

Controls on soil methane fluxes: Tests of biophysical mechanisms using stable isotope tracers

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[1] Understanding factors that control methane exchange between soils and the atmosphere remains one of the highest priorities for climate change research. Here we use a novel isotope-based technique to investigate the relative importance of three mechanisms for explaining landscape-scale variations in soil methane emissions: (1) consumption of methane by methanotrophic bacteria, (2) quantity of carbon mineralization, or (3) relative amounts of carbon flow through nonmethanogenic versus methanogenic mineralization pathways. Application of a new, nondisruptive, $^{13}\text{CH}_4$ isotope pool dilution technique permitted us to evaluate these mechanisms by distinguishing gross methane fluxes through both productive and consumptive pathways. We quantified each of these pathways in surface soils across broad moisture gradients in tropical montane environments in the Hawaiian Islands and temperate ecosystems in the northeastern United States. We found only limited support for the consumption control hypothesis because consumption was only important in dry soils. We also failed to find support for the carbon supply hypothesis, in that rates of carbon mineralization did not explain the observed variability in net fluxes across landscapes. Rather, dramatic differences in methane production, and thus emission, depended on surprisingly small diversions of soil carbon flow from nonmethanogenic to methanogenic pathways: on average, soils were a net source of methane to the atmosphere if more than 0.04% of total carbon mineralization passed through methanogenic pathways. We infer that fine-scale heterogeneity of soil redox status is critical for regulating soil methane fluxes.

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1. Introduction

[2] While historic [Chappellaz *et al.*, 1993; Petit *et al.*, 1999], modern [Lelieveld *et al.*, 1998; Walter and Heimann, 2000] and future [Intergovernmental Panel on Climate Change, 2001] variations in atmospheric methane have been linked to the moisture regime of ecosystems [Chappellaz *et al.*, 1993; Petit *et al.*, 1999; Walter and Heimann, 2000], there remains considerable uncertainty about the biophysical mechanisms that control this potential feedback between climate and methane emissions from soils [e.g., Torn and Harte, 2006].

[3] A major challenge is that methane emissions have been linked empirically to a diverse and often overlapping group of soil properties that include water content, pore size distribution, organic matter quality, temperature and the presence of vascular rooting systems [Kruger *et al.*,

2002]. Underlying these complex soil properties, however, is a set of proximate biophysical factors that act to determine methane transformations at scales of local microbial environments. From this perspective, methane exchange can be viewed as resulting from the local balance of methane production and consumption, which, in turn, closely depends upon the supplies of energy (i.e., from decaying plant material) and oxygen to local environments (Figure 1).

[4] Here we seek to examine the biophysical model of Figure 1 as a function of variations in one key property of ecosystems: soil moisture. We examine the response of governing biophysical factors to gradients in soil moisture in both temperate and tropical climates. We are specifically interested in three alternative hypotheses, which have been proposed to explain variability in the exchange of methane between soils and the atmosphere.

[5] First, net methane fluxes may be controlled by local methane consumption by methanotrophic bacteria (mechanism 1 in Figure 1) if the consumptive activity of methanotrophs tracks or exceeds rates of methane production [Oremland and Culbertson, 1992; Reeburgh *et al.*, 1993; Moosavi and Crill, 1998; Frenzel and Karofeld, 2000]. Such “consumptive control” predicts that variations in gross consumption would act to limit methane emissions,

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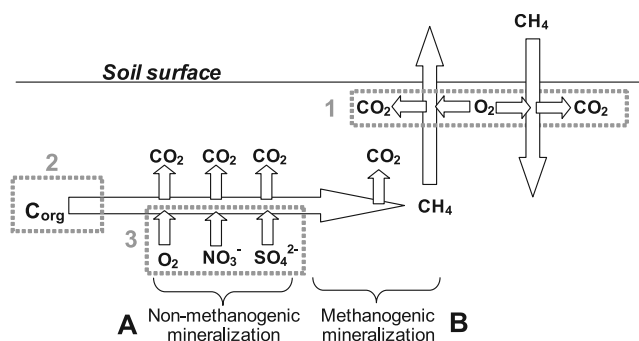


Figure 1. Conceptual model for soil methane production and consumption, and hypothesized biophysical controls of net methane flux. Large horizontal arrow illustrates that organic carbon (C_{org}) is mineralized via pathways in decreasing order of energetic yield. We refer to these respiratory pathways (small vertical arrows) collectively as nonmethanogenic mineralization (region A in diagram). Supplies of C_{org} in excess of electron acceptor supply can be mineralized through fermentative and methanogenic pathways to CO_2 and CH_4 (region B in diagram). Once methane is produced in the soil, it can either escape to the atmosphere (large upward vertical arrow) or be oxidized by methane consumption (small horizontal arrow). When rates of methane consumption are high, soils may be a net sink for atmospheric methane (downward vertical arrow at the soil surface). Root respiration, which can account for half of soil respiration, is included in this depiction as an O_2 consuming process. Gray boxes and numbers indicate hypothesized locations of biophysical control of net methane flux as described in the text: (1) consumptive control, (2) carbon supply control, and (3) methane pathway control.

yielding a negative correlation between net flux and gross consumption across soils. In dry soils, for example, *Del Grosso et al.* [2000] hypothesized that gross methane consumption can be responsible for variations in net methane flux. In wet soils, however, where high rates of methane production can occur, consumption can still be a significant factor if methanotroph communities are sufficiently active in the oxic layer that often separates the producing region from the atmosphere. Such layers have been identified on the surface of inundated soils [*Sundh et al.*, 1994] and in the rhizosphere of wetland plants [*Popp et al.*, 2000].

