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INVITED REVIEW

Methane emissions from wetlands: biogeochemical, microbial, and modeling perspectives from local to global scales

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Abstract

Understanding the dynamics of methane (CH_4) emissions is of paramount importance because CH_4 has 25 times the global warming potential of carbon dioxide (CO_2) and is currently the second most important anthropogenic greenhouse gas. Wetlands are the single largest natural CH_4 source with median emissions from published studies of 164 Tg yr^{-1}, which is about a third of total global emissions. We provide a perspective on important new frontiers in obtaining a better understanding of CH_4 dynamics in natural systems, with a focus on wetlands. One of the most exciting recent developments in this field is the attempt to integrate the different methodologies and spatial scales of biogeochemistry, molecular microbiology, and modeling, and thus this is a major focus of this review. Our specific objectives are to provide an up-to-date synthesis of estimates of global CH_4 emissions from wetlands and other freshwater aquatic ecosystems, briefly summarize major biogeophysical controls over CH_4 emissions from wetlands, suggest new frontiers in CH_4 biogeochemistry, examine relationships between methanogen community structure and CH_4 dynamics *in situ*, and to review the current generation of CH_4 models. We highlight throughout some of the most pressing issues concerning global change and feedbacks on CH_4 emissions from natural ecosystems. Major uncertainties in estimating current and future CH_4 emissions from natural ecosystems include the following: (i) A number of important controls over CH_4 production, consumption, and transport have not been, or are inadequately, incorporated into existing CH_4 biogeochemistry models. (ii) Significant errors in regional and global emission estimates are derived from large spatial-scale extrapolations from highly heterogeneous and often poorly mapped wetland complexes. (iii) The limited number of observations of CH_4 fluxes and their associated environmental variables loosely constrains the parameterization of process-based biogeochemistry models.

Keywords: anaerobic carbon cycling, climate change, methane, methane models, methanogen communities, wetlands

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Introduction

Methane (CH_4) has 25 times the global warming potential of carbon dioxide (CO_2) over a 100-year time frame (Forster *et al.*, 2007), so small changes in its atmospheric concentration have large implications for future climate. Methane is responsible for about 18% of human-induced radiative forcing, making it the second most important greenhouse gas after CO_2 (Forster *et al.*, 2007). Moreover, this estimate of the global warming potential of CH_4 may be 10–40% too low because the indirect effects of CH_4 on aerosols and other chemical compounds (e.g. O_3) were not considered (Shindell *et al.*, 2009).

Anthropogenic CH_4 emissions make up 54–72% of the total global flux (Fig. 1, Table S1), with livestock, biomass burning, landfills and other waste management, fossil fuel production, and rice agriculture being the largest anthropogenic sources (Denman *et al.*, 2007). Wetlands are the single largest natural source (Fig. 1), and though included as an anthropogenic source, rice fields are essentially agricultural wetlands, sharing the same fundamental set of controls over CH_4 emissions as natural wetlands. There is also major concern about potential feedbacks between global change perturbations and CH_4 emissions from wetlands, as climate, atmospheric CO_2 concentrations, and deposition of sulfate and nitrogen are all known to affect CH_4 emissions positively or negatively (Roulet, 2000; Gauci *et al.*, 2004; Bridgham *et al.*, 2006; Zhuang *et al.*, 2006). Moreover,

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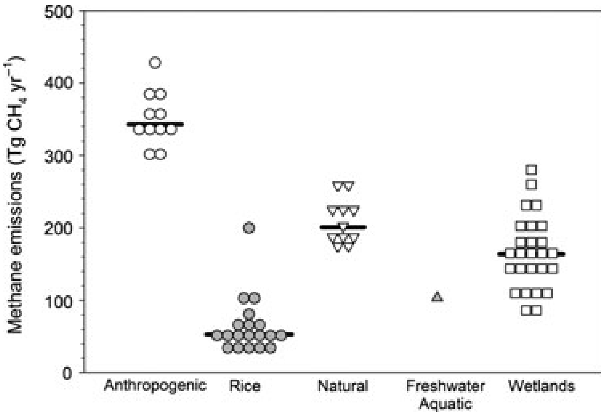

Fig. 1 Dot density graph of global methane sources. Horizontal lines are the median for each category. Anthropogenic sources include rice fields and natural sources include freshwater aquatic ecosystems and wetlands, but they are also presented separately. Data for figure are in Tables S1 and S2, and when ranges are given, the mean value was used.

there is strong evidence that wetlands have provided an important radiative feedback in past glacial-interglacial cycles (Chappellaz *et al.*, 1993a,b; Blunier *et al.*, 1995; Loulergue *et al.*, 2008). As discussed in the next section, a number of lines of evidence suggest that the effects of interannual variations in climate on CH_4 fluxes from wetlands have been large enough to drive many of the observed variations in global atmospheric CH_4 concentrations during the last several decades. Thus, there is compelling evidence that CH_4 emissions from wetlands have been strongly responsive to climate in the past, and will likely continue to be responsive to anthropogenic-driven climate change in the future.

