Supporting information

Title

Streambed organic matter controls on carbon dioxide and methane emissions from streams

Authors

Paul Romeijn[*,‡], Sophie A. Comer-Warner[‡], Sami Ullah, David M. Hannah, Stefan Krause

‡ *Co-first authors.*

Author affiliations (all)

University of Birmingham, School of Geography, Earth and Environmental Sciences, Edgbaston, Birmingham B15 2TT, United Kingdom

Corresponding author

*Paul Romeijn: +44 121 414 5682; p.romeijn@bham.ac.uk

ORCiD: https://orcid.org/0000-0001-9270-2453

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Earth and environmental sciences; biogeochemistry; carbon cycle; ecology; freshwater ecology; microbial ecology, greenhouse gas, carbon dioxide, methane .

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Figure S1

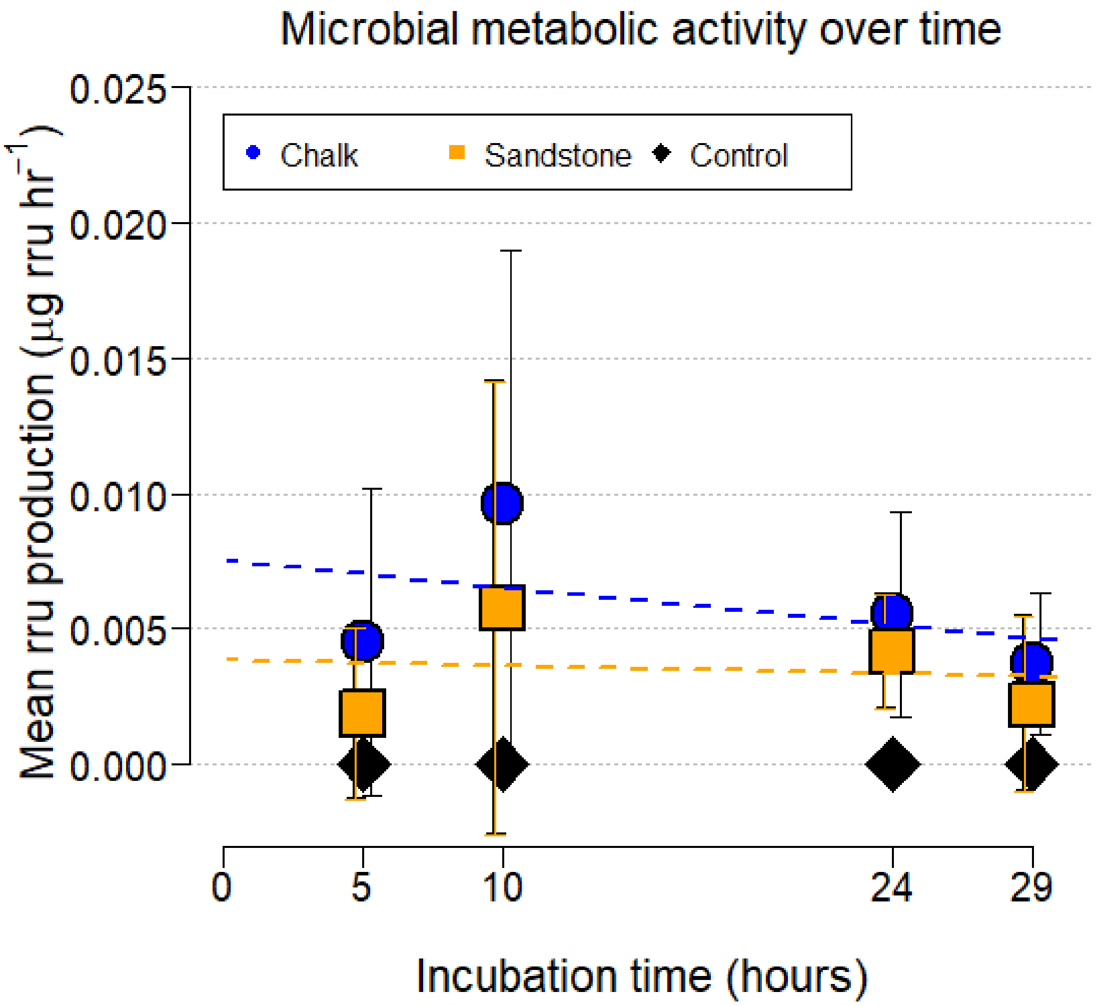