[6] Second, net methane flux may be limited by available energy as a function of the total supply of mineralizable carbon available to sustain microbial metabolism and methanogenesis (mechanism 2 in Figure 1). Such “carbon supply control” has been indirectly inferred from positive correlations between net methane flux and net ecosystem production (i.e., net CO_2 balance at the ecosystem scale) [*Whiting and Chanton*, 1993; *Bellisario et al.*, 1999; *Updegraff et al.*, 2001]. Because some soils have significant pools of recalcitrant organic matter, it is important to clarify that this hypothesis depends on the supply of labile carbon available to the community of decomposers, including aerobic heterotrophs, anaerobic heterotrophs, and fermenters; it is the fermentation of labile carbon that generates H_2 and acetate

used by methanogenic organisms [*Zinder*, 1993]. We expect to find support for this hypothesis if supplies of alternative electron acceptors such as nitrate and sulfate are small and do not vary across landscapes when compared to variability in carbon supply. This hypothesis predicts that both gross methane production and net flux should be positively correlated with total carbon mineralization (i.e., production of $\text{CO}_2 + \text{CH}_4$) [*Hedin et al.*, 1998].

[7] Third, net methane exchange may be controlled by the diversion of carbon flow from nonmethanogenic to methanogenic pathways (mechanism 3 in Figure 1), as occurs in anaerobic zones that form when local supplies of electron acceptors are diminished (e.g., decreased O_2 diffusion caused by soil moisture) relative to carbon supply. This methane pathway hypothesis differs from the “carbon supply” hypothesis in that methane production does not necessarily respond to the quantity of carbon mineralized, but rather by qualitative changes in the nature of carbon flow caused by local exhaustion of oxygen and other electron acceptors (e.g., nitrate, sulfate) in soil micro-environments. This hypothesis predicts a positive correlation between gross methane production and the fraction of total mineralized carbon that proceeds through methanogenic pathways.

[8] It is important to note that these biophysical responses are, in turn, sensitive to variations in more complex soil properties such as pore size distribution (which influences oxygen supply, methane diffusivity, and local soil moisture) or temperature (which influences biological rates such as carbon mineralization). While we do not seek to unravel such secondary relationships, we nevertheless aim to abstract some of the proximate mechanisms that determine the responsiveness of the soil methane systems to more complex soil properties.

2. Approach

[9] While the specific mechanisms outlined above have been appreciated for some time, evidence for their importance (or lack thereof) has relied on either speculation or indirect and sometimes causally weak correlations between methane fluxes and ecosystem or soil parameters [e.g., *Reeburgh et al.*, 1993; *Sundh et al.*, 1994; *Bellisario et al.*, 1999; *Del Grosso et al.*, 2000; *Verchot et al.*, 2000]. This lack of strong inference arises because direct evaluation of these mechanisms is only made possible by separately quantifying gross rates of methane production and consumption. We here report on a new, isotope-based method that, for the first time, allows such separation, thereby permitting us to directly examine the three competing biophysical mechanisms.

[10] Our technique depends on trace additions of ^{13}C -labeled methane [*von Fischer and Hedin*, 2002] to intact soil cores, and it permits clear and quantitative separation of gross methane transformations using short, in-field incubations. As we have previously reviewed [*von Fischer and Hedin*, 2002], this isotope-based pool dilution technique allows mechanistic understanding of methane production and consumption that is significantly expanded beyond traditional approaches (e.g., use of chemical inhibitors or alteration of the soil oxygen status) because it is not

subject to the disturbances and uncertainties that limit those methods.

[11] To provide a geographically broad evaluation of the three competing hypotheses, we sampled soil moisture gradients within both tropical and temperate biomes: two well-defined orographic moisture gradients on the Hawaiian islands of Maui and Kauai (holding temperature and geologic substrate constant within each location), and two topographic moisture gradients near Ithaca, New York, US, along uphill-to-wetland transects on similar parent material.

3. Methods

3.1. Study Sites and Soils

[12] We identified two different soil moisture gradients in natural environments of tropical (Hawaii) and temperate (New York State) biomes. Our study sites in Hawaii were distributed along orographic precipitation gradients (<1000 to >5000 mm mean annual precipitation) that extended across several kilometers of montane tropical forests on the islands of Maui [Schuur *et al.*, 2001; Houlton *et al.*, 2006] and Kauai [Giambelluca *et al.*, 1986]. Both the Maui and Kauai gradients were dominated by one of two native tree species: *Acacia koa*, which is only present in the drier two sites of each gradient, and *Meterosideros polymorpha*, which is present in all sites but dominant only in wetter environments. Soils on both gradients were derived from volcanic shield material (~500,000 years old in Maui and ~4,100,000 years old in Kauai) and displayed changes in iron redox state as indicated by increased gleying and soil carbon content with increased soil moisture. The topographic cline in New York extended approximately 500 m from a forested upland to riparian wetland. Sites were vegetated by mixed maple and oak (*Acer* spp., *Quercus* spp.) woodland on the most well-drained site, sedge (*Carex* spp.) in the intermediate moisture sites, and unvegetated stream sediment at the wet end; water was only present above the soil surface in the wettest site, though it was only a few centimeters below the soil surface on the carex-dominated site. Soils in this part of New York State are derived from shale with high clay content. We also sampled two contrasting sites in a hemlock (*Tsuga canadensis*) forest in New York State: one site on well drained and one site on permanently wet, poorly drained soils. The mineral soils in both these sites were overlain with a thick organic horizon, >8 cm in the dry site and >30 cm in the wet site.

