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Temperature dependence of methane emissions: consistent scaling from methanogenesis to ecosystem-level fluxes

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Methane (CH_4) is an important greenhouse gas because it has 25 times the global warming potential of carbon dioxide (CO_2) by mass over a century[1]. Recent calculations suggest that atmospheric CH_4 emissions have been responsible for approximately 20% of planet's warming since pre-industrial times[2]. Understanding how CH_4 emissions from ecosystems will respond to expected increases in global temperature is therefore fundamental for predicting the magnitude of feedbacks between the carbon cycle and climate change. Methanogenesis is the terminal step in the remineralisation of organic matter and is carried out by strictly anaerobic Archaea[3]. Like most other enzymatically mediated forms of metabolism, methanogenesis is temperature dependent[4,5]. However, it is not yet known how this physiological response combines with other biotic – e.g. methanotrophy[6], substrate supply[3,7], microbial community composition[8] – and abiotic – e.g. water-table depth[9,10] – processes to determine the temperature sensitivity of ecosystem-level CH_4 emissions. Nor is it known whether CH_4 emissions at the ecosystem-level have a fundamentally different temperature dependence than other key fluxes in the carbon cycle, such as photosynthesis and respiration. Here we use meta-analyses to show that seasonal variations in CH_4 emissions from a wide range of ecosystems exhibit an average temperature dependence similar to that of CH_4 production derived from pure cultures of methanogens and anaerobic sediment slurries. This average temperature dependence (0.98 electron volts (eV)), which corresponds to a 61-fold increase between 0 – 30°C, is considerably higher than previously observed for respiration (approximately 0.65 eV)[11] and photosynthesis (approximately 0.3 eV)[12]. As a result, we show that both the emission of CH_4 and the ratio of CH_4:CO_2 emissions increase markedly with seasonal increases in temperature.

Our findings suggest that global warming may have a large impact on the relative contributions of CO_2 and CH_4 to total greenhouse gas emissions from continental aquatic ecosystems, terrestrial wetlands and rice paddies.

Biogenic methane (CH_4) fluxes are a major component of global CH_4 emissions, yet they are poorly constrained[2,13,14]. There are large uncertainties not only in the current magnitude of these fluxes, but also in the factors that regulate them[2,13]. In particular, there is substantial uncertainty in the parameterisation of the temperature dependence of natural CH_4 emissions in process-based biogeochemistry models[15-18], which greatly hinders our ability to predict the response of this key component of the carbon cycle to global warming. For example, temperature sensitivities for ecosystem-level CH_4 emissions have reported apparent activation energies that range from 0.2 to 2.5 eV[6,19-21] (1 eV = 96 kJ mol^{-1}).

In a bid to reduce this uncertainty, which is fundamental to improving projections of future carbon cycle-climate change feedbacks[15-18], we quantified variation in the temperature dependence of CH_4 fluxes for three different types of experiments – i.e. methanogenic cultures, anaerobic sediment slurries, and seasonal field surveys of CH_4 emissions – that correspond to three distinct levels of biological organisation – i.e. population, community, and ecosystem, respectively. In particular, we assess whether ecosystem-level CH_4 emissions exhibit a temperature dependence similar to that of the underlying methanogenic process, and quantify the magnitude of between site deviations from this physiological response. To do this, we first establish the magnitude and variability of the temperature dependence of key metabolic rate processes (i.e. methanogenesis, growth) for populations of methanogens in culture, as well as the temperature dependence of CH_4 production for anaerobic microbial communities in slurries. We then assess whether these temperature dependencies

differ from those observed in an ecosystem-level analysis of the seasonal temperature dependence of natural CH_4 emissions from aquatic, wetland and rice paddy ecosystems (see S1 of the Supplementary Information). Our ecosystem analysis includes both new and previously published data that together encompass 1553 paired estimates of CH_4 emission and temperature taken from 126 field sites.

