Potential of biochar to mitigate methane production in paddy soils - application of a new incubation and modelling approach

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1. Calculations steps from gas sampling to amount of substance concentrations

By the use of defined CO_2 and CH_4 standards, calibration lines could be created with which the measured peak areas could be converted into mixing ratios. Multiplying the mixing ratio *r* (ppm) with the measured air pressure *p* (atm) in the incubation bottle, the partial pressure of the respective gas can be determined. In the following step, this is multiplied by the headspace volume of the bottle *Vg* (0.086 l) and divided by the product of the measured air temperature *T* (K) and general gas constant *R* (0.082057 l atm mol^{-1} K^{-1}):

$$n_g = \frac{g*p*Vg}{R*T} \quad \text{(eqn. S1)}$$

This results in the amount of substance n_g (µmol) of the respective gas in the headspace of the incubation bottle. In order to calculate the amount of substance of the respective gas in the dissolved phase in the next step, the equilibrium state according to the solubility of each gas was assumed (Table S1).

Table S1: Henry constants (Sander 2015) applied for carbon dioxide and methane solubility

	$KH_{25°C}$ (mol l^{-1} atm^{-1})	Correction factor *f* (K^{-1})
CO_2	0.035	2400
CH_4	0.0014	1600

With the actual temperature, the real Henry's constant results in *KHr* (mol l^{-1} atm^{-1}):

$$KHr = e^{-\left(f*\left(\left(\frac{1}{298.15\,K}\right)-\left(\frac{1}{T}\right)-\ln(KH)\right)\right)} \quad \text{(eqn. S2)}$$

This is used to calculate the amount of dissolved gas n_d (µmol) in the soil solution *Vd* (l):

$$n_d = g * p * Vd * KHr \left(* (1 + 10^{pH-6,4} + 10^{2*pH-6,4-10,25})\right) \quad \text{(eqn. S3)}$$

The last factor is a correction factor for the pH-dependent carbonate speciation (Stumm and Morgan 1996), which is not included in the case of methane. Finally, to calculate the absolute amount of substance production, the amounts of substance in the gas (n_g) and liquid phases (n_d) as well as the amount of substance of all gas samples taken up to the respective point in time were added. The sum was divided by the weight of the initial soil sample to obtain the mass-specific gas accumulation (µmol g^{-1} soil).

2. Tables

Table S2: Results of the ordinary least squares regressions for the response variable ***d* (delay of methanogenesis)**. The first rows show the results for the effect of each explanatory variable, the statistical significance (* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$) and the standard error in parentheses. General statistical parameters are shown for each model in the last three rows. Blank cells mean that the explanatory variable was not used in the respective model. Dummy variables (0/1) were used for all predictors except pH. For the model of "texture", the data from experiment 1 and all values from control groups were removed to distinguish only between fine and coarse texture biochar.

Explanatory var.	***d* ~ biochar**	***d* ~ feedstock**	***d* ~ texture**	***d* ~ pH**
All biochars	10.774 (6.335)	-	-	-12.23 (13.03)
Sorghum	-	9.745 (7.650)	-	-
Wood	-	15.287 (7.650)	-	-
Wheat	-	7.289 (7.650)	-	-
Coarse texture	-	-	-22.184 *** (4.715)	-
Experiment 2	-80.932 *** (5.486)	-80.932 *** (5.534)	-	-
pH	-	-	-	139.77 *** (28.78)
Observations	46	46	24	46
Multiple R^2	0.836	0.840	0.502	0.356
Adjusted R^2	0.828	0.825	0.479	0.326

Table S3: Results of the ordinary least squares regressions for the response variable ***pmCO₂* (pre-methanogenic respiration)**. The first rows show the results for the effect of each explanatory variable, the statistical significance (* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$) and the standard error in parentheses. General statistical parameters are shown for each model in the last three rows. Blank cells mean that the explanatory variable was not used in the respective model. Dummy variables (0/1) were used for all predictors except pH. For the model of "texture", the data from experiment 1 and all values from control groups were removed to distinguish only between fine and coarse texture biochar.