Figure S1. Change of mean hourly microbial metabolic activity over the duration of the experiment. Hourly means are calculated as means over time T_x-$T_{previous}$ (e.g. T_{24} is the mean between T_{10} and T_{24}), where for each point $n=3$. The plotted trendlines represent fitted simple linear regression models, which were not found to be significant for either Chalk (F(34)=0.8975, p=0.35, R^2=0.026, n=36) or Sandstone sediments F(34)=0.0491, p=0.826, R^2=0.001, n=36.

Figure S2

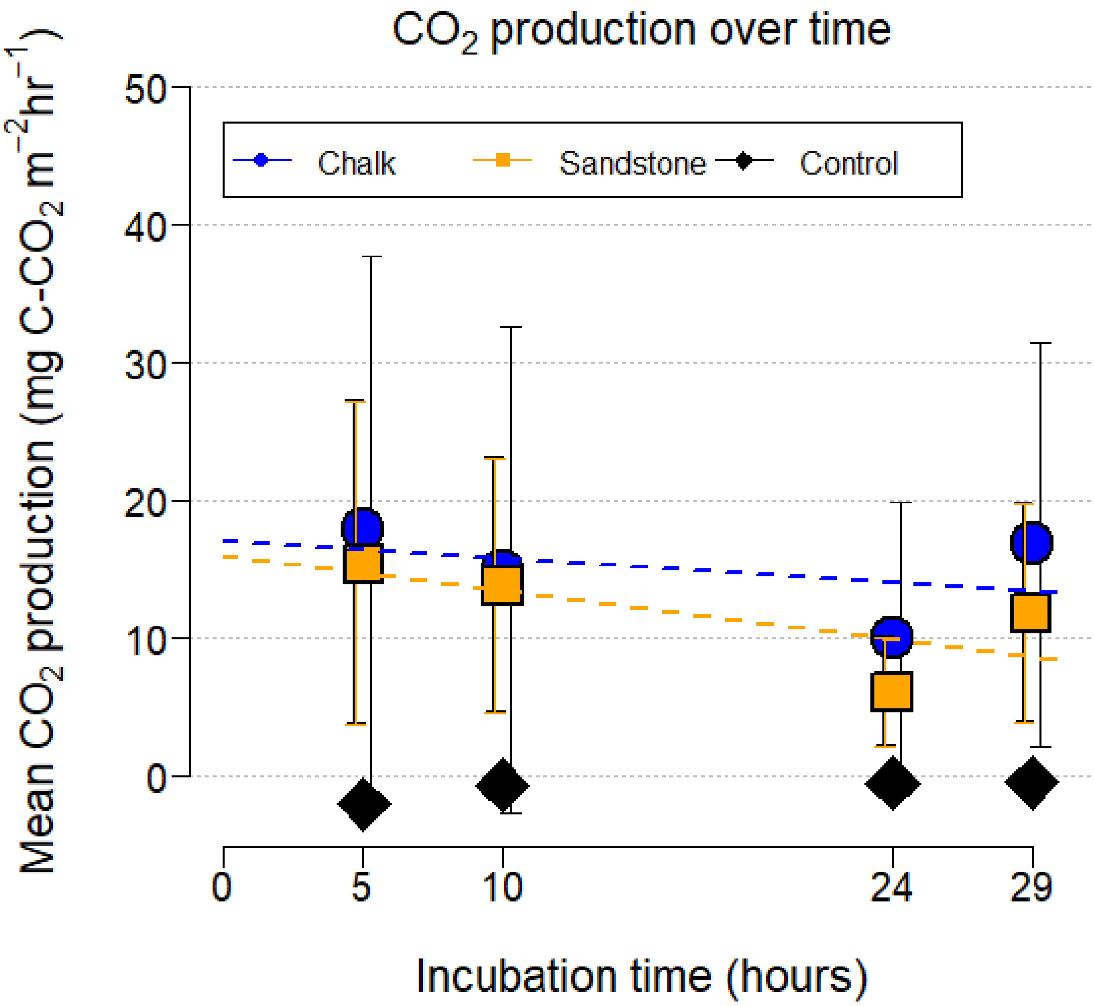

Figure S2. Change of mean hourly CO_2 production over the duration of the experiment. Hourly means are calculated as means over time T_x-$T_{previous}$ (e.g. T_{24} is the mean between T_{10} and T_{24}), where for each point $n=3$. The plotted trendlines represent fitted simple linear regression models, which were not found to be significant for either Chalk (F(34)=0.2066, p=0.65, R^2=0.006, n=36) or Sandstone sediments F(34)=2.824, p=0.102, R^2=0.077, n=36.

