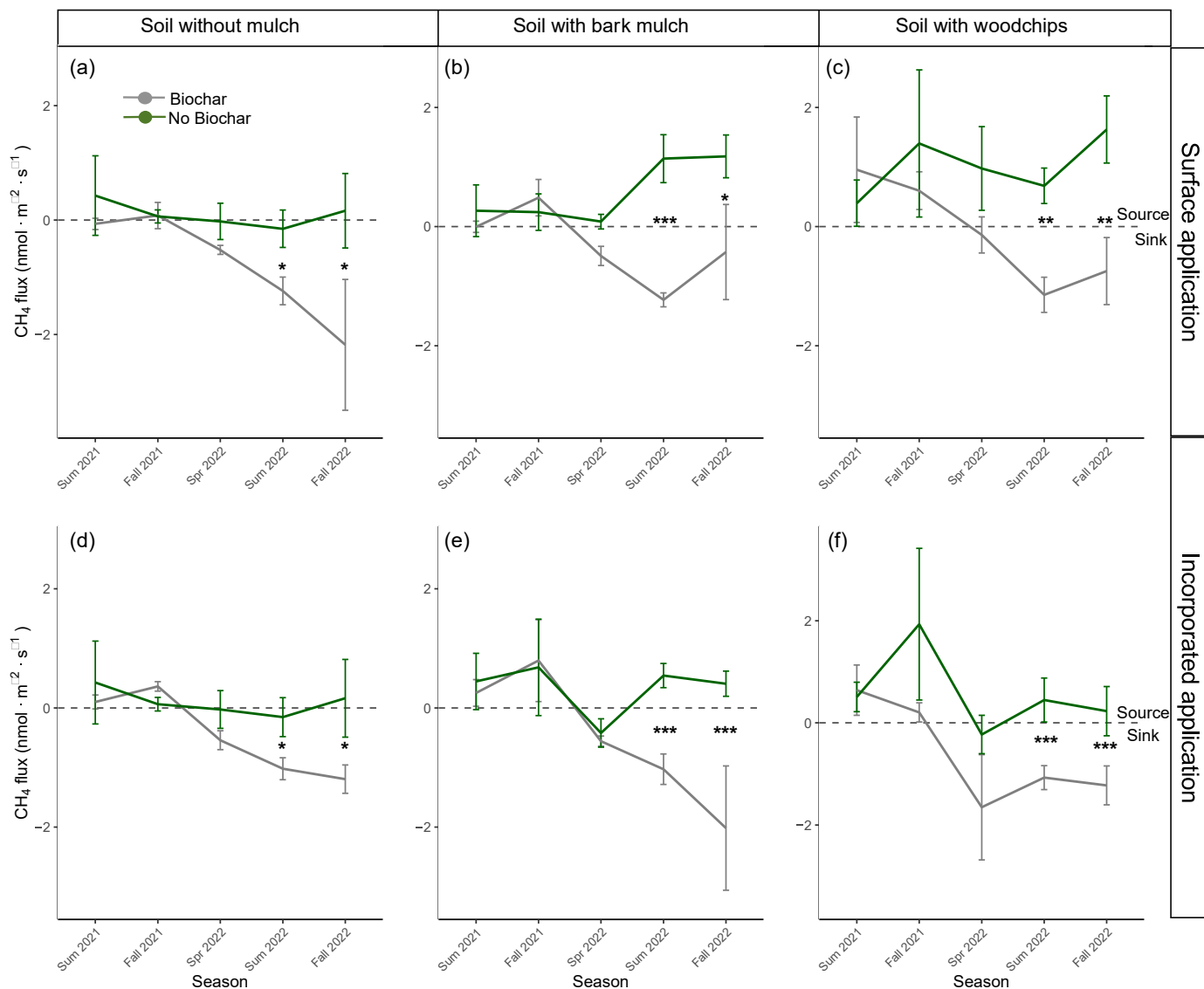


Fig. 1. Effects of biochar treatment on substrate CH_4 flux across control soil, bark mulch and woodchips in both surface and incorporate application mode measured through Summer 2021 to Fall 2022. Each data point represents the mean (\pm SE) flux values measured throughout the growing season. ANOVA results are given in Table 1. Significance of post-hoc comparisons between biochar and no biochar treatment within measurement seasons are indicated by asterisks: (*) $p \leq 0.10$; * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$.

applications resulted in a significant sink in both the case of surface ($-0.52 \pm 0.08 \text{ nmol m}^{-2}\text{s}^{-1}$) and incorporated ($-0.54 \pm 0.16 \text{ nmol m}^{-2}\text{s}^{-1}$) treatments (Fig. 1a–d).

By summer 2022, both woodchips and bark mulch treatments without biochar (both surface and incorporated applications) showed CH_4 emission, while consumption was found in with biochar treatments with significant differences in all cases ($p < 0.01$). Biochar also increased the rate of CH_4 uptake in the control soil for both surface and incorporate application (Fig. 1). In this measurement period, the highest CH_4 emission rate was found in surface-applied bark mulch with a mean (\pm se) of $1.14 \pm 0.46 \text{ nmol m}^{-2}\text{s}^{-1}$, while biochar addition resulted in CH_4 uptake with a mean (\pm se) rate of $-1.23 \pm 0.24 \text{ nmol m}^{-2}\text{s}^{-1}$. A similar pattern was found in the case of incorporated bark mulch with a slightly lower CH_4 emission without biochar ($0.54 \pm 0.23 \text{ nmol m}^{-2}\text{s}^{-1}$) and consumption with biochar ($-1.03 \pm 0.24 \text{ nmol m}^{-2}\text{s}^{-1}$) (Fig. 1b–e). In the case of woodchip mulch, biochar significantly favored CH_4 uptake in both the surface and incorporated treatments ($p < 0.01$). Regardless of the mode of application, woodchips without biochar emitted CH_4 but the effect was most pronounced in the surface-applied

treatment, with a mean (\pm se) emission rate of $0.68 \pm 0.33 \text{ nmol m}^{-2}\text{s}^{-1}$, compared to the incorporated application with mean (\pm se) emission rate of $0.45 \pm 0.37 \text{ nmol m}^{-2}\text{s}^{-1}$. Conversely, for woodchips with biochar, CH_4 uptake was higher in the incorporated than the surface application (Fig. 1c–f).