[13] We determined gravimetric soil moisture by oven drying and percent water-filled pore space from bulk density and soil particle density. We report soil moisture levels in units of percent water-filled pore spaces (WFPS) because both theoretical and applied studies have shown WFPS to be mechanistically related and strongly correlated with soil diffusivity and thus soil gas exchange rates [Millington and Sherer, 1971].

3.2. Analytical Techniques

[14] Our measures of gross methane production and consumption are based on trace additions of $^{13}\text{CH}_4$ to soil cores and subsequent analysis of the abundance and isotopic

composition of methane in the incubation container. At each site we took four soil cores (5 cm diameter \times 12 cm depth) and began incubations within 30 min. The details of this method are described elsewhere [von Fischer and Hedin, 2002]. Briefly, sleeved soil cores were capped on the bottom and placed in 1 L canning jars. We added labeled methane to the containers, enriching the headspace methane to 2–10 atom percent ^{13}C , and incubated them in the field for 3–6 hours sampling 4 times during the incubation. Samples were taken by syringe and stored <14 days in stoppered serum vials. Gas standards were also stored in bottles and samples were corrected for any systematic changes in standards. We determined methane concentration by gas chromatography using an FID and measured carbon isotopic composition using a modified Europa ANCA TG preparation unit connected to a Europa GEO 20-20 mass spectrometer.

[15] We calculated rates of gross methane production and consumption from measures of methane concentration and isotopic composition by fitting a model to the data. The model assumed methane production had been constant during the incubation, methane consumption was first-order with respect to methane concentration, new methane produced during the incubation had an isotopic composition of -60‰ , and the instantaneous fractionation rate of methane consumption was 20‰ . We have previously shown [von Fischer and Hedin, 2002] that the model is robust to biologically plausible departures from these assumptions. The assumption of first-order dependence of methane consumption is based on (1) the stoichiometric excess of oxygen as compared to methane in environments where methanotrophs are exposed to the atmosphere, and (2) our observation that maximum methane concentrations were typically lower than the Michaelis-Menten constant (i.e., Km) for methane oxidation [von Fischer and Hedin, 2002].

[16] We specifically tested whether variation in the isotopic composition of produced methane ($\delta^{13}\text{C}$ typically -100 to -40‰) could influence our estimated rates of methane production. Such effects were small to negligible because this range in $\delta^{13}\text{C}$ is negligible when compared to our isotopic enrichment, which typically increased $\delta^{13}\text{C}$ by 3000 to 5000‰. While our experimental setup did not permit us to examine rates of deep-soil methane consumption (e.g., in the rhizosphere of wetland plants), our technique does quantify methanotrophy on the soil surfaces where significant rates of methane oxidation can occur [Sundh *et al.*, 1994].

[17] Calculated rates that were below the minimum detection limits (0.1 and 0.04 mg $\text{CH}_4\text{-C m}^{-2} \text{d}^{-1}$ for consumption and production respectively) were assigned a value of half the detection limit. This isotopic pool-dilution technique is not subject to the disturbances and uncertainties of methods that depend on metabolic inhibitors and/or alterations of physicochemical conditions. We have previously examined these data on gross rates of methane production and consumption [von Fischer and Hedin, 2002], but only to verify the quality of the isotope pool dilution approach.

[18] In roughly half of the incubations, we measured soil CO_2 production ($n = 70$ of 128) by periodically sampling air