There is an extensive literature on many aspects of this topic, including several recent reviews (Le Mer & Roger, 2001; Blodau, 2002; Megonigal *et al.*, 2004; Lai, 2009; Laanbroek, 2010). Therefore, this article provides a more focused perspective on important recent frontiers in obtaining a better understanding of CH_4 dynamics in natural systems, with a focus on wetlands. One of the most exciting recent developments in this field is the attempt to integrate the different methodologies and spatial scales of biogeochemistry, molecular microbiology, and modeling perspectives, and thus this is a major focus of this review. Our specific objectives are to (i) provide an up-to-date synthesis of estimates of global CH_4 emissions from wetlands and other freshwater aquatic ecosystems, (ii) briefly summarize major biogeophysical controls over CH_4 emissions from wetlands, (iii) suggest new frontiers in CH_4 biogeochemistry, (iv) examine relationships between methanogen community structure and CH_4 dynamics *in situ*, (v) and to review the current generation of CH_4 models. We highlight throughout some of the most pressing issues concerning global change and feedbacks on CH_4 emissions from natural ecosystems.

A global accounting of wetland (and other) atmospheric CH_4 sources

Methodology

Methods for estimating global CH_4 emissions and their geographic distribution can be divided into 'bottom-up' and 'top-down' approaches. Bottom-up methods involve scaling CH_4 fluxes estimated with empirical ground-based or model-derived flux estimates by wetland area. Typically, this is done zonally and/or by wetland type. Ground-based CH_4 emission data via chambers or eddy-flux towers are typically highly variable spatially and have undersampled some wetland types, such as tropical wetlands. Model-derived estimates of CH_4 fluxes are limited to the extent that models accurately capture CH_4 dynamics, which is discussed in greater detail below (*Modeling methane emissions from wetlands*).

Top-down methods estimate regional CH_4 emissions by combining data on the global distribution of atmospheric CH_4 concentrations, models of atmospheric CH_4 transport, and estimates of atmospheric CH_4 removal (primarily by the hydroxyl radical). The $\delta^{13}C$ signature of CH_4 is also sometimes used as an additional constraint on its sources. Then in an 'inverse' Bayesian statistical approach, prior information on the spatial distribution of CH_4 sources and sinks is combined with the atmospheric data to provide the most robust estimate of regional CH_4 sources. Top-down studies have been invaluable for placing constraints on regional CH_4 sources, but they are limited by the density of the sampling network for surface measurements (Dlugokencky *et al.*, 2011), the accuracy of *a priori* estimates used in the Bayesian modeling (e.g. Neef *et al.*, 2010; Bousquet *et al.*, 2011), and sometimes by an inability to uniquely resolve sources (e.g. Spahni *et al.*, 2011). Satellite-based measurements of atmospheric CH_4 concentrations have recently begun to be used with inverse modeling (see Tables S1 and S2), which can help alleviate the large gaps in surface sampling networks, but the retrieval of the data from satellite measurements is complex and can result in strong biases (Meirink *et al.*, 2006; Frankenberg *et al.*, 2011).

Very poor estimates of the global area and geographic distribution of wetlands have limited the ability to accurately estimate global wetland CH_4 fluxes (Zhuang *et al.*, 2009; Ringeval *et al.*, 2010; Zhu *et al.*, 2011; Melton *et al.*, 2012). In particular, the total area of northern wetlands is very poorly constrained to between