The fall of 2022 presented the largest differences in CH_4 fluxes among treatments, with a mean efflux of $0.41 \pm 0.58 \text{ nmol m}^{-2}\text{s}^{-1}$, while the incorporated application of bark with biochar demonstrated a mean uptake of $-2.02 \pm 1.02 \text{ nmol m}^{-2}\text{s}^{-1}$. This measurement period highlighted the cumulative effect of biochar over time, with biochar-amended treatments consistently showing greater CH_4 uptake compared to non-biochar treatments in all cases. Significant differences were observed between several treatment combinations, including between surface-applied woodchips without biochar in fall 2021 and control soil with biochar in fall 2022 ($p < 0.01$) (Fig. 1).

3.2. Mulch and biochar effects on CO_2 flux

The mixed effect model demonstrated significant effects of the mode

of application ($\chi^2 = 69.08, p < 0.001$), substrate type ($\chi^2 = 86.12, p < 0.001$), biochar ($\chi^2 = 193.51, p < 0.001$), and CTE ($\chi^2 = 24.42, p < 0.001$) on CO₂ flux (Table 1). Additionally, significant interactions between application mode and substrate type ($\chi^2 = 48.36, p < 0.001$), mode and biochar ($\chi^2 = 5.06, p = 0.024$), and substrate type and CTE ($\chi^2 = 19.10, p = 0.014$) were observed (Table 2). Overall, CO₂ fluxes were highest during the summer across both years, particularly in treatments involving biochar. Biochar consistently resulted in higher CO₂ fluxes compared to non-biochar treatments across all substrates. Incorporated applications generally produced higher CO₂ fluxes than surface applications, especially during the summer. Fall seasons exhibited the lowest CO₂ fluxes, with significant differences between biochar and non-biochar treatments, particularly in incorporated applications ($p < 0.01$) (Fig. 2).

In the summer of 2021, CO₂ fluxes were consistently higher with biochar treatments compared to non-biochar treatments across all substrates. For surface applications, biochar resulted in a 49.1% increase in flux for bark mulch, a 2.4% increase for woodchips, and a 43.3% increase for control soil, with a mean flux of 6.62 ± 1.8 , 8.16 ± 3.75 , and $8.94 \pm 2.4 \mu\text{mol m}^{-2}\text{s}^{-1}$, respectively. For incorporated applications, woodchips with biochar showed a 22.9% increase in CO₂ flux compared to those without biochar. By fall 2021, CO₂ fluxes decreased across all treatments, but biochar amendments still exhibited significantly higher emissions than non-biochar treatments. For incorporated applications, biochar-treated bark mulch and woodchips produced fluxes of 4.79 ± 2.66 and $5.44 \pm 2.42 \mu\text{mol m}^{-2}\text{s}^{-1}$, respectively, compared to 2.52 ± 1.53 and $2.46 \pm 1.75 \mu\text{mol m}^{-2}\text{s}^{-1}$ for non-biochar treatments, representing increases of 90.1% and 121.1% ($p < 0.01$). In spring 2022, biochar treatments continued to show higher CO₂ fluxes. For surface applications, biochar resulted in mean fluxes of 3.92 ± 0.6 for bark mulch and $4.98 \pm 0.97 \mu\text{mol m}^{-2}\text{s}^{-1}$ for woodchips, which were 43.6% and 90.1% higher than non-biochar treatments, respectively. In summer 2022, biochar treatments for surface applications yielded fluxes of 6.35 ± 1.86 for bark mulch and $6.88 \pm 1.38 \mu\text{mol m}^{-2}\text{s}^{-1}$ for woodchips, reflecting increases of 26.7% and 58.2% compared to non-biochar treatments. By fall 2022, for surface applications, biochar-treated

woodchips produced fluxes of $5.05 \pm 1.61 \mu\text{mol m}^{-2}\text{s}^{-1}$, which was 102% higher than non-biochar treatments, while bark mulch showed a 43.1% increase compared to non-biochar treatments (Fig. 2).

3.3. Mulch and biochar effects on H₂O flux

Analysis revealed that, substrate type ($\chi^2 = 12.95, p < 0.01$) and CTE ($\chi^2 = 228.63, p < 0.001$) showed significant impact on H₂O flux (Table 1). Notably, significant interaction effects were observed between the mode of application and biochar ($\chi^2 = 6.45, p = 0.01$), indicating that the way in which mulches and biochar are applied—whether on the surface or incorporate into the soil—can lead to differing outcomes in terms of H₂O flux. Similarly, the interaction between substrate type and CTE was also significant ($\chi^2 = 27.43, p < 0.01$) as was the three-way interaction between substrate, biochar, and CTE ($\chi^2 = 17.92, p = 0.02$) (Table 1).

The post-hoc analyses provide insights into how H₂O flux varied across different seasons and treatments, particularly when comparing the fall of 2021 with the spring of 2022. During the fall of 2021, H₂O fluxes in soils treated with biochar were relatively moderate, with values ranging between 0.138 and $0.229 \mu\text{mol m}^{-2}\text{s}^{-1}$ across various substrates and application modes. For instance, in biochar-amended soil substrates, H₂O flux averaged $0.138 \mu\text{mol m}^{-2}\text{s}^{-1}$ under mixed application and $0.153 \mu\text{mol m}^{-2}\text{s}^{-1}$ under surface application. However, a marked increase in H₂O flux was observed during the spring of 2022, particularly in biochar-amended woodchip substrates applied on the soil surface, where the flux reached a peak mean of $1.080 \mu\text{mol m}^{-2}\text{s}^{-1}$. This significant seasonal escalation highlights the pronounced effect of spring climate conditions on soil moisture dynamics, especially in substrates that benefit from the water-retentive properties of biochar. In contrast, soils without biochar also exhibited an increase in H₂O flux during the spring of 2022, though the effect was less pronounced compared to biochar-treated soils. For example, in mixed soil substrates without biochar, the H₂O flux reached $0.842.17 \mu\text{mol m}^{-2}\text{s}^{-1}$, indicating that the interaction between substrate type and biochar presence is a crucial determinant of water flux, particularly under the mixed application mode.

During the fall of 2021, the surface application of woodchips combined with biochar resulted in a mean flux of $0.229 \mu\text{mol m}^{-2}\text{s}^{-1}$, which was higher than the flux observed in bark ($0.196 \mu\text{mol m}^{-2}\text{s}^{-1}$) or soil substrates ($0.153 \mu\text{mol m}^{-2}\text{s}^{-1}$) treated with biochar. In fall 2022, the mixed application of woodchips without biochar resulted in a mean flux of $0.628 \mu\text{mol m}^{-2}\text{s}^{-1}$, significantly higher than the flux observed in other substrates under similar conditions (Fig. 3). This highlights the role of substrate-specific properties in influencing water flux, with woodchips exhibiting a unique ability to retain moisture, especially when applied in a mixed mode.

