

## S1. DERIVATION OF EQUATION 2: TEMPERATURE DEPENDENCE OF CH<sub>4</sub>:CO<sub>2</sub>.

Net CO<sub>2</sub> flux from the surface water at temperature  $T$ ,  $\Delta C(T)$ , is equal to the differences between ecosystem respiration,  $R(T)$ , and gross primary production,  $P(T)$ ,

$$\Delta C(T) = R(T) - P(T) = R(T_C)e^{E_R\left(\frac{1}{kT_C} - \frac{1}{kT}\right)} - P(T_C)e^{E_P\left(\frac{1}{kT_C} - \frac{1}{kT}\right)} \quad (\text{S1})$$

where  $E_R$  and  $E_P$  are the apparent activation energies for respiration ( $\sim 0.65$  eV)<sup>1</sup> and photosynthesis ( $\sim 0.30$  eV)<sup>2</sup>, and  $T_C$  is a fixed, arbitrary temperature centered within the temperature range. Assuming that  $T_C = 15^\circ\text{C}$ , Eq. (S1) demonstrates that if  $R(T_C) \geq 2.2P(T_C)$ , net CO<sub>2</sub> flux is expected to be positive for all temperatures  $> 0^\circ\text{C}$ , and to increase with increasing temperature, due to the greater temperature sensitivity of respiration than photosynthesis.

The form of Eq. (S1) implies that net CO<sub>2</sub> flux is not expected to follow the Boltzmann-Arrhenius equation, meaning that the relationship between  $\ln\Delta C(T)$  and  $1/kT_C - 1/kT$  is non-linear. Nevertheless, we can approximate the apparent activation energy,  $E_{\Delta C}$ , in the vicinity of  $T_C$ , as

$$E_{\Delta C} \equiv \left. \frac{d\ln\Delta C(T)}{d(1/kT)} \right|_{T=T_C} = \frac{E_R R(T_C) - E_P P(T_C)}{R(T_C) - P(T_C)} \quad (\text{S2})$$

and thus derive a Boltzmann-Arrhenius approximation for the temperature dependence of net CO<sub>2</sub> flux

$$\Delta C(T) \approx (R(T_C) - P(T_C))e^{E_{\Delta C}\left(\frac{1}{kT_C} - \frac{1}{kT}\right)} \quad (\text{S3})$$

This approximation becomes more accurate as the relative magnitude of  $R(T_C)$  increases. For example, if  $R(T_C) = 2.5P(T_C)$ , the correlation between the arithmetic estimates obtained using Eq. (S1) and its approximation (Eq. S2 with  $T_C = 288$  K) is  $r^2 = 0.997$  over the temperature range  $5\text{--}25^\circ\text{C}$ , whereas if  $R(T_C) = 4P(T_C)$ , this

correlation increases to  $r^2 = 0.999$ . These high correlations indicate that the predicted temperature dependence of net CO<sub>2</sub> flux can be reasonably approximated by the Boltzmann-Arrhenius relationship. Importantly, however, this approximation breaks down if  $P(T_C)$  is of similar or greater magnitude than  $R(T_C)$ , in which case net CO<sub>2</sub> flux can be negative, particularly at lower temperatures. Our use of the approximation in Eq. (S3) is supported by the observation that net CO<sub>2</sub> flux was never observed to be negative for the ecosystems included in our analysis.

Given that the temperature dependence of net CO<sub>2</sub> flux can be approximated by the Boltzmann-Arrhenius relationship (following Eq. S3), and that results in the main text (Fig. 2) demonstrate that the temperature dependence of methane flux is well characterized by the expression

$$F(T) = F(T_C) e^{E_M \left( \frac{1}{kT_C} - \frac{1}{kT} \right)} \quad (\text{S4})$$

the ratio of methane emissions to net CO<sub>2</sub> emissions can also be approximated by a Boltzmann-Arrhenius-type expression of the form

$$Q(T) \equiv F(T)/\Delta C(T) \approx (F(T_C)/(R(T_C) - P(T_C))) e^{E_{M:C} \left( \frac{1}{kT_C} - \frac{1}{kT} \right)} \quad (\text{S5})$$

where  $E_{M:C} \approx E_M - E_{\Delta C}$ , and  $Q(T_C) \approx (F(T_C)/(R(T_C) - P(T_C)))$ . Equation (S5) provides justification for Eq. (2) in the text. It also demonstrates that this ratio is expected to increase with temperature whenever  $E_{\Delta C} < E_M \approx 1$  eV, as is predicted if  $R(T_C) > 2P(T_C)$  (following Eq. S2). For example, if  $R(T_C) = 3P(T_C)$  and  $T_C = 293$  K,  $E_{\Delta C} = 0.825$  eV. This derivation also demonstrates, however, that the magnitude of this ratio, and its temperature dependence, depend in detail on the relative magnitudes of the normalisations  $F(T_C)$ ,  $R(T_C)$ , and  $P(T_C)$ . Hence, site-specific differences in the balance of carbon emissions attributable to respiration, photosynthesis, and

methanogenesis are expected to influence the random effects terms for the mixed-model expression given in Eq. (2) of the text.