To directly characterise the physiological temperature dependence of key metabolic rate processes for methanogens, we compiled data on rates of methanogenesis and growth from laboratory cultures of methanogen populations as well as rates of CH_4 production from microbial communities in anaerobic sediment slurries (see S1 of the Supplementary Information). We then separately fit the data compiled for each type of experiment to a Boltzmann-Arrhenius function, which characterises the exponential relationship between metabolic rate and temperature assuming a single enzyme catalysed reaction is rate-limiting[22], using a linear mixed-effects model (see S2 of the Supplementary Information) of the form[23]

$$\ln F_i(T) = \left(\overline{E_M} + \varepsilon_{E_M,i}\right)\left(1/kT_C - 1/kT\right) + \left(\overline{\ln F(T_C)} + \varepsilon_{F,i}\right) \quad (1)$$

where $\ln F_i(T)$ is the natural logarithm of the measured rate of CH_4 production or growth rate at absolute temperature, T (K), for some arbitrary experimental unit, i. In this expression, each experimental unit, i, corresponds to a distinct strain of methanogen (culture analysis) or sediment community (slurry analysis) that has been subjected to a range of temperatures. The parameter $\overline{E_M}$ (in eV; 1 eV = 96 kJ mol^{-1}) corresponds to an average among experimental units for the apparent activation energy, which characterises the temperature sensitivity of $F_i(T)$, and k is the Boltzmann constant (8.62×10^{-5} eV K^{-1}). We centred the temperature data using the mean temperature, T_C, across experimental units, so that $\overline{\ln F(T_C)}$ corresponds to an

average rate at T_C. For each analysis, we expect estimates of E_M and $\ln F(T_C)$ to vary between experimental units due, for example, to differences between cultures in cell densities, and variation between slurries in community composition. We account for these factors in our linear mixed-effects models by treating the slopes and intercepts as random variables with averages of $\overline{E_M}$ and $\overline{\ln F(T_C)}$, respectively, and deviations from these averages of $\varepsilon_{E_M,i}$ and $\varepsilon_{F,i}$ for each experimental unit, *i* (see S2 of the Supplementary Information for details of the statistical analysis).

The population-level analysis of the culture data reveal that the average apparent activation energies, $\overline{E_M}$, for the rates of methanogenesis and growth are statistically indistinguishable (likelihood ratio test; χ^2 = 0.39, d.f. = 1, P = 0.53), and therefore have a similar temperature sensitivity (Fig. 1a; $\overline{E_M}$ = 1.10 eV, 95% confidence interval: 0.93 – 1.27 eV). The community-level analysis of CH_4 production rates in anaerobic slurries yields a similar value for $\overline{E_M}$ (0.93 eV, 95% confidence interval: 0.82 – 1.03 eV), indicating that the temperature dependence of CH_4 production at the community level largely reflects the kinetics of the physiological processes generating this flux. More detailed analyses indicate that the estimates of $\overline{E_M}$ for sediment slurries obtained from three broadly defined ecosystem types (i.e. aquatic, wetlands, rice paddies; see S1 of the Supplementary Information for details of the data) are statistically indistinguishable (likelihood ratio test: χ^2 = 1.62, d.f. = 2, P = 0.44). Consistent with our expectations, E_M does vary between experimental units, *i*, as reflected by the magnitude of the standard deviation of the random effect on the slope of the Arrhenius model, $\varepsilon_{E_M,i}$, in both analyses (see Table 1).