Explanatory var.	***pmCO₂* ~ biochar**	***pmCO₂* ~ feedstock**	***pmCO₂* ~ texture**	***pmCO₂* ~ pH**
All biochars	2.846 * (1.237)	-	-	2.434 (1.357)
Sorghum	-	0.941 (1.350)	-	-
Wood	-	2.496 (1.350)	-	-
Wheat	-	5.102 *** (1.350)	-	-
Coarse texture	-	-	-2.916 * (1.227)	-
Experiment 2	-2.487 * (1.071)	-2.487 * (0.977)	-	-
pH	-	-	-	1.959 (2.997)
Observations	46	46	24	46
Multiple R^2	0.190	0.358	0.204	0.098
Adjusted R^2	0.153	0.295	0.168	0.056

Table S4: Results of the ordinary least squares regressions for the response variable ***m* (methanogenesis production rate)**. The first rows show the results for the effect of each explanatory variable, the statistical significance (* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$) and the standard error in parentheses. General statistical parameters are shown for each model in the last three rows. Blank cells mean that the explanatory variable was not used in the respective model. Dummy variables (0/1) were used for all predictors except pH. For the model of "texture", the data from experiment 1 and all values from control groups were removed to distinguish only between fine and coarse texture biochar.

Explanatory var.	***m* ~ biochar**	***m* ~ feedstock**	***m* ~ texture**	***m* ~ biochar + pH**
All biochars	-0.019 ** (0.006)	-	-	-0.015 * (0.006)
Sorghum	-	-0.020 ** (0.007)	-	-
Wood	-	-0.023 ** (0.007)	-	-
Wheat	-	-0.014 (0.007)	-	-
Coarse texture	-	-	-0.010 (0.006)	-
Experiment 2	0.013 * (0.005)	0.013 * (0.005)	-	-
pH	-	-	-	-0.025 (0.014)
Observations	46	46	24	46
Multiple R^2	0.270	0.297	0.134	0.216
Adjusted R^2	0.236	0.229	0.095	0.179

3. Figures

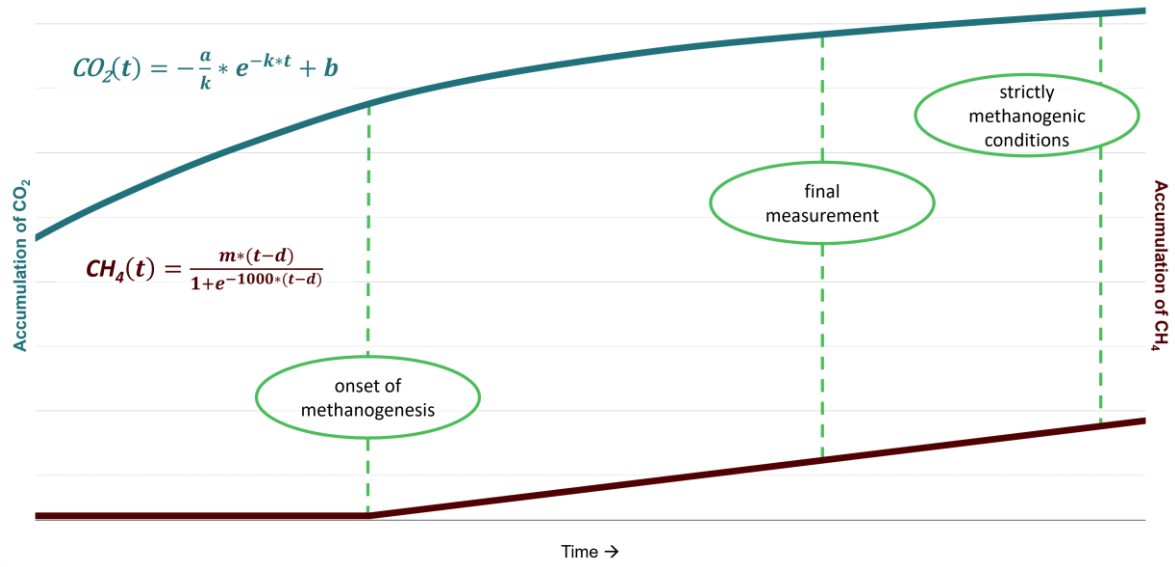

Figure S1: Schematic illustration of the accumulation models of CO_2 and CH_4 and the incubation time points (green dashed lines) relevant for the analysis.