3.4. Biochar placement effect on CH₄ flux

The analysis revealed that biochar placement and substrate type had no significant effects on CH₄ flux (Table 2). However, a highly significant seasonal effect was detected ($\chi^2 = 49.03, p < 0.001$). Interactions between placement and substrate ($p = 0.94$), placement and CTE ($p = 0.29$), substrate and CTE ($p = 0.56$), and the three-way interaction among placement, substrate, and CTE ($p = 0.56$) were all non-significant, suggesting that these factors did not significantly alter CH₄ fluxes with time (Table 2).

3.5. Biochar placement effects on CO₂ flux

The analysis of deviance indicated a significant effect of biochar placement on CO₂ flux ($p = 0.047$), with a marginal effect of substrate type ($p = 0.057$). A highly significant time effect was also observed ($\chi^2 = 111.90, p < 0.001$). Interactive effects of placement and substrate ($p = 0.583$), placement and CTE ($p = 0.056$), substrate and CTE ($p = 0.382$),

Table 2

Results from the generalized linear mixed effect model predicting CH₄, CO₂ and H₂O flux with biochar placement (biochar above vs. below the mulch), substrate (woodchips and bark mulch) as fixed effects and cumulative temporal effects (season and year) as random effects.

Greenhouse gas	Effects	Chisq (DF _{between} , DF _{within})	p-value
CH ₄	Placement	0.07 (1,80)	0.779
	Substrate	0.26 (1,80)	0.607
	CTE	49.03 (4,80)	<0.001
	Placement × Substrate	0.006 (1,80)	0.607
	Placement × CTE	4.92 (4,80)	0.294
	Substrate × CTE	2.95 (4,80)	0.567
	Placement × Substrate × CTE	2.96 (4,80)	0.564
CO ₂	Placement	3.93 (1,80)	0.047
	Substrate	3.60 (1,80)	0.057
	CTE	111.89 (4,80)	<0.001
	Placement × Substrate	0.30 (1,80)	0.582
	Placement × CTE	9.22 (4,80)	0.056
	Substrate × CTE	4.18 (4,80)	0.381
	Placement × Substrate × CTE	4.94 (4,80)	0.293
H ₂ O	Placement	4.96 (1,80)	0.025
	Substrate	13.50 (1,80)	<0.001
	CTE	190.25 (4,80)	<0.001
	Placement × Substrate	2.64 (1,80)	0.104
	Placement × CTE	49.56 (4,80)	<0.001
	Substrate × CTE	15.70 (4,80)	<0.001
	Placement × Substrate × CTE	10.99 (4,80)	0.027

Cumulative Temporal Effect (CTE) is the cumulative effect of season and year.

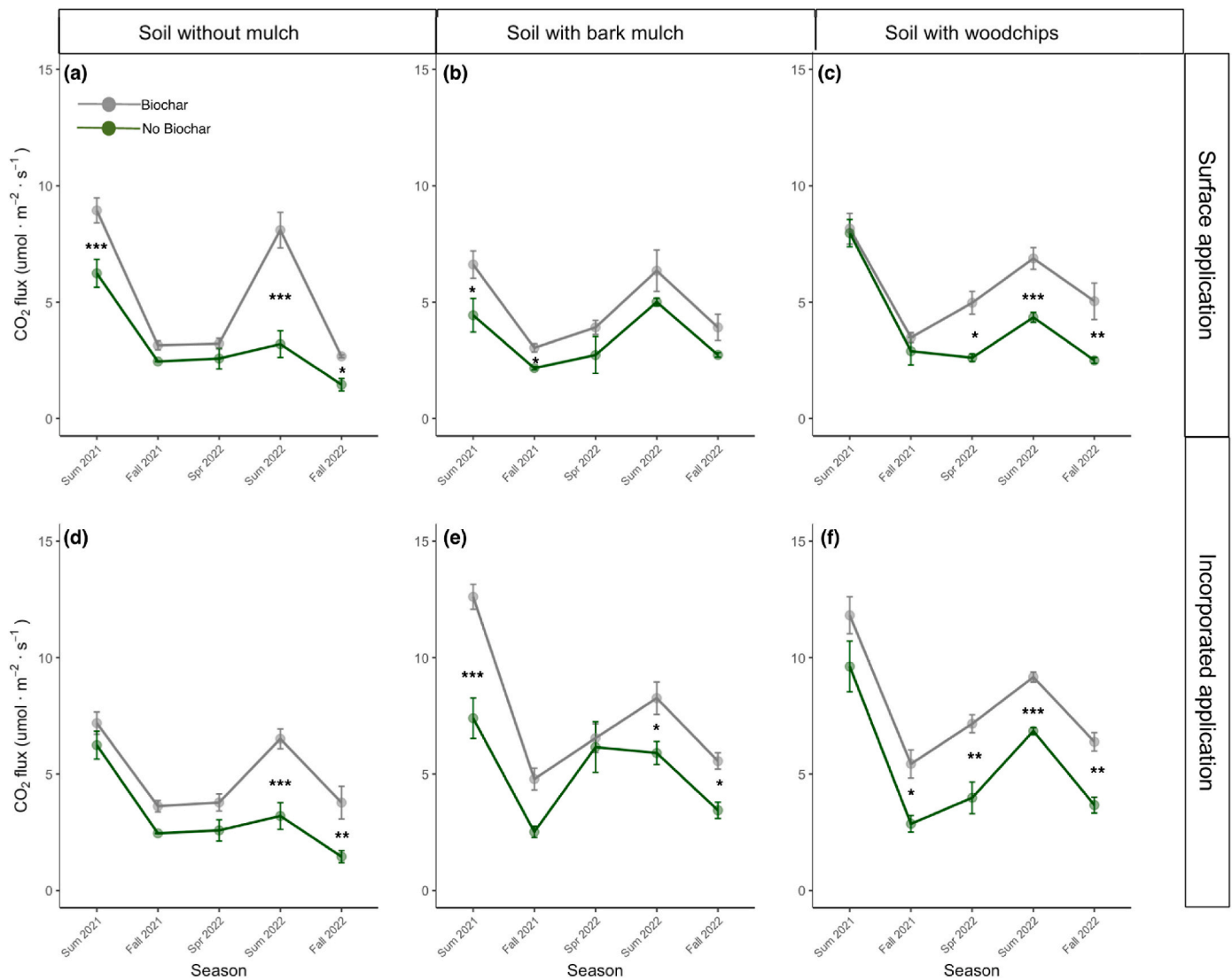


Fig. 2. Effects of biochar treatment on substrate CO₂ flux across control soil, bark mulch and woodchips in both surface and incorporate application mode measured through Summer 2021 to Fall 2022. Each data point represents the mean (\pm SE) flux values measured throughout the growing season. ANOVA results are given in Table 1. Significance of post-hoc comparisons between biochar and no biochar treatment within measurement seasons are indicated by asterisks: (*) $p \leq 0.10$; * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$.

and the three-way interaction of placement, substrate, and CTE ($p = 0.293$) were non-significant, suggesting that these factors did not significantly influence CO₂ fluxes across different seasons (Table 2).