2.6 and 9.0 × 10^6 km^2 (Petrescu *et al*., 2010). The historical estimate of global wetland area by Matthews & Fung (1987) of 5.3 × 10^6 km^2 was based upon three independent digital sources, vegetation, soils, and fractional inundation, and it has been used by most bottom-up studies since. A subsequent estimate of global wetland area of 5.7 × 10^6 km^2 using country and regional wetland inventories (Aselmann & Crutzen, 1989) appeared to largely support the estimate of Matthews & Fung. However, subsequent wetland inventory data suggested that these early estimates were more than two times too low (Finlayson *et al*., 1999). Lehner & Döll (2004) combined a number of different datasets to estimate a global wetland area of 9.2 × 10^6 km^2. Prigent *et al.* (2007) used several satellite datasets to determine that the minimum and maximum extent of inundated area (including wetlands, rivers, small lakes, and irrigated rice) ranges from 2.2 × 10^6 km^2 to 5.9 × 10^6 km^2, which compares well with the extent of wetlands and irrigated rice in Matthews & Fung (1987). However, many wetlands rarely if ever have standing water, so the actual global wetland area is likely substantially greater. The study by Prigent *et al.* reinforces the importance of considering the seasonality of wetland inundation in estimating CH_4 emissions. Similarly, Kaplan (2002) used a simple algorithm of slope and volumetric soil wetness to estimate a global wetland area of 11.0 × 10^6 km^2, of which 61% was seasonal. As for aquatic ecosystems, existing estimates often do not account for small lakes, which can result in an underestimation of regional lake area by more than half (Walter *et al*., 2007). See Lehner & Döll (2004) and Melton *et al.* (2012) for detailed comparisons of the total area and geographic distributions of lakes and wetlands from previous studies. What is clear at this point is that without a robust estimate of the current distribution of global wetlands by type, there is little possibility of accurately portraying how future global change will affect their CH_4 emissions.

Global CH_4 emission estimates

Atmospheric observations of CH_4 concentrations and estimates of its atmospheric lifetime constrain total global emissions to between 500 and 600 Tg CH_4 yr^{-1} (Dlugokencky *et al*., 2011). However, the relative contributions of individual sources are still poorly known (Fig. 1, Tables S1 and S2).

Global wetland CH_4 emissions from both bottom-up and top-down methods range from 80 to 280 Tg CH_4 yr^{-1} (1 Tg = 10^{12} g), with a median value of 164 Tg CH_4 yr^{-1} (mean = 166, Fig. 1, Table S2). Scaling of empirical emission data has given a narrow range of low emission estimates (range 80-111, median 107 Tg CH_4 yr^{-1}), modeling studies have given widely variable estimates (range 92-280, median 181 Tg CH_4 yr^{-1}), and atmospheric inversion studies typically have given relatively high estimates with modest variability (range 115–232, median 163 Tg CH_4 yr^{-1}) (Fig. 2a). A recent inter model comparison gave a mean global CH_4 emission of 190 Tg yr^{-1}, but model results varied by ±40% around this mean (Melton *et al*., 2012). The zonal breakdown of these estimates is significant because most peatlands are in the boreal region and most mineral soil wetlands are in the tropics, and these two types of wetlands have fundamentally different sets of ecosystem controls (Spahni *et al*., 2011) and response of CH_4 emissions to climate (Bloom *et al*., 2010b; Hodson *et al*., 2011). Atmospheric inversion studies estimate that from 47 to 89% (median 73%) of global wetland CH_4 emissions originate from tropical wetlands (Table S2) with their large areal extent and high CH_4 fluxes per area. However, the dominant research effort has focused on CH_4 dynamics in northern wetlands, probably mostly because of the density of more developed countries at northern latitudes with their greater research

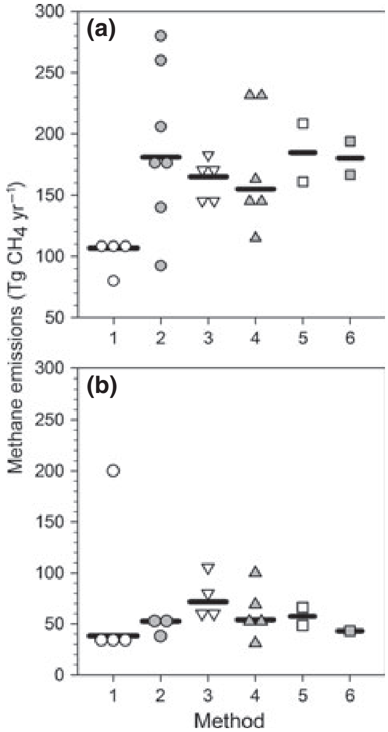

Fig. 2 Global methane sources in (a) wetlands and (b) rice fields determined by different methods. 1 = scaling from empirical measurements, 2 = process-based models, 3 = inverse atmospheric modeling with ground-based measurements, 4 = inverse atmospheric modeling with ground-based measurements constrained by $\delta^{13}CH_4$, 5 = inverse modeling with satellite-based measurements, and 6 = a combination of 2 and 5. Horizontal lines are the median for each category.

expenditures. However, northern peatlands contain ca. 392 Pg C (1 Pg = 10^{15} g) (Maltby & Immirzi, 1993) and northern permafrost regions contain 1,672 Pg C (278 Pg C in peatlands) (Tarnocai *et al.*, 2009), with the permafrost pool being 50% of the terrestrial soil carbon pool. In addition, the largest temperature increases are predicted to occur at high latitudes in the next century (Meehl *et al.*, 2007). Thus, there is justifiable concern that future climate change may disproportionately increase CH_4 emissions from northern wetlands.