To explore how the temperature dependence of methanogenic populations and communities, compare to that of natural ecosystem-level CH_4 emissions, we fit equation (1) – here experimental units, *i*, correspond to sites – to a database of 1553 measurements of CH_4 emission and temperature, measured seasonally for 126 field sites that span the globe and encompass three distinct ecosystem types (aquatic, wetlands, rice paddies – see S1 of the Supplementary Information for definitions). Analyses reveal that estimates of $\overline{E_M}$ are statistically indistinguishable among ecosystem types (likelihood ratio test: χ^2 = 4.97, d.f. = 2, P = 0.10), and therefore that the average temperature dependence of CH_4 emissions from diverse ecosystem types can be characterised by a common apparent activation energy ($\overline{E_M}$ = 0.98 eV; 95% confidence interval: 0.88 – 1.08; see Fig. 2). This average temperature dependence is strikingly similar to that observed for methane production in cultures and sediment slurries (Fig. 1), which is remarkable given the multitude of processes – e.g. methanotrophy[6], water-table depth[9,10], substrate supply[7], community composition[8] – that may confound the temperature dependence of CH_4 emissions over a seasonal cycle at the ecosystem-level. Our analysis is broadly consistent with the hypothesis that the seasonal temperature dependence of CH_4 emissions at the ecosystem-level largely reflects the kinetics of the methanogenic process generating this flux (see S4 for further discussion of the potential mechanisms constraining the scaling of the temperature dependence of CH_4 emissions). Importantly, the average apparent activation energy we report here for the seasonal temperature dependence of ecosystem-level CH_4 emissions ($\overline{E_M}$ = 0.98 eV) is considerably higher than that reported previously for CO_2 fluxes attributable to respiration (~0.65 eV)[11], which could have important implications for the effect of global warming on the balance of CH_4 and CO_2 emissions from ecosystems[24].

Given the average seasonal temperature dependencies of CH_4 emissions reported here ($\overline{E_M}$ = 0.98 eV), and that previously documented for respiration (~0.65 eV)[11], we expected the ratio of CH_4 to CO_2 emission to increase, on average, with seasonal increases temperature across a collection of sites (see S3 of the Supplementary Information). While the temperature dependence of this ratio is not expected to adhere to a Boltzmann-Arrhenius relationship, we can approximate it using an expression of the form (see S3 of the Supplementary Information for a derivation of Eq. 2)

$$\ln Q_i(T) = \left(\overline{E_{M:C}} + \varepsilon_{E_{M:C},i}\right)\left(1/kT_C - 1/kT\right) + \left(\overline{\ln Q(T_C)} + \varepsilon_{Q,i}\right) \quad (2)$$

where $Q_i(T)$ is the ratio of CH_4 to CO_2 emissions for site *i* at temperature *T*, $\overline{E_{M:C}}$ and $\overline{\ln Q(T_C)}$ are averages across sites for the temperature dependence of this ratio and the magnitude of the ratio at temperature T_C, and $\varepsilon_{E_{M:C},i}$ and $\varepsilon_{Q,i}$ are random-effects terms used to represent site-level deviations from these respective averages.

To test this prediction, we analyse ecosystem-level data for the subset of studies in our compilation that report simultaneous measurements of ecosystem-level fluxes of CH_4 and CO_2, enabling us to calculate the efflux ratio of these greenhouse gases in response to seasonal variation in temperature. This dataset comprises 177 estimates from 38 field sites. In exactly the same way as for the analyses of CH_4 emissions, we fit a linear mixed effects model using the Boltzmann-Arrhenius function to the natural logarithm of the CH_4:CO_2 flux data (see Eq. 2). As predicted, this ratio increases with increasing temperature for the majority of the field sites (35 of 38), yielding average temperature dependence across sites of $\overline{E_{M:C}}$ = 0.71 eV (95% confidence interval: 0.46 – 0.97; see Fig. 3). This finding suggests that, on average, the relative contribution of methane to total greenhouse gas emissions from aquatic

ecosystems increases with seasonal increases in temperature due to the differences in the biochemical kinetics of methanogenesis, respiration and photosynthesis.

Our analyses demonstrate that the average apparent activation energy of CH_4 emissions across a wide range of ecosystems scales consistently with that of populations of methanogens in culture, and laboratory incubations of microbial communities. Moreover, this temperature dependence is much higher than that of both respiration[11] and photosynthesis[12], resulting in a greater relative contribution of CH_4 to total C emissions from aquatic ecosystems at higher temperatures. While this scaling of the temperature dependence of CH_4 fluxes across levels of biological organisation is remarkable, our results also emphasise that temperature is not the only variable that controls CH_4 emissions. Indeed, the substantial site-to-site variation we report for the temperature dependence of ecosystem-level CH_4 emissions (characterized by $\varepsilon_{E_M,i}$ in our mixed-effects model; see also Fig. 2b & Table 1), highlights the importance of other variables in driving deviations from the underlying physiological response. It is also important to note, that the average within-site apparent activation energy we report here for CH_4 emissions ($\overline{E_M}$ = 0.98 eV) does not hold for the temperature response derived from geographic variation in average CH_4 emissions and temperature across sites. For example, average site temperature is a poor predictor of spatial variation in average emissions for each ecosystem type (see Extended Data Figures 1 & 2), suggesting that other biotic – e.g. methanotrophy[6], substrate supply[3,7], microbial community composition[8] – and abiotic – e.g. water-table depth[9,10] – variables, besides temperature, may be more important for driving differences in total CH_4 emissions among ecosystems.