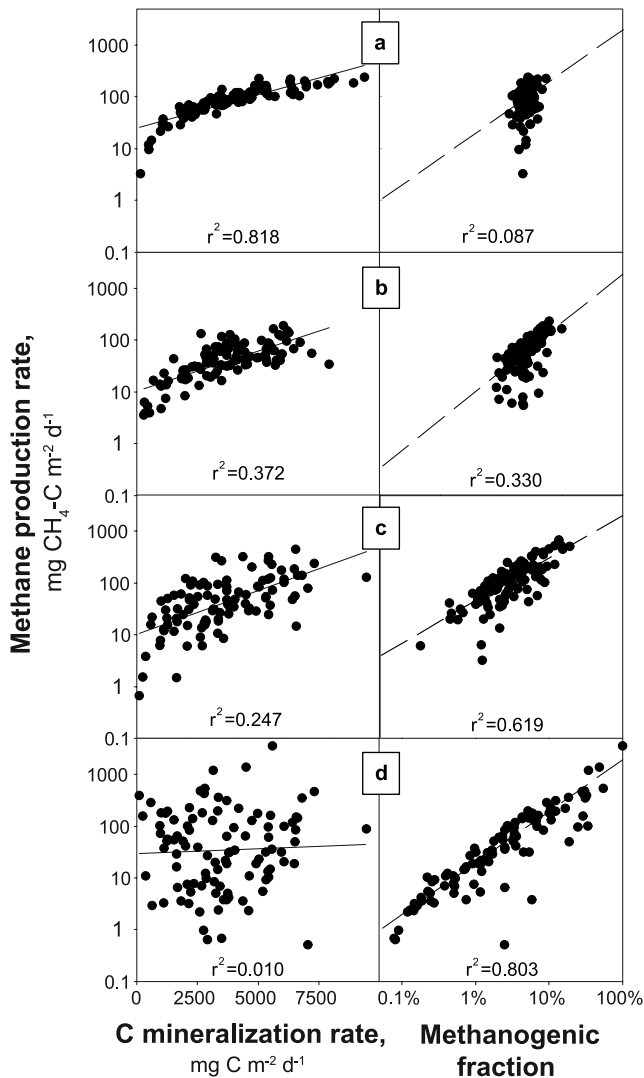


Figure 2. Results of Monte Carlo simulations to illustrate relationships among variables as predicted by the carbon supply hypothesis (i.e., low variance in the methanogenic fraction, F_{MP}) and the methane pathway hypothesis (i.e., high variance in F_{MP}). Simulations with (a) low variance, (b) medium variance, (c) high variance, and (d) very high variance in F_{MP} . Lines in the left column are linear regression fits, and r^2 values are for the regression. Lines in the right column predict variance in methane production as a function of the mean carbon supply rate and variance in F_{MP} according to equation (1); the r^2 values in these plots indicate the proportion of variance in methane production explained by the model line.

and analyzing CO₂ by gas chromatography using a methanizer and FID.

[19] We estimated the rate of soil carbon mineralization empirically as the sum of soil CO₂ and CH₄ production. Assuming steady state microbial biomass, which is reasonable given our brief field incubations, this metric reflects the carbon supplies available to soil biota [Parton *et al.*, 1994;

Del Grosso *et al.*, 2005]. Our measures of total mineralization rate include both heterotrophic and autotrophic respiration and have particular relevance for understanding methane production since most methane emitted from wetland soils is derived from recently fixed carbon [King and Reeburgh, 2002], and since both heterotrophic and autotrophic respiration deplete soil electron acceptor pools.

[20] We calculated the fraction of mineralized carbon that proceeded through methanogenic pathways (hereafter the “methanogenic fraction” or F_{MP}) for each incubation. In principle, the rate of methanogenic mineralization equals total soil C mineralization rate multiplied by the methanogenic fraction

$$(CH_4 + CO_2)_{\text{methanogenic}} = \text{Soil } C_{\text{mineralized}} \cdot F_{MP} \quad (1)$$

where CH_4 and CO_2 refer to the methane and carbon dioxide produced during methanogenic mineralization (B in Figure 1), and where “Soil C mineralized” refers to the rate of soil C mineralization through both methanogenic and nonmethanogenic pathways (A and B in Figure 1). To determine the methanogenic fraction from measures of methane and carbon dioxide production in soil samples, we rearranged equation (1) to solve for F_{MP} . Then, since methanogenic mineralization generates both methane and carbon dioxide, we used a scaling value of $(CH_4 + CO_2)_{\text{methanogenic}} = 2 \times CH_4$ based on both theoretical and empirical results [Grant, 1998]; with this scaling factor, we assume methanogenic fermentation of organic material generates half methane and half carbon dioxide. The result is

$$F_{MP} = \frac{(CH_4 + CO_2)_{\text{methanogenic}}}{\text{Soil } C_{\text{mineralized}}} = \frac{2 \cdot CH_4}{(CH_4 + CO_2)_{\text{total}}} \quad (2)$$

3.3. Hypothesis Testing

[21] To evaluate each hypothesis, we compared our observed results to patterns generated by “null” models that predict how data would be distributed when a particular mechanism is not the primary determinant of the observed variability across soils [Gotelli and Graves, 1996]. In the null model for the consumption control hypothesis (mechanism 1), we assume that methane consumption and production vary independently, so that net methane exchange is not solely controlled by consumption. Thus variation in net methane flux is generated from variance in both methane production and consumption. This null model predicts a weak, negative or absent correlation between observed methane consumption and net flux rates. We rejected the null hypothesis if we observed a significant positive correlation between methane production and methane consumption.