Post-hoc tests revealed significant seasonal differences in CO₂ flux among placement treatments. In particular, CO₂ flux was significantly higher in Summer 2021 under the bark mulch biochar above treatment compared to all other seasons and treatments, with an average flux of $5.53 \pm 1.01 \mu\text{mol m}^{-2}\text{s}^{-1}$ ($p < 0.01$). Although CO₂ fluxes were lower in Summer 2022 compared to Summer 2021, they remained higher than in other seasons, particularly under the woodchip mulch biochar above treatment ($3.72 \pm 1.01 \mu\text{mol m}^{-2}\text{s}^{-1}$, $p < 0.05$) (Fig. 4).

3.6. Biochar placement effects on H₂O flux

The analysis revealed significant effects of biochar placement ($p = 0.026$), substrate type ($p < 0.001$), and CTE ($p < 0.001$) on H₂O flux. Significant interactions were also observed between placement and CTE ($\chi^2 = 49.56$, $p < 0.001$), substrate and CTE ($\chi^2 = 15.7$, $p < 0.01$), and the three-way interaction among placement, substrate, and CTE ($\chi^2 = 10.99$, $p < 0.05$), indicating that these factors significantly influenced H₂O flux across different seasons (Table 2).

Significant seasonal differences in H₂O flux were observed in the post-hoc analysis. In Summer 2021, the biochar above for bark mulch treatment exhibited the highest H₂O flux ($0.465 \pm 0.077 \mu\text{mol m}^{-2}\text{s}^{-1}$, $p < 0.01$) compared to all other seasons and treatments, indicating increased evaporation rates during this period. By Summer 2022, high H₂O fluxes were observed under the biochar below treatment in bark mulch ($0.609 \pm 0.077 \mu\text{mol m}^{-2}\text{s}^{-1}$, $p < 0.01$) (Fig. 4).

3.7. Structural equation models and relationships between CH₄ and CO₂ flux

The results of the Structural Equation Models (SEM) are presented in Fig. 5, while the regression analysis illustrating the relationship between CH₄ and CO₂ fluxes is provided in Fig. 6. In the first SEM model (Fig. 5A), CH₄ flux showed a significant negative relationship with CO₂ flux ($Z = -3.325$, $p < 0.01$) while significant positive relationships with TOC ($Z = 7.285$, $p < 0.01$) and MC ($Z = 3.831$, $p < 0.01$). In second model (5B), CH₄ flux showed a significant negative relationship with CO₂ flux ($Z = -2.653$, $p = 0.008$), substrate carbon-to-nitrogen ratio ($Z = -3.49$, $p < 0.01$) and bulk density ($Z = -2.235$, $p < 0.01$) and a positive relationship with substrate MC ($Z = 2.55$, $p = 0.01$) and pH ($Z = 1.985$, $p =$

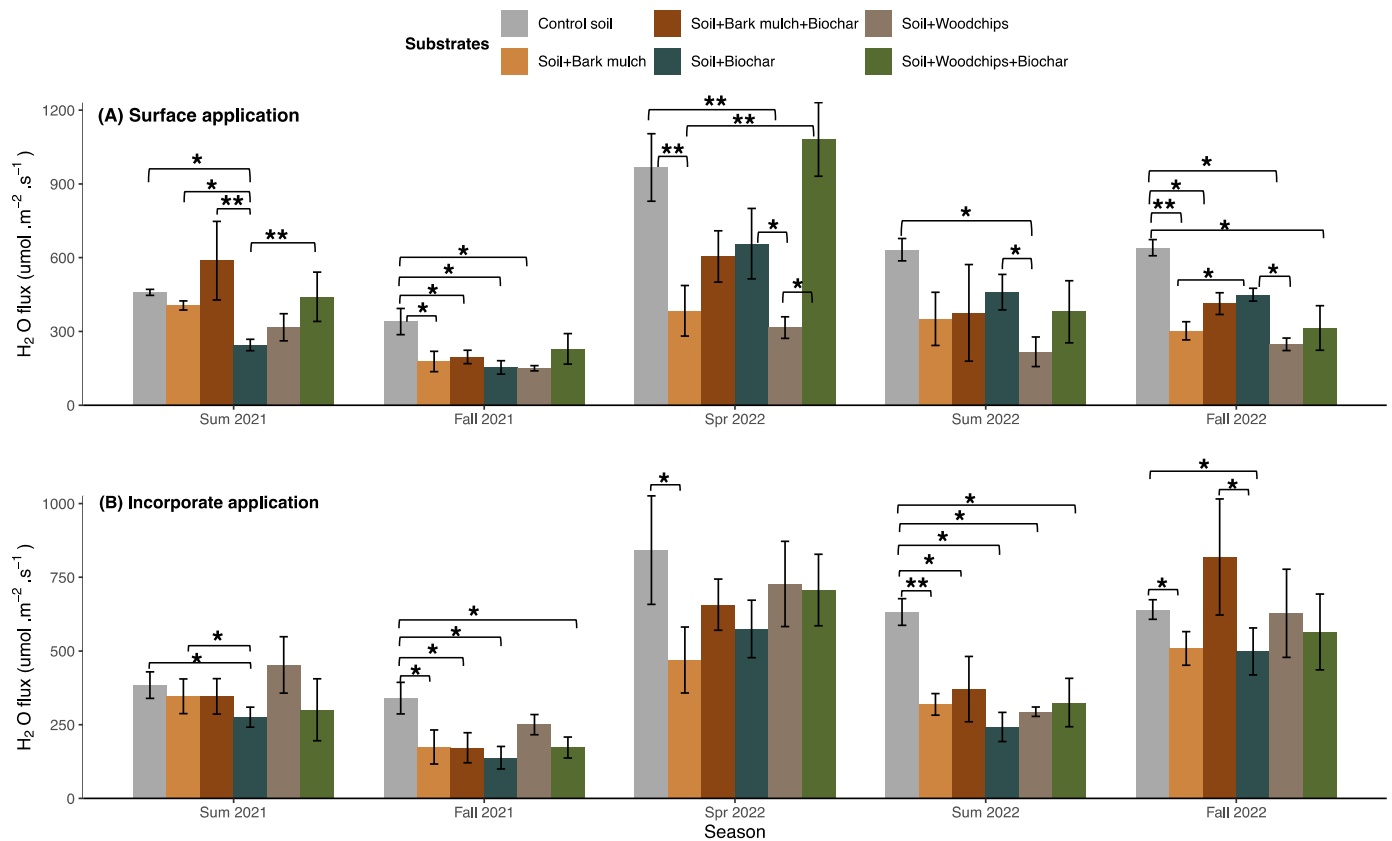


Fig. 3. Effects of substrate types on H_2O flux (evaporation) in both surface and incorporated application mode measured through Summer 2021 to Fall 2022. Each data point represents the mean (\pm SE) flux values measured throughout the growing season. ANOVA results are given in Table 1. Significance of post-hoc comparisons between biochar and no biochar treatment within measurement seasons are indicated by asterisks: * $p < 0.05$; ** $p < 0.01$.