Overall, our findings provide a robust basis for refining parameterisation of the temperature sensitivity of CH_4 fluxes in global coupled climate-carbon cycle

models, a factor that until now yielded significant uncertainty in these models[15]. Furthermore, the observation of a general increase in the CH_4:CO_2 ratio with increasing temperature, driven by the high temperature sensitivity of CH_4 production, has important implications for the magnitude of future positive feedbacks between global warming and the carbon cycle given the relative potency of CH_4 compared to CO_2 as a greenhouse gas[2,13]. In fact, a recent sensitivity analysis of the temperature dependence of CH_4 production in CLM4Me[16], a process-based wetland biogeochemistry model embedded within the land surface component of an Earth system model, demonstrates that a Q_{10} value of 4, equivalent to the activation energies we identify ($\overline{E_M} \approx 1.0$ eV), would result in an 50% increase in high latitude CH_4 emissions over the 21st Century, relative to the model's baseline Q_{10} of 2 at 20°C ($\overline{E_M} \approx 0.5$ eV). Our analyses give strong evidence to support temperature sensitivities for methanogenesis and CH_4 emissions that are substantially higher than other key fluxes in the carbon cycle, like heterotrophic respiration and photosynthesis, and suggest that current predictions of carbon cycle-climate change feedbacks[25], which fail to account for these differences, may be significantly underestimated.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

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Author contributions. GY-D, DB & CG had initial discussions. GY-D conceived the study, analysed the data, and wrote the first draft of the manuscript. DB, PdG, CG, NT-D, RC & AS contributed original data. APA wrote the theory for the CH_4:CO_2 temperature dependence. All authors contributed to revisions of the manuscript.

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Tables

Table 1| Estimates of the parameters used to characterise the temperature dependence of CH_4 flux or the CH_4: CO_2 efflux ratio. The standard deviations (s.d.) of site or experimental unit-specific estimates for $\varepsilon_{E_M,i}$ (equation 1) were significantly > 0 for each of the analyses ($P < 0.05$), indicating differences among sites or experimental units in apparent activation energies. The standard deviations of site or experimental unit-specific estimates for $\varepsilon_{F,i}$ (equation 1) were significantly >0 in all analyses ($P < 0.001$), indicating differences among sites or experimental units in CH_4 flux or the CO_2:CH_4 efflux ratio at the average temperature.

Flux Type	$\overline{E_M}$ **(95% CI)**	**s.d.** $\varepsilon_{E_M,i}$	**s.d.** $\varepsilon_{F,i}$
Laboratory Studies			
Pure culture methanogens	1.10 (0.93 – 1.27)	0.42	2.28
Slurries CH_4 production	0.93 (0.82 – 1.03)	0.32	2.45
Whole Ecosystem CH_4 Efflux	0.98 (0.88 – 1.08)	0.36	2.16
CO_2:CH_4 ratio	0.71 (0.46 – 0.97)	0.59	1.03