Figure S3

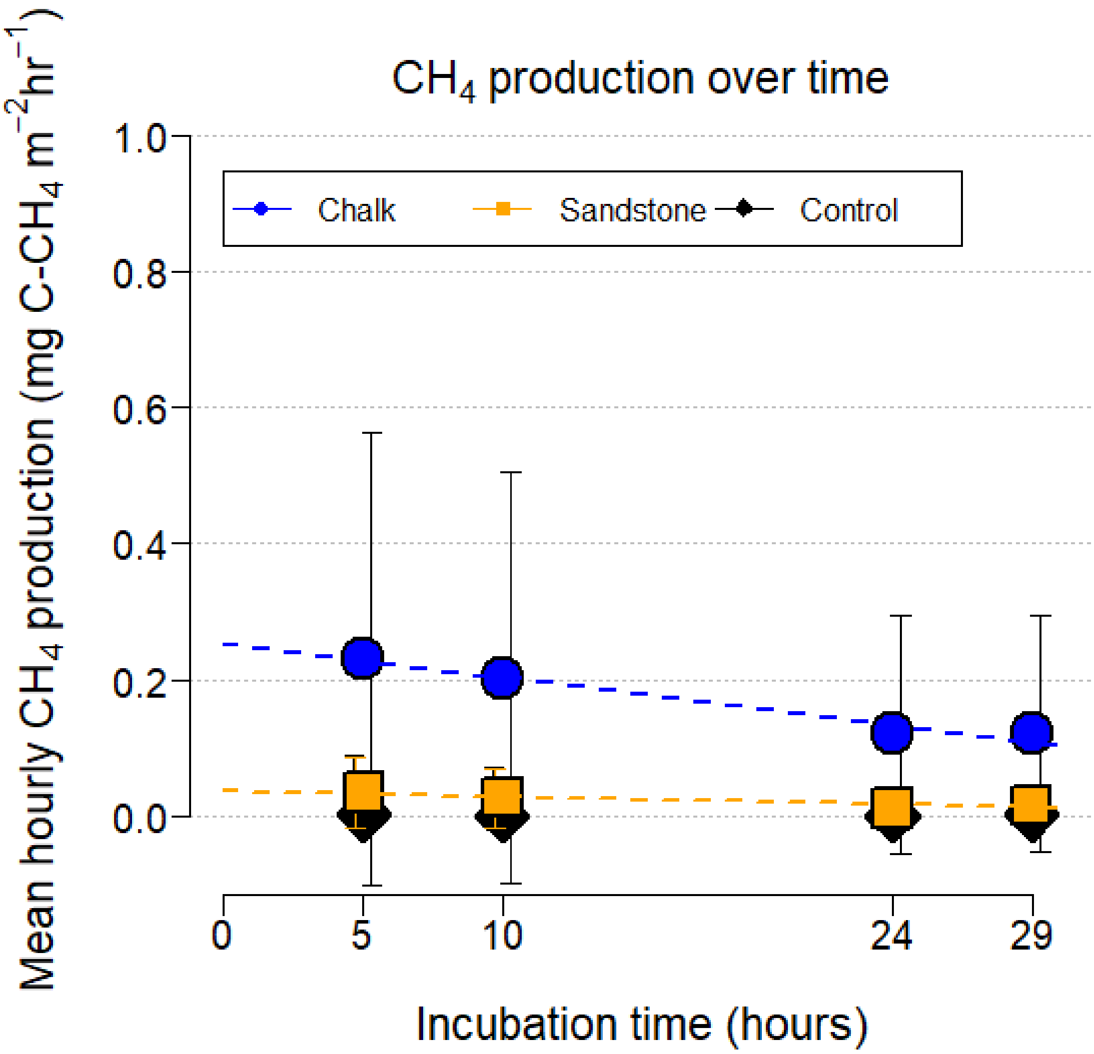

Figure S3. Change of mean hourly CH_4 production over the duration of the experiment. Hourly means are calculated as means over time T_x-$T_{previous}$ (e.g. T_{24} is the mean between T_{10} and T_{24}), where for each point *n=3*. The plotted trendlines represent fitted simple linear regression models, which were not found to be significant for either Chalk (F(34)=1.365, p=0.25, R^2=0.039, n=36) or Sandstone sediments F(34)=1.833, p=0.185, R^2=0.051, n=36.

Text S1

This is a detailed step-by-step walkthrough of our experimental procedure. During the experiment, the following steps were undertaken at T = 0, 5, 10, 24 and 29 hours after the microcosms were prepared as described above.

- Take microcosm out of the incubator
- Take two 15 ml headspace gas samples through septum and store in Exetainer, and then open lid (this step is skipped before the addition of raz). This sample will represent the final GHG concentration of this incubation time step
- Open jar and take a 15 ml water sample, filter and measure on fluorometer
- The first timestep only, follow these steps:
- Take 15 ml water sample from water column and store for calibrations
- Add 10 ml of raz stock solution and gently stir the water column, trying to minimise turbidity to bring raz to the target concentration
- Place sample from fluorometer back into microcosm using syringe
- Periodically check pH of water column
- Replace headspace air with ambient air by pushing in ambient air using a 100 ml syringe and repeat 5 times
- Close jar and take two 15 ml headspace samples again. This sample will represent starting headspace GHG concentration for this incubation time step
- Return microcosm back to the incubator

Table S1

Table S1. Sampling location characteristics from the River Tern and the River Lambourn.

River	Location	Dominating geology	Average discharge#	Stream order	Catchment size#