0.08).

The linear regression analysis, shown in Fig. 6, revealed a significant negative relationship between CH_4 and CO_2 flux in both the mulch and biochar treatments. The slope was greater for the biochar treatments, indicating higher CO_2 emissions compared to the mulch treatments. There was a significant positive relationship between CO_2 flux and temperature in both substrates, regardless of biochar treatment. However, the relationship between CH_4 flux and temperature in substrates containing biochar is marginally significant ($p = 0.09$), with a negative slope, indicating increased methane uptake with the increasing temperature (Fig. S2).

4. Discussion

We examined the effects of organic mulch and biochar on CH_4 , CO_2 and H_2O flux in urban soil mesocosms under various treatment combinations. We found that organic mulching, specifically the application of woodchips and bark mulch, enhanced CH_4 emissions, with the rate of emissions varying seasonally and with substrate age, supporting our hypothesis that organic mulches create an environment that facilitates methanogenesis, particularly under certain substrate conditions. As predicted, biochar additions substantially reduced CH_4 emissions in the mulched treatments; but beyond this, biochar additions converted CH_4 emissions resulting from mulch additions into net CH_4 sinks – a pattern consistently found in all treatments (Fig. 1). Contrary to our hypothesis, layering of biochar and mulch had similar effects to mixed amendments, though differences between layered and mixed treatments were more pronounced in the case of CO_2 and H_2O flux patterns.

Previous survey studies of urban soil GHG flux have generally not considered mulch effects on CH_4 flux (Groffman and Pouyat, 2009; Costa and Groffman, 2013; Zhang et al., 2014; van Delden et al., 2016; Bezyk

et al., 2022). We are aware of only a single prior study that has specifically addressed mulching effects on urban soil methane flux: Livesley et al. (2010) reported higher methane uptake in a mulched garden than a lawn site; however, this result was based on a non-replicated experiment and mulched and non-mulched sites differed in vegetation. In contrast, high CH_4 emissions were observed in urban soils in Moscow, Russia, which were attributed to waterlogged technosols (Kulachkova and Kovalenko, 2021). Similarly, Xue et al. (2023) reported that high organic matter was associated with increased CH_4 emissions, based on a structural equation model for a sponge city park in Chengdu, China.

4.1. Biochar converts mulch methane emissions into sink

We found all mulch treatments, both with and without biochar, initially emitted CH_4 during the first year. However, by the following spring, this pattern shifted—biochar amendments resulted in increased CH_4 uptake, effectively transforming CH_4 sources into sinks (Fig. 1). The structural equation model indicates that CH_4 emissions induced by mulch were mainly driven by its positive effects on total organic carbon (TOC) and soil moisture content (MC) (Fig. 5A). Woodchips and bark mulch increased water-holding capacity of the substrate while also contributing organic matter (OM). High soil moisture limits oxygen diffusion, leading to the development of low-oxygen (hypoxic) zones. This effect is even more pronounced in the case of fine-textured clayey soils common in urban area. Under conditions of high moisture mulches will also generate dissolved organic compounds, which support the growth of methanogenic microbes. Previous studies suggest that OM in soils can have varying effects on CH_4 fluxes: low levels of OM can improve soil porosity and enhance CH_4 oxidation (Savage et al., 1997); for example (Lee et al., 2023), reported OM determined rate of CH_4 oxidation in forest soils. However, high levels of OM increase soil water