Figures

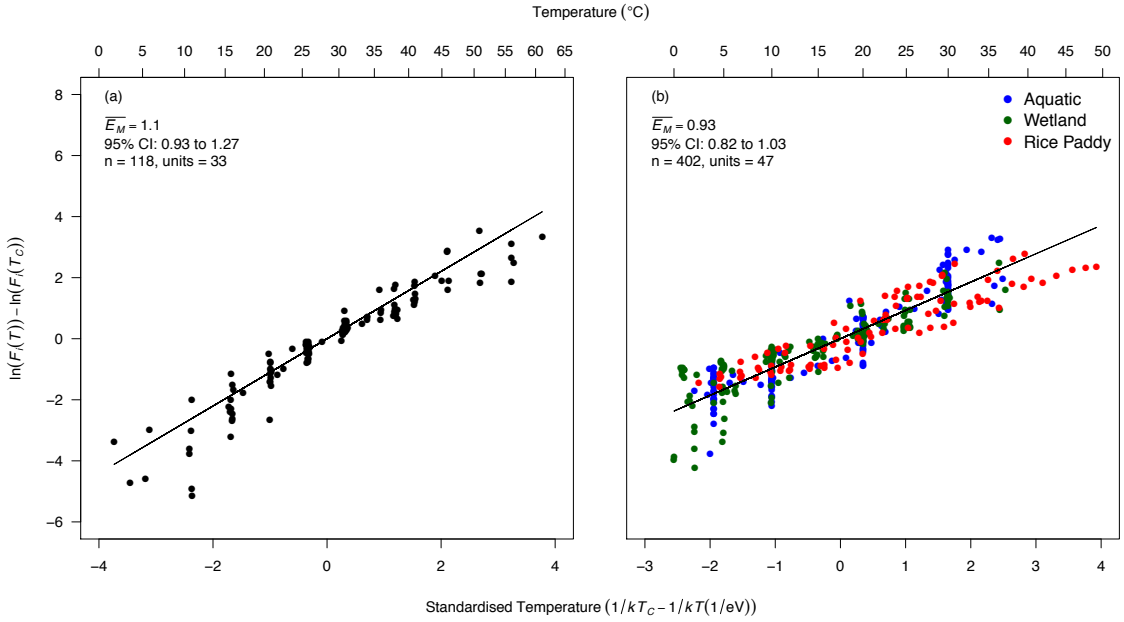

Figure 1| The temperature dependence of CH_4 production. Analyses fitting the Boltzmann-Arrhenius function to rate data, reveal similar temperature dependencies for (a) pure cultures of methanogens, and (b) slurries of aquatic (red), wetland (green) and rice-paddy (red) sediment samples incubated at different constant temperatures in the laboratory. In (b), the temperature dependence of CH_4 production is not significantly different among ecosystem types (see main text for details of statistics). In all plots, data have been standardised by subtracting from each measurement the estimated experiment-specific deviation from the average intercept predicted by the mixed-effects model. This standardisation was used for visualisation of the data only; raw values were used in the statistical analyses.