Rice agriculture is also a substantial source of CH_4, with a range of 25–300 Tg CH_4 yr^{-1} from both bottom-up and top-down methods, with a median value of 53 Tg CH_4 yr^{-1} (mean = 64, Fig. 1, Table S2). There is large overlap in estimates of CH_4 emissions from rice fields among different methods (Fig. 2b).

There are fewer estimates of global CH_4 fluxes from open-freshwater aquatic systems, and we focus here on the recent updated estimates from Bastviken *et al.* (2011). They used an inventory approach to estimate that open-freshwater aquatic systems emit 93 Tg CH_4 yr^{-1}, with another 10 Tg CH_4 yr^{-1} coming from plants in shallow littoral zones. This is a substantial, previously underappreciated flux, but other data suggest that it may still be too low. In a response to Bastviken *et al.*, Li & Lu (2011) suggested that their estimate of CH_4 fluxes from tropical reservoirs was too low, and predicted that these emissions could double in the next 40 years. Extrapolating from 16 sites to all lakes north of 45°N, Walter *et al.* (2007) suggested that northern lakes alone emit from 13.7 to 34.7 Tg CH_4 yr^{-1}. There may be some spatial overlap in Bastviken *et al.*'s estimate of aquatic CH_4 emissions with previous wetland estimates, but to the extent the areas are distinct it suggests that top-down estimate from wetlands may need to be reduced so they are more in line with bottom-up inventory estimates and that estimates of wetland CH_4 fluxes from models may also be too high.

Have wetlands affected recent variability in atmospheric CH_4 concentrations?

Atmospheric CH_4 concentrations increased by 12 ± 2 ppb yr^{-1} in the 1980s, but this growth rate sharply decreased in the 1990s and atmospheric CH_4 concentrations were relatively constant from the late 1990s to 2006, albeit with large interannual variability (Fig. 3). Atmospheric CH_4 concentrations began to increase again in 2007, and this increase has continued since. This atmospheric record has provided top-down methods with an invaluable dataset with which to attempt to examine sources and sinks of CH_4 over time (Dlugokencky *et al.*, 2011). In addition, if empirical evidence suggests that CH_4 emissions from wetlands are responding in a significant way to current interannual climate variability, that should be construed as strong evidence that they will have large feedbacks to future climate change.

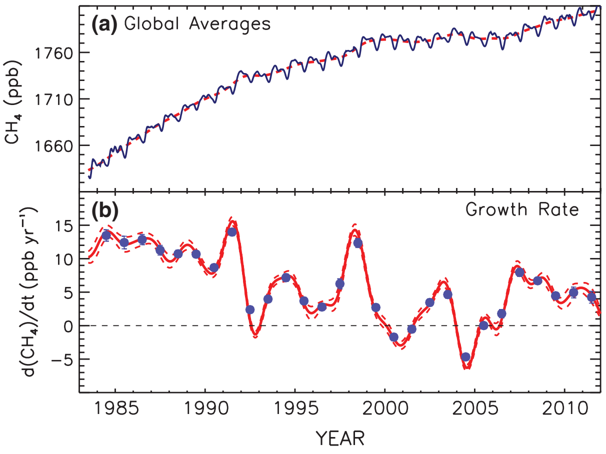

Fig. 3 Atmospheric growth rate of CH_4 in dry air mole fractions in blue and the deseasonalized trend curve as a red–dashed line. (b) The instantaneous growth rate of (a). The symbols are the annual increase calculated from January 1 in 1 year to January 1 in the next year, plotted in the middle of the year. Data and graphic are from E. Dlugokencky (Dlugokencky *et al.*, 2009).

The long-term trend of the decreasing growth rate of atmospheric CH_4 from 1984 to 2003 was driven by a decrease in anthropogenic sources (Bousquet *et al.*, 2006; Aydin *et al.*, 2011). However, wetlands explained 70% of the substantial interannual variations in atmospheric CH_4 concentrations during this period, with tropical wetlands being particularly significant in this regard (Bousquet *et al.*, 2006). Anthropogenic emissions began to increase again after 2000, but this was largely offset by a coincident drop in emissions from northern wetlands due to drier conditions (Bousquet *et al.*, 2006, 2011). However, this decrease in CH_4 emissions from wetlands was short-lived. There was an increase in emissions from northern wetlands, but not in tropical wetlands, from 2003 to 2007 that was mainly due to increasing temperatures (Bloom *et al.*, 2010b). The large increases in atmospheric CH_4 concentrations in 2007 and 2008 were primarily driven by higher emissions in tropical wetlands, with secondary contributions from boreal wetlands and anthropogenic sources (Bousquet *et al.*, 2011).