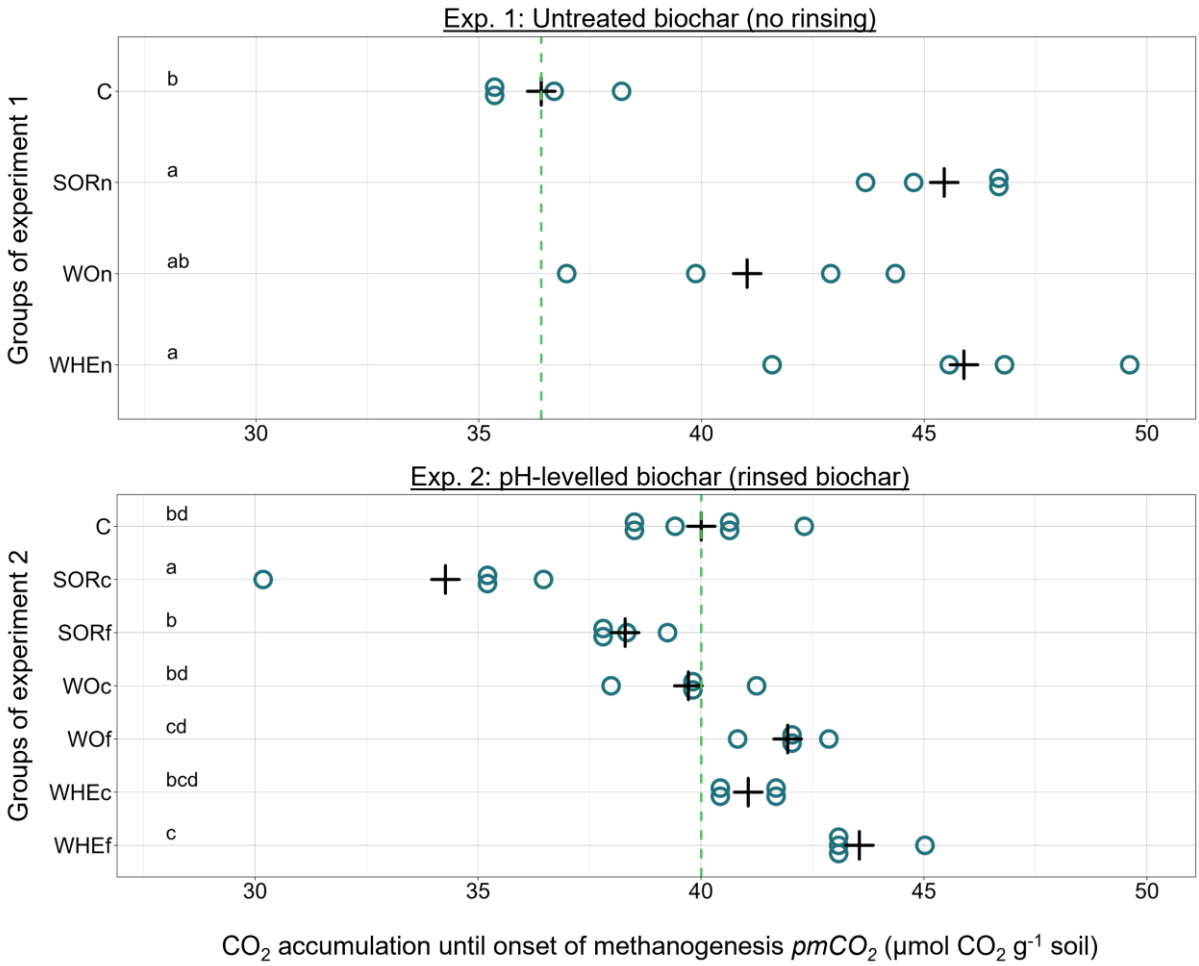

Figure S2: Distribution of the **pre-methanogenic respiration** ***pmCO₂*** among the experimental groups. Rings show the modelled results of each replicate. Groups contain C) no biochar, SOR) sorghum biochar WO) wood biochar and WHE) wheat biochar. Small letters of the experimental groups mean n) no rinsing, c) coarse biochar or f) fine biochar. Black crosses show mean values and green lines mean values of control groups. Letters (at x = 0) indicate significant differences between groups ($p < 0.05$), separated by experiments (exp. 1 & 2: Tukey's test).

4. References of supporting information

Sander, R. 2015. 'Compilation of Henry's Law Constants (Version 4.0) for Water as Solvent'. *Atmospheric Chemistry and Physics* 15 (8): 4399–4981. https://doi.org/10.5194/acp-15-4399-2015.

Stumm, Werner, and James J. Morgan. 1996. *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*. 3rd ed. Environmental Science and Technology. New York: Wiley.