## **S2. MECHANISMS CONSTRAINING THE TEMPERATURE DEPENDENCE OF CH<sub>4</sub> EMISSIONS**

Our analyses demonstrate that the average temperature dependencies of CH<sub>4</sub> emissions from laboratory-incubated anaerobic communities and entire ecosystems are similar to each other and to the temperature dependencies of methanogenesis and growth rate for cultures of methanogens. This result is surprising given the complexity of the microbial metabolic pathways involved in organic matter breakdown, as well as the physical and chemical processes that influence the ultimate emission of CH<sub>4</sub> from ecosystems. We propose two hypotheses that could explain this phenomenon.

*(i) The catabolism of methanogenic Archaea generally limits CH<sub>4</sub> production, and thereby constrains the temperature dependence observed in the field studies and the experiments on anaerobic sediment communities included in this data synthesis.*

This hypothesis assumes that the preceding steps in organic carbon mineralisation (e.g. hydrolysis, fermentation, acetogenesis) are not rate limiting. For field-scale emissions, it predicts that the products of microbial fermentation (e.g. acetate, formate, hydrogen) should be detectable in natural habitats. And it implies that, over the time scales of the seasonal field surveys and the slurry experiments, methanogenesis and the upstream metabolisms that generate the methanogenic precursors – e.g. acetogenesis, fermentation – exhibit non-steady state dynamics.

*(ii) The upstream metabolic processes, like acetogenesis, hydrolysis and fermentation, that supply the dominant methanogenic precursors, have temperature*

*dependencies comparable to that of methanogenesis.* If the temperature dependencies of metabolic processes upstream are similar to that of methanogenesis, then consistent scaling of the temperature response will still be expressed irrespective of a steady-state between fermentation and methanogenesis.

There is some empirical evidence in support of the first hypothesis. For example, Shannon & White<sup>3</sup> and Duddleston *et al.*<sup>4</sup> document strong seasonal accumulation of acetate during colder periods of the year, followed by drawdown of acetate concentrations during the summer due to acetoclastic methanogenesis in natural wetland ecosystems. These data indicate a pronounced seasonal asymmetry in the accumulation of fermentation products and subsequent mineralisation to CH<sub>4</sub>, which is indicative of non-steady state dynamics between these metabolic processes. In such cases it is highly likely that, when derived over an annual cycle, the temperature dependence of CH<sub>4</sub> emissions would not be constrained by that of the upstream metabolic processes, provided that there is strong temporal asynchrony between substrate supply through fermentation and consumption by acetoclastic methanogenesis. In support of this perspective, von Fisher & Hedin<sup>5</sup> have recently demonstrated, using a novel isotope pool dilution technique, that carbon substrate supply rates do not tend to regulate CH<sub>4</sub> formation rates.

On the other hand, others<sup>6,7</sup> have shown that acetate rarely accumulates in some less productive systems, where organic carbon input to the sediment is limiting, but rather turns over rapidly due to uptake by acetoclastic methanogens and sulphate reducers. In these systems, one could argue that steady state dynamics between fermentation and methanogenesis may exist and upstream metabolisms will constrain the temperature dependence of CH<sub>4</sub> emissions.

These two sets of studies highlight that a generalisation of the relative steady state between fermentation and methanogenesis is unlikely to apply across ecosystems. Furthermore, none of the studies included in our meta-analysis, in which seasonal dynamics of *in-situ* temperature and CH<sub>4</sub> emission are given, supply additional data on the seasonal dynamics of acetate (or other fermentation products). Thus, given the field data currently available, it is not yet possible to explicitly assess the extent to which these processes influence CH<sub>4</sub> emissions in ecosystems, and their temperature dependence.

With respect to our second hypothesis – i.e. that upstream metabolisms and methanogens have coevolved comparable temperature dependencies – recent work by Finke & Jorgensen<sup>8</sup> demonstrate that acetate production and sulphate reduction are tightly coupled in sediment cores from temperate and Arctic marine sediments. They demonstrate that both of these fluxes exhibit seemingly identical temperature response curves, and that given consistently low concentrations of H<sub>2</sub> below the thermal optima for the sulphate reducing community, terminal oxidizers exhibit high levels of substrate limitation from fermentation. Therefore, despite a steady state between sulphate reduction and fermentation, terminal oxidation of organic carbon remained highly temperature dependent.

Disentangling the mechanisms that constrain the temperature dependence of CH<sub>4</sub> emission is clearly a significant challenge. However, our analyses demonstrate that for the majority of the 127 sites, which span wetlands, rice paddies and aquatic systems, the temperature dependence of CH<sub>4</sub> emissions closely matches that of the underlying methanogenic process. Irrespective of the underlying mechanisms involved, this finding is significant, with consequences spanning climate change-carbon cycle feedbacks, and aquatic biogeochemistry.

## References

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