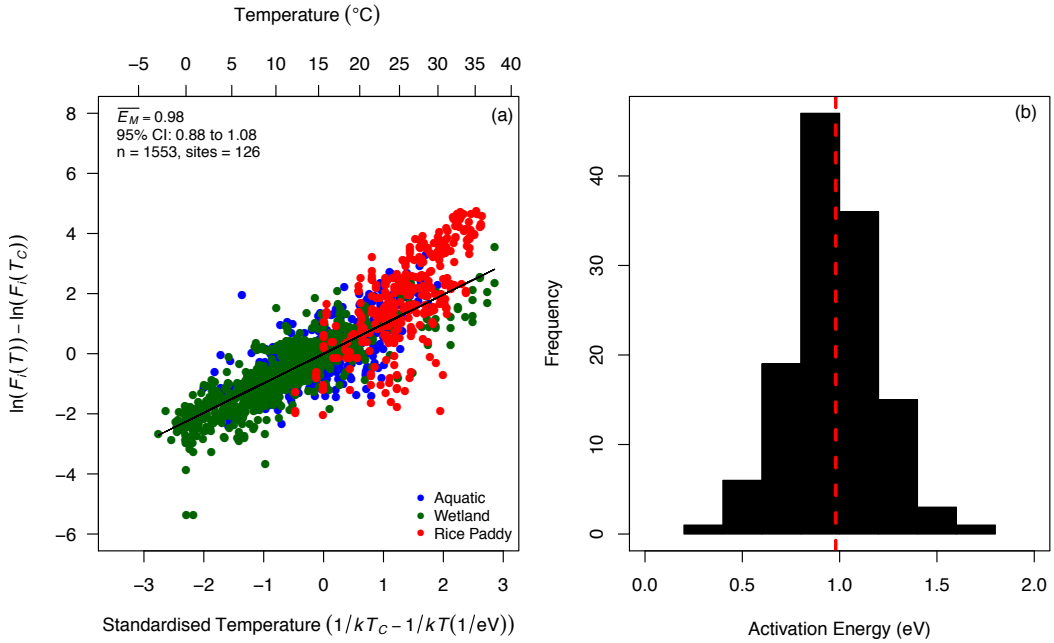

Figure 2| The temperature dependence of CH_4 emissions at the ecosystem scale. Analysis reveals a consistent temperature dependence for the emission of CH_4 from aquatic (red), wetland (green) and rice-paddy (red) ecosystems (a). Histogram of the site-level activation energies is also given (b), note that the majority of estimated apparent activation energies are very close to the average value derived from experiments using pure cultures and anaerobic sediment communities (see Fig. 1). The red dashed line in (b) corresponds to $\overline{E_M}$ = 0.98 eV, estimated from the mixed effects model. In the Arrhenius plot, data have been standardised by subtracting from each measurement the estimated site-specific deviation from the average intercept predicted by the mixed-effects model. This standardisation was for visualisation of the data only; raw values were used in the statistical analyses.

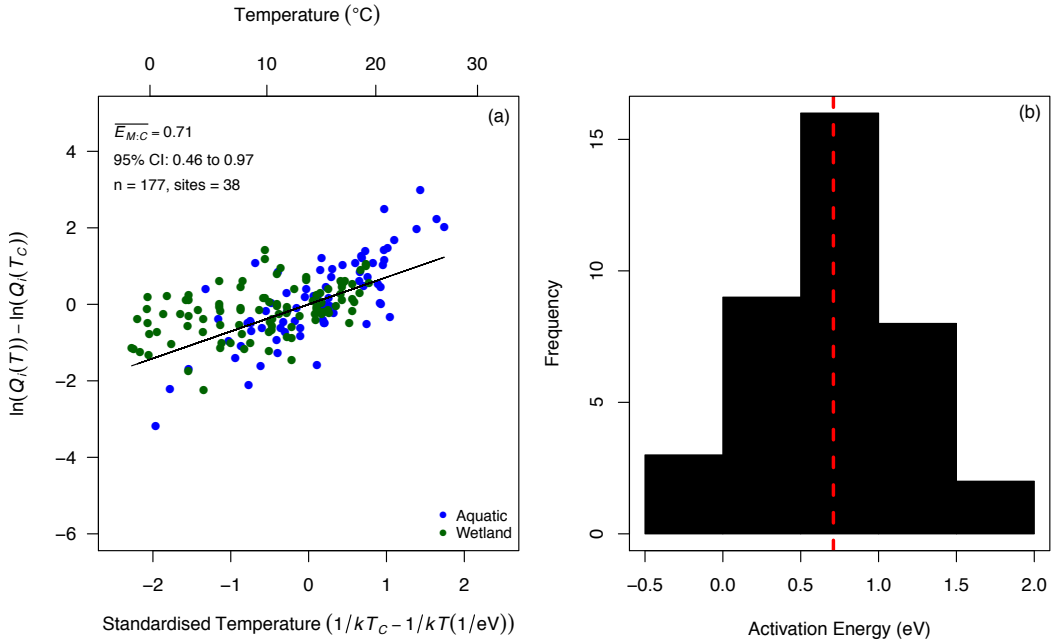

Figure 3| The temperature dependence of the CH_4:CO_2 emission ratio. Analyses reveal a high temperature dependence in the CH_4 to CO_2 emission ratio (a). A histogram of the site-level apparent activation energies is also given (b). The red dashed line in (b) corresponds to $\overline{E_{M:C}}$ = 0.71 eV, estimated from the mixed effects model. As with Figs. 1 & 2, data for the Arrhenius plot have been standardised by subtracting from each measurement the estimated site-specific deviation from the average intercept predicted by the mixed-effects model. This standardisation was for visualisation of the data only; raw values were used in the statistical analyses.