[22] The carbon supply hypothesis (mechanism 2) and methane pathway hypothesis (mechanism 3) reflect two end-members of control that depend on whether total carbon supply or the methanogenic fraction is more variable across the landscape. In the carbon supply hypothesis the methanogenic fraction remains relatively constant while variation in carbon supply drives methane production (which, in turn, generates the observed variations in net methane

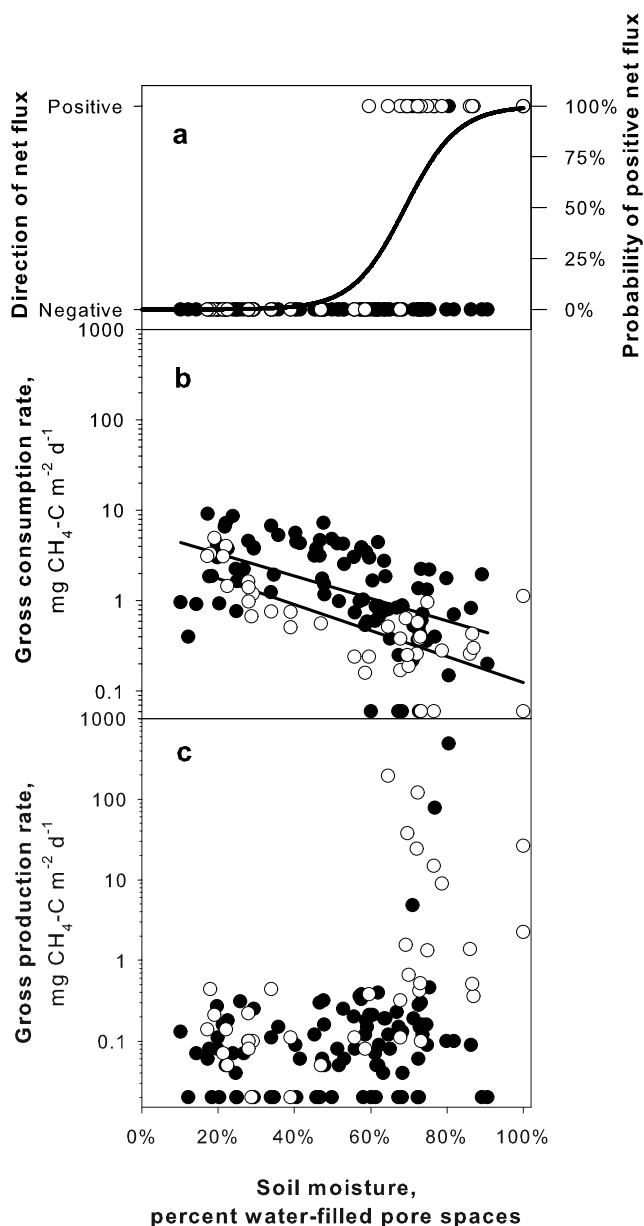


Figure 3. Responses of net methane flux, gross methane consumption, and gross production to variation in soil moisture. Solid symbols are from tropical environments, and open symbols are temperate environments. (a) Net methane flux from individual soil cores, categorized as negative (i.e., net consuming) or positive (i.e., net producing) as indicated on the left y axis. The line is a logistic regression for the probability of positive methane flux, as indicated by values on the right y axis. (b) Response of gross methane consumption to variation in soil moisture with linear regression fits. (c) Response of gross methane production to variation in soil moisture.

exchange). Our null hypothesis therefore is the absence of correlation between carbon supply and methane production.

[23] In contrast, the methane pathway hypothesis assumes that variance in methane production is primarily caused by

variations in the fraction of mineralized carbon that flows through the methanogenic pathway, while total carbon mineralization varies less. Methane production therefore should be correlated with the methanogenic fraction of carbon flow; our null model is the absence of such a correlation.

[24] To illustrate the quantitative predictions generated by these two hypotheses, we performed four Monte Carlo simulations of our data set across a range of conditions from strong carbon supply control to strong methane pathway control. For each simulation, we generated 100 soil incubations for which the total carbon supply rate was drawn randomly from a normal distribution with mean and variance equal to that observed in our data set (mean = $3.7 \text{ mg C m}^{-2} \text{ d}^{-1}$, $\text{SD} = 2.0$). We then calculated methane production in each incubation by multiplying the carbon supply by a methanogenic fraction (F_{MP}) following equation (1). This value for F_{MP} was also drawn randomly from a distribution. In our data set, we found that F_{MP} was distributed in a log-normal fashion, so we drew F_{MP} in the simulations from a log-normal distribution with the same mean as our data set (2.5%), but each of the four simulations differed in the magnitude of the variance for F_{MP} .

[25] We illustrate in Figure 2 the results of these simulations with variance in F_{MP} low ($\text{SD} \approx 0.5\%$, Figure 2a), medium ($\text{SD} \approx 1.3\%$ Figure 2b), high ($\text{SD} \approx 2.9\%$, Figure 2c) and very high ($\text{SD} \approx 9.1\%$, Figure 2d). Strong carbon supply control, characterized by small variance in F_{MP} , generates a strong correlation between methane production and carbon dioxide production, and a weak relationship between methane production and the methanogenic fraction. Conversely, strong control by the methanogenic fraction, characterized by relatively large variance in F_{MP} , leads to a weak relationship between methane production and carbon dioxide production, but instead a strong relationship between the methanogenic fraction and methane production. We examined our field data to identify which of these conditions were represented.

4. Results

[26] In all four transects we found strong increases in net methane flux with increased soil moisture. Probability analysis of data from all locations (Figure 3a) showed that positive net methane production (i.e., gross production > gross consumption) started to occur at soil moistures above 60% water filled pore space (WFPS), but that some soils above 90% WFPS still displayed net methane consumption. Although soil moisture was a moderately successful variable for predicting direction of net methane flux (logistic regression $r^2 = 0.42$; $p < 0.0001$), it was not effective for predicting magnitude of methane flux ($r^2 = 0.03$, $p > 0.12$, regression fit not shown).