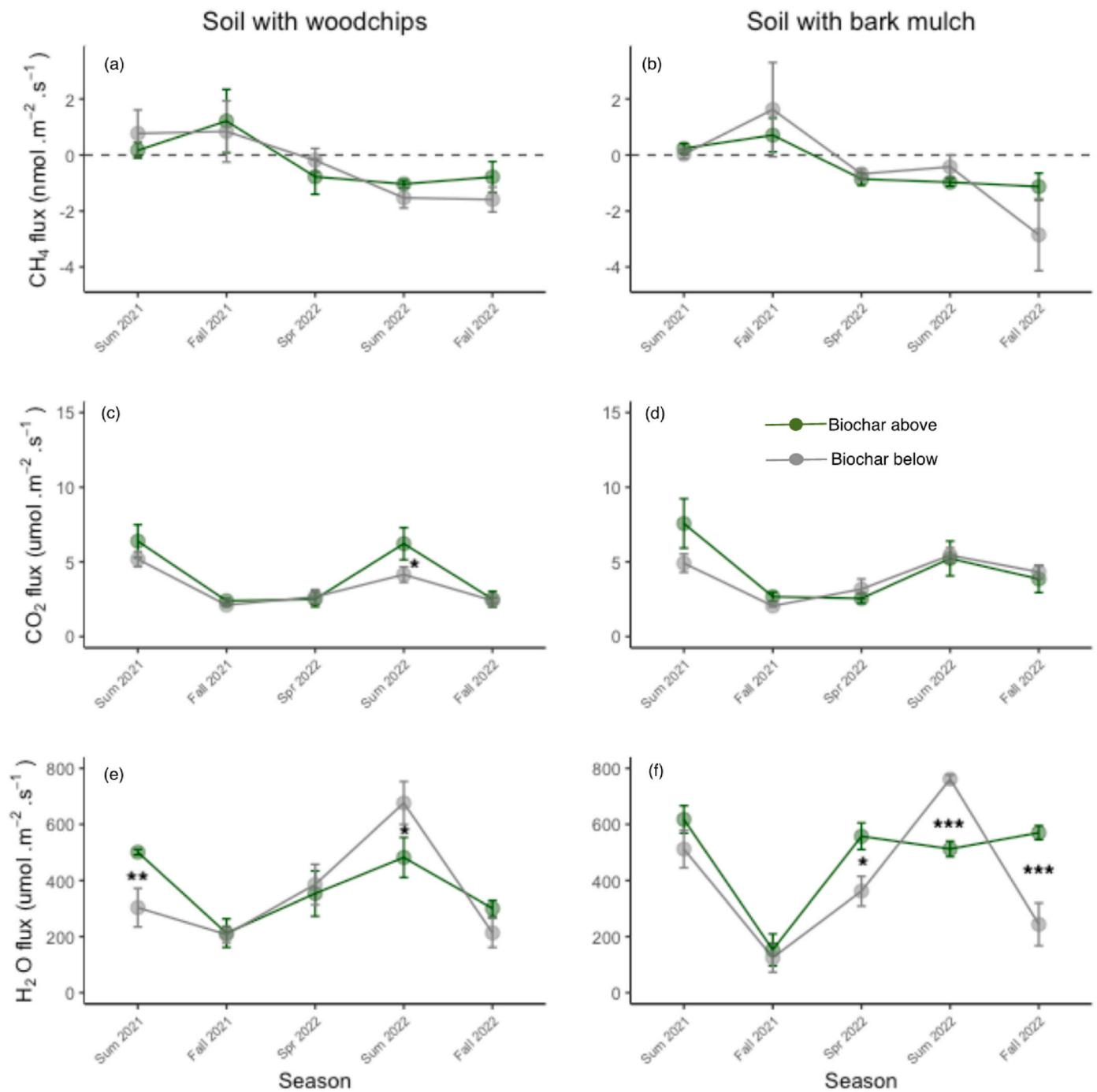


Fig. 4. Effects of biochar placement (above vs. below the mulch) on CH₄, CO₂ and H₂O (evaporation) flux from woodchips and bark mulches throughout the measurement period (Summer 2021-Fall 2022). Each data point represents the mean (\pm SE). ANOVA results are given in Table 2. Significance of post-hoc comparisons between biochar above and below within measurement seasons are indicated by asterisks: * $p < 0.05$; ** $p < 0.01$, *** $p < 0.001$.

holding capacity, which reduces oxygen availability and promotes methanogenesis (Lal, 2020). Vantellingen and Thomas (2021b) reported a situation closely analogous to mulch applications, in which buried wood fragments on log landings were a main driver of high CH₄ emissions. Our results for water flux also indicate that both woodchip and bark mulch amendments reduced evaporative water loss compared to controls (Fig. 3). Although reductions in soil evaporation are often considered a benefit of mulch use (Chalker-Scott, 2007; Li et al., 2020), this effect can clearly contribute to hypoxic conditions under mulch.

We observed significantly higher CH₄ emissions in mulch treatments in the spring season of the second year compared to first year (Fig. 1) and

the emission continued to increase with time. There was seasonal variation in CH₄ flux as well, with increased emissions observed during summer 2022 (Fig. 1). Seasonal fluctuations in temperature and moisture availability are known to influence the dynamics of soil microbial communities, including methanogens (Xue et al., 2023). Our results also showed a positive relationship between both CH₄ and CO₂ flux and substrate temperature based on pooled data, although temperature-dependence was not statistically significant for CH₄ flux in control treatments (Fig. 6). Higher temperatures not only accelerate the decomposition of organic material but also increase microbial activity (van den Pol-van Dasselaar et al., 1998). This potentially led to

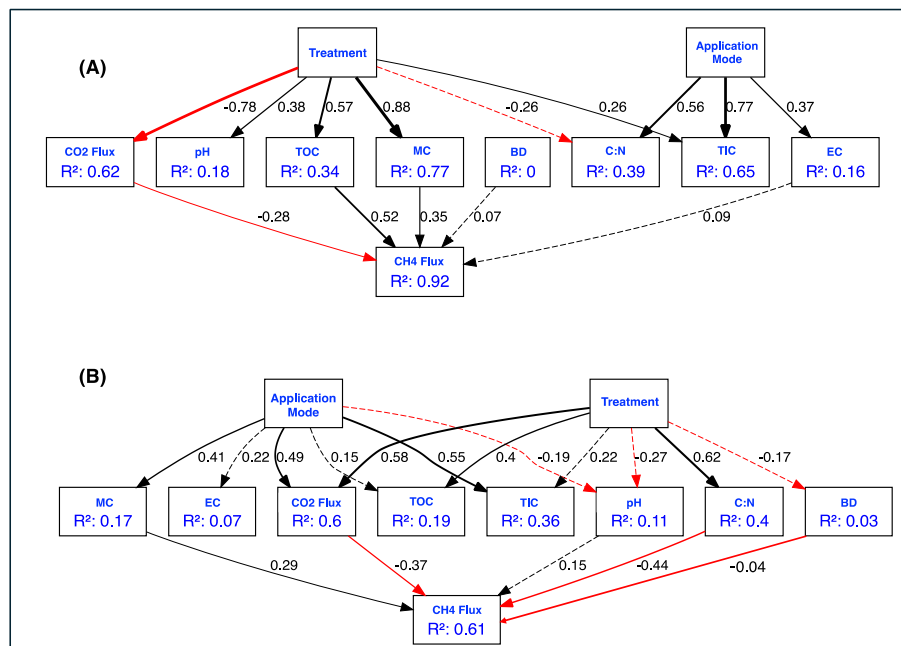


Fig. 5. Final structural equation models generated from full mediation through continuous variables structural equation modelling, a confirmatory path analysis method. In the first model (A) (CFI = 0.82, $p < 0.01$), categorical variables—Treatments comprised of “mulch only (woodchips and bark mulch pooled)” and “biochar” and application mode compares “surface vs incorporated” were specified to influence CH₄ flux exclusively through continuous variables including CO₂ flux, pH, total organic carbon (TOC), moisture content (MC), bulk density (BD), carbon nitrogen ratio (C:N), total inorganic carbon (TIC) and electric conductivity (EC). In the second model (B) (CFI = 0.61, $p < 0.01$), categorical variables—Treatments comprised of “mulch only” and “mulch with biochar” and “Application mode compares “surface vs incorporated” were specified to influence CH₄ flux exclusively through the similar continuous variables. Single-headed arrows represent a causal effect on the response variable. Solid black arrows depict positive relationships between variables, solid red arrows negative relationships, and dashed grey arrows depict paths with marginal significance ($p > 0.05$). In the case of CH₄ flux, a positive relationship depicts increases in CH₄ emissions, while negative effects depict uptake. Arrow thickness is proportional to the standardized coefficient, which is also represented numerically with the arrow, non-significant relationships have been omitted for clarity. R² values represent conditional pseudo-R² values, which take into account measure variables and unmeasured latent variables (in this case, unmeasured latent variable was not significant thus, not shown in path diagram).

enhanced production of labile carbon compounds, which served as substrates for methanogens.