Lambourn	Berkshire, UK, 52°51'20.5" N 2°32'44.7" W	Chalk[1]	1.03 $m^3 s^{-1}$	2	234 km^2
Tern	Shropshire, UK, 51°26'41.7" N 1°22'59.1" W	Permotriassic Sandstone[1]	0.856 $m^3 s^{-1}$	2	192 km^2

#Averages over 1962 – 2015, measured at Eaton upon Tern and Newbury, obtained from the National River Flow Archive[2]

Table S2

Tabel S2. Accuracy, precision and limit of detection for fluorometers used. All concentrations are in ng l^{-1}.

(ng L^{-1})	Accuracy	Precision	Limit of detection[3]	Standard concentration
raz	0.06	0.19	1	108.67
rru	0.08	0.43	1	95.33

Table S3

Table S3. Limits of detection, precision and accuracy for GHG measurements on Agilent 7890A gas chromatograph, based on standards with listed concentration. All units in parts-per-million (ppm).

(ppm)	Accuracy	Precision	Limit of detection	Standard concentration
CO_2	13.4	14.8	8.2	1051
CH_4	0.07	0.11	0.15	9.8

Table S4

Table S4. Results from comparing hourly microbial metabolic activity (rru production) between the different sediment groups by statistical tests. Values are P-values from the corresponding tests. Whole groups are also compared, indicated with ‘all’. For groups CH, CM, CL, SH, SM, SL and Control, n=12 and, depending on group normality, T-test or Mann-Whitney U test was used. For Chalk (all) and Sandst. (all), n=36 and, depending on group normality, T-test or Kruskall-Wallis test was used. T or U values are in brackets.

	CM	*CL*	*SH*	*SM*	*SL*	*Control*	*Sandst. (all)*
CH	*0.002 (U=123)*	*7.63E-05 (U=141)*	*0.078 (U=103)*	*0.0002 (U=136)*	*3.60E-05 (U=144)*	*1.03E-05 (U=144)*	
CM		*0.099 (T=1.761)*	*0.22 (U=50)*	*0.11 (T=1.688)*	*0.013 (T=2.851)*	*1.03E-05 (U=144)*	
CL			*0.01 (U=27)*	*0.73 (T=0.358)*	*0.06 (T=1.963)*	*0.000125 (U=132)*	
SH				*0.012 (U=116)*	*0.0009 (U=130)*	*1.03E-05 (U=126)*	
SM					*0.46 (T=0.756)*	*0.005874 (U=144)*	
SL						*0.0004 (U=114)*	
Chalk (all)						*8.73E-07* (χ^2*=24.189)*	*0.012* (χ^2*=6.316)*
Sandst. (all)						*3.96E-05* (χ^2*=16.888)*	