[27] Underlying the variations in net methane exchange across the moisture gradients were distinct trends in gross methane transformations. Methane consumption declined (Figure 3b) with increasing soil moisture in both tropical and temperate sites ($p < 0.0001$; ANCOVA for consumption as a function of WFPS, biome and WFPS*biome),

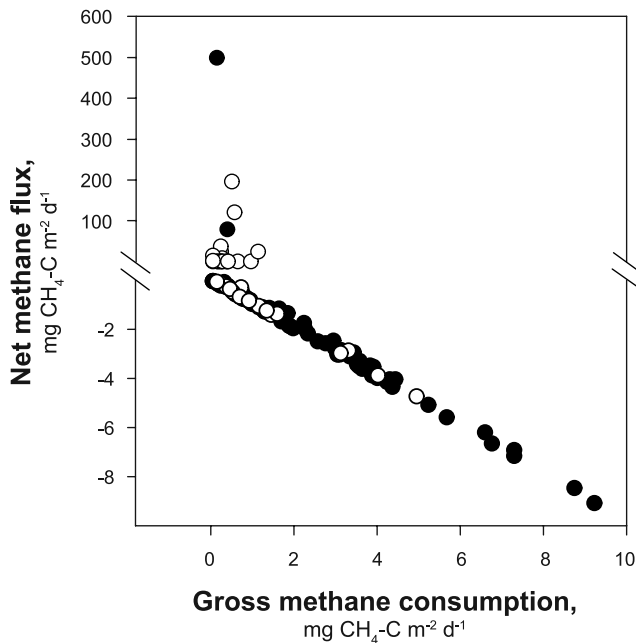


Figure 4. Correlation of net methane flux to gross methane consumption. Open symbols are from tropical environments, and solid symbols from temperate environments. Note the axis break and change in y axis intervals at the point where net flux = 0.

with average consumption rates ca. 49% lower in temperate compared to tropical sites ($p < 0.01$). Consumption rates fell within a relatively narrow range from below detection limits to $9.2 \text{ mg CH}_4\text{-C m}^{-2} \text{ d}^{-1}$ (mean = $1.7 \text{ mg CH}_4\text{-C m}^{-2} \text{ d}^{-1}$, SD = 1.9).

[28] In contrast to the monotonic declines in methane consumption, gross rates of methane production increased abruptly (Figure 3c) from a narrow range of low rates below 60% WFPS (mean = $0.15 \text{ mg CH}_4\text{-C m}^{-2} \text{ d}^{-1}$, CV = 88%, range = 0.02 to 0.55), to a wide range that included very high rates above 60% WFPS (mean = $19.8 \text{ mg CH}_4\text{-C m}^{-2} \text{ d}^{-1}$, CV = 383%, range = 0.02 to 501). There was no evidence that methane production differed significantly between biomes ($p > 0.6$; ANCOVA for production rate as a function of WFPS, biome and WFPS*biome).

[29] The strength of methane consumption as a predictor for net methane flux depends pivotally on the direction of net methane flux. When considering all biomes and net flux rates together, methane consumption was a poor predictor of net methane flux (Figure 4, $r^2 < 0.03$). However, in soils with negative net flux, methane consumption rates were strongly correlated with the net flux rate ($r^2 = 0.996$) with no difference between temperate and tropical soils ($p > 0.7$). In soils with high rates of methane production and positive net methane flux, gross consumption rates were poorly correlated with net flux rates ($r^2 = 0.003$). In these methane emitting soils, we found that methane consumption rates were low, with median rates of consumption only 5% of production rates.

[30] Methane production proved the strongest predictor of variation in net flux at the landscape scale. Across all soils, net flux was strongly correlated with production ($r^2 = 0.999$).

The correlation was similarly strong in some subsets of soils that we sampled including tropical ($r^2 = 0.999$) and temperate ($r^2 = 0.999$) sites, and soils with positive net flux ($r^2 > 0.999$). However, in soils with negative net flux, production was a weak but significant predictor of net flux ($r^2 = 0.072$, $p = 0.005$).

[31] We found that total carbon mineralization was not an important factor of control for methane production. We show in Figure 5a that methane production was not statistically related to carbon mineralization when considering all biomes and net flux rates together ($r^2 = 0.008$, $p > 0.4$ for regression). In examining subsets of the data, we found a significant correlation only for sites with net negative flux. Here a small fraction of the variability in methane production was driven by carbon mineralization ($r^2 = 0.012$, $p < 0.09$). However, we found no indication of such a relationship within tropical or temperate biomes ($p > 0.25$ for each biome), or in soils with positive net methane flux ($p > 0.5$). While methane production could conceivably increase suddenly above a certain level of carbon mineralization, we found no evidence for such threshold effects.