Both mulches used in the study were derived from woody tissues of conifers. Monoterpenes, commonly produced by coniferous and some tropical angiosperms, have been found to strongly inhibit methanotrophic activity in soils (Amaral and Knowles, 1998; Maurer et al., 2008). This effect could also contribute to the observed patterns of CH₄ emission from mulch addition treatments.

4.2. Relationship between CO₂ and methane fluxes

Substrate respiration is expected to contribute to hypoxic conditions as oxygen is depleted. Results revealed that biochar treatments showed higher CO₂ flux than mulch treatments (Fig. 2). SEM analysis showed negative relationship between CH₄ and CO₂ fluxes (Fig. 5). Regression analysis also revealed a significant negative relationship between CH₄ and CO₂ flux with a higher slope in case of substrate with biochar treatment indicating higher microbial respiration (Fig. 6). Biogenic CH₄ is produced by methanogenic archaea under anaerobic or hypoxic conditions, typically in waterlogged soils, whereas CO₂ is generated primarily through aerobic respiration by microbes, plants, and other organisms in oxygen-rich environments. The observed negative relationship between CO₂ and CH₄ flux in both mulch and biochar treatments suggests a shift in microbial activity driven by changes in oxygen availability and substrate competition. Mulch application increased soil moisture (Fig. 5), promoting hypoxic conditions that might favored methanogenesis while inhibiting aerobic respiration, resulting in higher CH₄ and lower CO₂ emissions. The enhanced moisture and organic matter under mulch may have also altered microbial community composition, favoring methanogens over aerobic microbes.

The observed negative relationship between CO₂ and CH₄ flux in biochar-amended substrates also suggests enhanced microbial activity dominated by methanotrophs. In general, CO₂ emission in soil is primarily driven by autotrophic and heterotrophic microbial processes. Since there was no autotrophic component, CO₂ emission in this case was from heterotrophic respiration either from organic matter decomposition, or CH₄ oxidation in the aerobic microsites. Our results showed that biochar application reduced substrate bulk density, indicating improved aeration. We found a small but significant negative relationship between substrate bulk density and CH₄ flux (Fig. 5B). The porous structure of biochar provides a favorable habitat for microbial communities (Lehmann et al., 2011). When biochar was applied alongside mulch, it likely improved soil aeration, increasing oxygen availability. This enhanced oxygen levels may have supported methanotrophic microorganisms, leading to methane oxidation. The increase in CO₂ emissions observed could have resulted, in part, from this methane oxidation occurring in the aerobic microsites over heterotrophic organic matter decomposition. Previous studies in agricultural systems have reported similar findings, with biochar generally enhancing methane oxidation (Lehmann et al., 2011; Wu et al., 2019; Zhao et al., 2021). Although biochar increased CO₂ emissions from the mulch treatments, the overall radiative forcing would be lower compared to the CH₄ emissions that occur with mulching alone.

We found only weak effects of pH on either CO₂ or CH₄ flux (Fig. 5). The optimum pH for methanogenesis typically falls between 6.5 and 7.5 (Yao et al., 2023), where higher methane emissions are observed at elevated pH levels within this range. In the present study, the soil used was generally neutral to slightly alkaline, with a mean pH of 7.33 ± 0.18 (Table S1), with a relatively high cation, primarily Ca²⁺, content. Organic mulch generally reduces soil pH through organic acid release

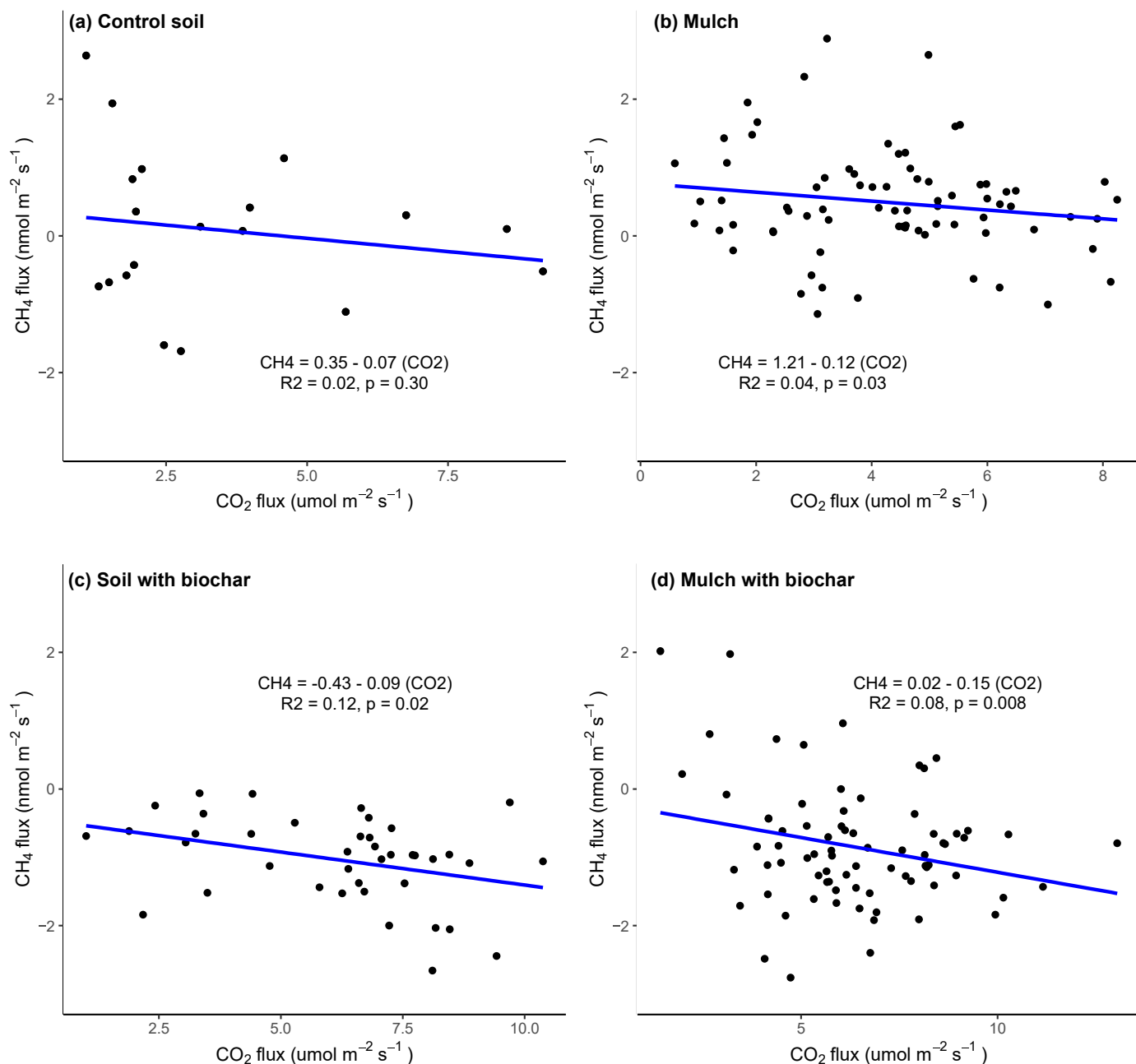


Fig. 6. Relationship between CH_4 and CO_2 fluxes, based on data pooled across all seasons measured in 2022, where (a) Control soil ($n = 20$), (b) Mulch, woodchips and bark mulch pooled together ($n = 80$), (c) Soil with biochar ($n = 40$) and, (d) Mulch with biochar, woodchips and bark mulch pooled together ($n = 80$). The grey shaded area around the fitted regression line represents the 95% confidence interval.