Table S5

Table S5. Results from comparing hourly CO_2 between the different sediment groups by statistical tests. Values are P-values from the corresponding tests. Whole groups are also compared, indicated with 'all'. For groups CH, CM, CL, SH, SM, SL and Control, n=12 and, depending on group normality, T-test or Mann-Whitney U test was used. For Chalk (all) and Sandst. (all), n=36 and, depending on group normality, T-test or Kruskall-Wallis test was used. T or U values are in brackets.

	CM	*CL*	*SH*	*SM*	*SL*	*Control*	*Sandst. (all)*
CH	6.7E-06 *(T=6.391)*	2.3E-07 *(T=10.749)*	0.009 *(T=2.881)*	2.1E-06 *(T=8.274)*	1.4E-06 *(T=9.031)*	7.4E-07 *(U=0.000)*	
CM		2.7E-05 *(T=6.352)*	0.0006 *(T=4.063)*	0.053 *(T=2.091)*	0.006 *(T=3.295)*	0.0002 *(U=0.000)*	
CL			4.5E-07 *(T=9.762)*	2.5E-07 *(T=7.877)*	1.6E-07 *(T=7.524)*	0.017 *(U=0.000)*	
SH				1.9E-05 *(T=6.410)*	7.4E-06 *(T=7.440)*	7.4E-07 *(U=0.000)*	
SM					0.054 *(T=2.055)*	7.4E-07 *(U=0.000)*	
SL						7.4E-07 *(U=0.000)*	
Chalk (all)						3.8E-05 (χ^2=16.967)	0.86 (χ^2=0.032)
Sandst. (all)						2.7E-07 (χ^2=26.449)	

Table S6

Table S6. Results from comparing hourly CH_4 production between the different sediment groups by statistical tests. Values are P-values from the corresponding tests. Whole groups are also compared, indicated with 'all'. For groups CH, CM, CL, SH, SM, SL and Control, n=12 and, depending on group normality, T-test or Mann-Whitney U test was used. For Chalk (all) and Sandst. (all), n=36 and, depending on group normality, T-test or Kruskall-Wallis test was used. T or U values are in brackets.

	CM	*CL*	*SH*	*SM*	*SL*	*Control*	*Sandst. (all)*
CH	7.4E-07 *(U=144)*	5.9E-06 *(T=8.091)*	1.8E-05 *(T=6.921)*	3.6E-05 *(U=144)*	5.8E-06 *(T=8.099)*	5.8E-06 *(T=8.102)*	
CM		0.0001 *(U=133)*	0.003 *(U=22)*	0.0005 *(U=133)*	0.0006 *(U=132)*	0.0001 *(U=134)*	
CL			0.0001 *(T=5.859)*	0.285 *(U=91)*	0.207 *(T=1.310)*	0.113 *(T=1.656)*	
SH				3.6E-05 *(U=144)*	0.0001 *(T=5.904)*	9.9E-05 *(T=5.919)*	
SM					0.773 *(U=77.5)*	0.885 *(U=75)*	
SL						0.573 *(T=0.573)*	
Chalk (all)						9.4E-05 (χ^2=15.247)	0.004 (χ^2=8.119)
Sandst. (all)						0.051 (χ^2=3.812)	

References

(1) Wheater, H. S.; Peach, D. Developing Interdisciplinary Science for Integrated Catchment Management: The UK Lowland Catchment Research (LOCAR) Programme. *Int. J. Water Resour. Dev.* **2004**, *20* (3), 369–385.

(2) NRFA. National River Flow Archive; UK Daily Flow Data http://nrfa.ceh.ac.uk/data/search (accessed Oct 24, 2016).

(3) Lemke, D.; Schnegg, P.-A.; Schwientek, M.; Osenbrück, K.; Cirpka, O. a. On-Line Fluorometry of Multiple Reactive and Conservative Tracers in Streams. *Environ. Earth Sci.* **2013**, *69* (2), 349–358.