[32] In contrast, we found a strong relationship between methane production and the methanogenic fraction of carbon flow in each soil core (Figure 5b). Using equation (1), we model this relationship, assuming: (1) the carbon supply rate equals the mean observed across all soils ($3600 \text{ mg C m}^{-2} \text{ d}^{-1}$), and (2) methanogenic mineralization yields half CH_4 and half CO_2 . This model predicts that F_{MP} generates variation in methane production (line in Figure 5b, $r^2 = 0.925$) and predicts a theoretical maximum rate of methane production (at 100% F_{MP}) of $1800 \text{ mg CH}_4\text{-C m}^{-2} \text{ d}^{-1}$ (black triangle in Figure 5b). The fit was strong across soils with net positive flux ($r^2 = 0.916$) and across tropical sites ($r^2 = 0.999$), but somewhat weaker across temperate sites ($r^2 = 0.583$) or soils with net negative flux ($r^2 = 0.493$). In contrast, we found no relationship between the methanogenic fraction and total carbon mineralization across our data as a whole ($p > 0.05$), within temperate or tropical biomes ($p > 0.15$), within soils with net negative flux ($p > 0.05$) or within soils with a net positive flux ($p > 0.2$).

[33] Using logistic regression, we determined the average point at which net methane flux shifts from net consumption to net production. This analysis, illustrated in Figure 6, reveals that on average only 0.04% of carbon mineralization (identified by gray lines in Figures 5b and 6) need pass through methanogenic pathways before soils become net sources of methane to the atmosphere. Although some samples had positive net methane flux with a methanogenic fraction as low as 0.01%, we found that all samples with methanogenic fractions above 0.06% were associated with positive net flux.

5. Discussion

[34] Our isotope-based approach, coupled with quantitative null model predictions, permit us to directly and independently test the contribution of each of the three biophysical mechanisms hypothesized to control methane fluxes across our field moisture gradients. Despite some

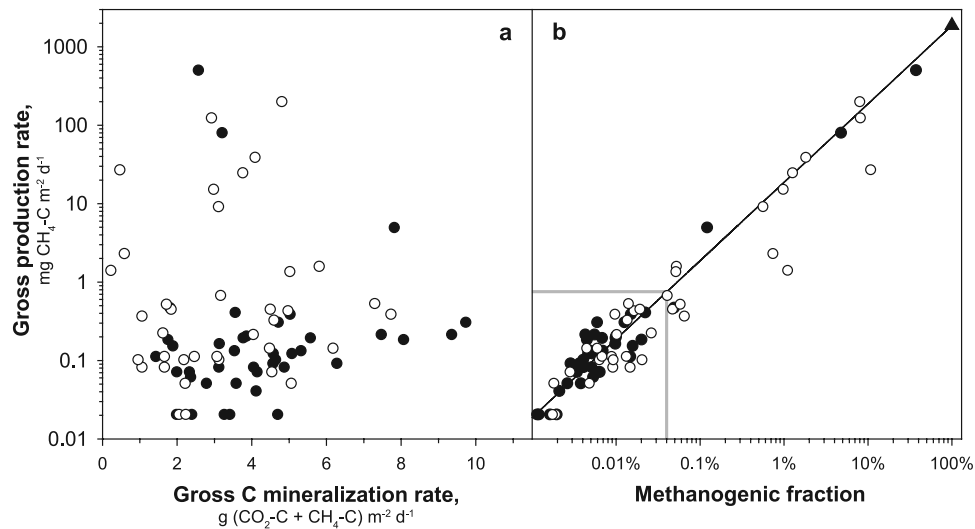


Figure 5. Correlation of gross methane production to total carbon mineralization rate and gross methane production as a function of the methanogenic fraction (F_{MP} in equation (1)). Open symbols are from tropical environments, and solid symbols are from temperate environments. (a) Total carbon mineralization rate is not correlated with methane production rates ($p > 0.25$ for slope). (b) The black line is the relationship predicted by equation (1) based on average mineralization rate of all samples ($3.7 \text{ g C m}^{-2} \text{ d}^{-1}$). Gray lines indicate the point at which average net methane flux shifts from negative to positive: methanogenic fraction = 0.04% and methane production = $0.7 \text{ mg CH}_4\text{-C m}^{-2} \text{ d}^{-1}$.

qualitatively clear relationships between methane transformations and soil moisture (Figures 3a–3c), soil moisture was only a weak quantitative predictor of net methane flux, characterized by substantial residual variance that can be attributed to factors other than moisture. Such observations raise concerns about the way that moisture information is used in models to predict the contribution and dynamics of different soils to local and global methane balances. Other studies have similarly found that soil moisture is a poor predictor of landscape variations in net methane fluxes [Potter, 1997; Verchot *et al.*, 2000]. We conclude that additional factors must be understood mechanistically in order to capture the fundamental dynamics that link soil methane transformations and climate.