during decomposition (Goldin and Hutchinson, 2013). However, the presence of cations in wood-based mulches can, in some cases, increase soil pH instead (Escuer and Vabrit, 2017). Biochar, although alkaline, also has the capacity to adsorb cations and exert a buffering effect, stabilizing soil pH (Qi et al., 2024).

4.3. Impacts of biochar placement on methane flux

The placement of biochar, whether at the top or below the mulch layer, did not seem to provide additional CH_4 mitigation benefits beyond what was achieved through biochar addition itself, implying that the mechanisms by which biochar mitigates methane emissions from organic mulching—such as modifying substrate properties conducive to methanotrophs—are not particularly sensitive to its placement.

Lehmann et al. (2011) reported that biochar enhances soil aeration and stimulates methanotrophs, however these effects are still likely to occur regardless of whether biochar is applied on the top or under the mulch layers.

While surface application of biochar is more convenient, it presents challenges due to biochar's lightweight nature, which makes it vulnerable to wind erosion and runoff. Given that our results show no significant difference in methane mitigation between surface and subsurface biochar placement, it is advisable to apply biochar below the mulch layer. This strategy not only minimizes the risk of biochar loss but also ensures optimal contact with the soil. Sohi et al. (2010) emphasize that deeper placement of biochar helps prevent environmental loss while maximizing its soil-improving effects.

4.4. Mulch and biochar reduce soil evaporation

Our results show that mulch amendments reduced evaporative water loss (Fig. 3), consistent with the generalization that organic mulching is effective in reducing water loss from soil by forming a protective layer that limits soil exposure to sunlight, wind, and heat (Chalker-Scott, 2007). Although this effect has long been recognized, essentially all data pertaining to mulch effects on water loss derives from agricultural systems (Iqbal et al., 2020; Li et al., 2020; Ramos et al., 2024). Consistent with our observations (Fig. 3), the impact of mulch is generally most pronounced during the summer months when evaporative demand is highest. By reducing soil temperature and limiting evaporative loss, mulch preserves moisture within the soil. Agricultural studies indicate that organic mulch reduces soil evaporation by 25–45% during the summer months (Iqbal et al., 2020; Ramos et al., 2024). We found even more pronounced effects in the present study, with ~60% reduction in evaporative water loss averaged across treatments for summer measurements (Fig. 3). Biochar also generally enhances soil moisture retention (Razzaghi et al., 2020). A number of studies have specifically tested for biochar effects on soil surface evaporation in agricultural systems: in general biochar applications result in moderate reductions in evaporative water loss (Wang et al., 2018; Zhao et al., 2021; Feng et al., 2023), but some studies have not detected an effect (Zhang et al., 2016). The combined effects of biochar and organic mulches do not appear to have been investigated in this regard. Here we found interactive effects of biochar and mulch additions, such that biochar in some cases enhanced evaporative water loss. Nevertheless, in second summer measurements where water loss would be of concern and mulch effects were pronounced, all biochar-mulch combinations showed reduced surface water flux relative to controls (Fig. 3).

4.5. Research limitations and perspectives for the future

In this experiment, we used conifer mulch applied to fine-textured, clayey, alkaline soil. Future research should explore different types of mulch feedstocks and variations in particle size across various soil textural classes to better understand these processes. Additionally, the impacts of biochar feedstock and dosage should be investigated to determine the most effective type of biochar for these applications. Long-term field experiments involving plant presence are also necessary to understand how mulch and biochar interact in real-world scenarios concerning soil CH₄ flux. While experimental studies have examined the effects of mulching on soil physical and chemical properties, research specifically targeting its impact on GHG flux, specifically CH₄, remains limited (Chalker-Scott, 2007; Livesley et al., 2010; Liao et al., 2022). Addressing this gap is important for developing effective strategies for urban sustainability and climate resilience.

Urban forestry and green infrastructures are important components of urban landscape management aimed at enhancing environmental resilience and sustainability. However, degraded urban soil often makes it challenging to establish trees. Organic mulching has long been recognized for its outstanding moisture retention and weed suppression benefits (Chalker-Scott, 2007; Li et al., 2020). As cities across the globe are implementing ambitious GHG emission reduction plans, our study reveals that organic mulching widely utilized in urban forestry can often become source of methane (CH₄), a potent GHG, particularly when it acts to hold excessive moisture. However, we also found that amending mulch with biochar can transform this source of CH₄ into a sink, indicating a promising avenue for optimizing mulching and biochar application as strategies for mitigating CH₄ emissions in urban landscapes while allowing for the ecological benefits of mulching to be maintained.

5. Conclusion

Our findings indicate that, while organic mulching is effective in reducing evaporative water loss, especially during periods of high

evaporative demand, the combination of high organic matter coupled with excessive water results in substantial methane emissions. However, biochar amendments were remarkably effective in converting mulch-amended soils into a methane sink by favoring methane oxidation. These results thus suggest that biochar can be a practical strategy for maintaining high soil moisture retention while also mitigating methane emissions in urban landscapes where mulch is used. Our findings also suggest that biochar placement (i.e., mixed vs. above or below mulch) did not differ substantially in terms of methane oxidation. In most cases, biochar application below mulch is recommended to warrant possible wind erosion and surface runoff. Given the limitations of mesocosm study without plants, further long-term *in-situ* studies are warranted to better understand interactive effects with vegetation with combinations of mulch and biochar under field conditions.

CRedit authorship contribution statement

Imrul Kayes: Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Md Abdul Halim:** Writing – review & editing, Validation, Methodology, Conceptualization. **Sean C. Thomas:** Writing – review & editing, Validation, Supervision, Resources, Methodology, Investigation, Funding acquisition, Conceptualization.

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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Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jenvman.2025.124525>.

Data availability

Data will be made available on request.

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