[35] We asked which of the biophysical mechanisms (Figure 1) could explain the nonlinear response and residual variability of methane transformations across our moisture transects (Figure 3). We found only partial support for the consumption control hypothesis. Methane consumption failed to control net methane flux across the landscape because it was only a potent force in dry soils; methane production dominated in wet soils, virtually unchecked by consumption. The observed decline in methane consumption with increasing soil moisture is consistent with a reduction in soil diffusivity resulting from increased soil moisture [Millington and Sherer, 1971]. At low soil moisture, diffusive supplies of methane likely limit methane consumption [Del Grosso *et al.*, 2000], while at higher moisture levels, diffusive supplies of O_2 likely limit [King, 1992]. Several studies have found that methane production does occur in dry, “oxic” soils [Andersen *et al.*, 1998; von Fischer, 2002; Teh *et al.*, 2005]; however, these rates are generally low. High rates of production and consumption

were therefore mutually exclusive, as expected if limits to oxygen diffusion simultaneously suppressed methane consumption and allowed increased production in wet soils. Although oxygen transport to the rhizosphere by some wetland plants has been shown to facilitate methane oxidation below the soil surface [Popp *et al.*, 2000], we cannot evaluate this effect as it was not captured by our core-based approach. High consumptive rates therefore appear limited to soils with high supply of atmospheric oxygen, while high

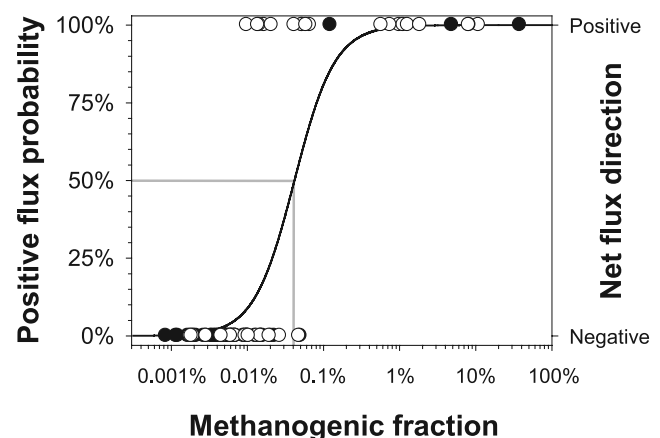


Figure 6. Logistic regression for likelihood of observing positive net methane flux (i.e., net methane emission) as a function of the methanogenic fraction (F_{MP} in equation (1)). The solid line illustrates the logistic regression and gray lines indicate the predicted threshold value for methanogenic fraction at which net methane flux turns positive, 0.04%.

rates of methane production depend on the formation of anoxic regions in soils with >60% WFPS. This also means that methane flux across landscapes with locally varying moisture levels depends more on factors that control gross methane production than on consumption.

[36] Laboratory and field studies have commonly found that additions of labile carbon to soils and sediments stimulate methane production [Winfrey and Zeikus, 1977; Williams and Crawford, 1984; Delwiche and Cicerone, 1993; Valentine *et al.*, 1994; Nusslein and Conrad, 2000] and, as a result, the notion has arisen that carbon supply is the primary determinant of methane production. However our results clearly show that differences in carbon supply cannot explain the observed variations in methane production (Figure 5a). We conclude that factors controlling variations in electron acceptors to local sites of decomposition (i.e., methanogenic pathway control) exert greater influence on methane production than does carbon supply alone.

[37] In fact, our results strongly support the methanogenic pathway hypothesis (Figure 5b), with variations in net and gross methane fluxes that can only be quantitatively explained by local variations in the methanogenic fraction across the landscape. The correlation patterns between net methane flux, total carbon mineralization, and fraction of methanogenic mineralization across our samples only rejected the null model that assumed absence of methanogenic pathway control; the data were consistent with the null model prediction for the absence of carbon supply control (see Figure 2 versus Figure 5). Although it is conceivable that carbon supply might affect the methanogenic fraction, we found no statistical evidence for this. In addition, the methanogenic fraction was only weakly related to variations in soil moisture (explaining 5% of variance); this observation explains the commonly observed, weak statistical correspondence between methane flux and soil moisture (e.g., Figure 3). Below 60% WFPS, the F_{MP} never rose above 0.01%, while above 60% WFPS, the fraction varied much more widely, reaching values near 40%.

[38] The point at which net methane flux shifts from negative to positive (indicated by gray lines in Figures 5b and 6) shows that only 0.04% of total mineralized carbon needed to proceed through methanogenic pathways before soils become net sources of methane to the atmosphere. This result indicates that methane production is highly sensitive to the development of anaerobic “microsites,” in which energy is diverted to methanogenic pathways in highly localized soil microenvironments. It is possible that such environments arise owing to small-scale hot spots in carbon supply [Wachinger *et al.*, 2000] or as regions where the supplies of electron acceptors are limited [Sexstone *et al.*, 1985]. Future research should seek to identify the factors that control the methanogenic fraction within and across soils, as well as the factors that determine the development and maintenance of small-scale heterogeneities that can have disproportionate effects on methane flux. We anticipate that distributions of microsites across soils may follow general scaling laws and may therefore allow for landscape-scale generalization about soil properties that

control anaerobic microsite formation. Efforts to address such phenomena might begin by characterizing soil properties that control the probability distribution function of the methanogenic fraction.

[39] While ecosystem carbon supply must ultimately constrain methane production from a mass balance perspective [Whiting and Chanton, 1993], our findings show that local-scale biophysical factors are essential for understanding the exceedingly large variance expressed within and across natural ecosystems. The spatial organization of soil methane production thus depends on factors that control local-scale pathways of carbon flux in soils. Global- and regional-scale models of methane flux should consider how such factors contribute to the nonlinear nature of the soil-methane-climate system.

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