Modeling approaches have also considered recent interannual variability in atmospheric CH_4 concentrations as a useful test case. Hodson *et al.* (2011) used a simple modeling approach to suggest that interannual variability in CH_4 emissions from wetlands is strongly influenced by the El Niño-Southern Oscillation (ENSO) cycle, with 44% of the interannual variability in CH_4

emissions from tropical wetlands explained by ENSO, 27% from Northern Hemisphere temperate wetlands, 12% from boreal wetlands, and 18% from nontropical wetlands in the Southern Hemisphere. Similar to Bloom *et al.* (2010b), they found that the interannual variability in CH_4 emissions in the tropics was driven by variation in the area of inundated wetlands, whereas it was driven by temperature in the boreal region. They also suggested stronger El Niño than La Niña events from 1980 to 1999 are partially responsible for the slowdown in the increase in atmospheric CH_4 concentrations over this period.

Spahni *et al.* (2011) used the LPJ-WHyMe model to show an increase in global wetland emissions of CH_4 from 1990 to 1998, a small decrease from 1999 to 2004, and an increase again from 2004 to 2008. Most of the increase from 2004 to 2008 came from wet mineral soils in the temperate and tropical zones, but there were also substantial contributions from all other wetland categories and from rice. In contrast, Kai *et al.* (2011) suggested that CH_4 emissions from rice agriculture were significantly reduced over the period 1960–2005 due to increased use of fertilizers and reduction in water use.

In summary, while changes in atmospheric CH_4 concentrations since the 1980s are likely due to both changes in anthropogenic (biogenic and non biogenic) and natural sources, both top-down and modeling studies consistently suggest that interannual variations in climate have resulted in significant changes in CH_4 emissions from wetlands and potentially other freshwater ecosystems. We suggest that these studies, along with the strong linkage between paleoclimate and atmospheric CH_4 concentrations (Chappellaz *et al.*, 1993a,b; Blunier *et al.*, 1995; Loulergue *et al.*, 2008), are compelling evidence that CH_4 fluxes from wetlands will provide a strong feedback response to future, anthropogenic climate change.

Mechanisms controlling CH_4 production and emissions – the current paradigm

The amount of CH_4 emitted from an ecosystem is the balance between CH_4 production (methanogenesis) and CH_4 oxidation (methanotrophy) (Fig. 4). While both of these processes are regulated by microbial activities, vegetation dynamics also serve as important controls over CH_4 flux by regulating CH_4 transport from the soil to the atmosphere and influencing both the production and consumption of CH_4 by microbes. An overview of relevant processes is presented here, but other recent reviews summarize these processes in greater detail (Le Mer & Roger, 2001; Blodau, 2002; Megonigal *et al.*, 2004; Lai, 2009; Laanbroek, 2010).

The CH_4 dynamics described in this section often vary in a fairly predictable manner in different types of wetlands. The most important characteristics defining wetland types are climatic zones (e.g. arctic, boreal, temperate, and tropical), the presence or absence of permafrost, the degree of any salinity influence, and the presence of peat or mineral soil. Peatlands are also defined within a regional hydrogeomorphic context along a minerotrophic-ombrotrophic gradient, with minerotrophic peatlands having groundwater and/or surface water inputs and ombrotrophic peatlands having only precipitation inputs. These larger scale characteristics subsequently control plant composition, hydrology, and the soil characteristics that drive anaerobic carbon cycling and the CH_4 dynamics described below.

CH_4 Production

The production of CH_4 is the result of a complex suite of microbial activities that include both syntrophic interactions and competition for key substrates. Heterotrophic microbes rely upon organic carbon as an electron donor to drive their metabolism, and rates of decomposition in wetlands are frequently correlated with various indexes of soil carbon quality (Yavitt & Lang, 1990; Valentine *et al.*, 1994; Updegraff *et al.*, 1995; Bridgham *et al.*, 1998; Chanton *et al.*, 2008). While complex organic polymers derived from senescent vegetation and soil organic matter represent an important source of carbon to soil microbes, methanogenesis is frequently closely correlated with plant productivity (Whiting & Chanton, 1993; Updegraff *et al.*, 2001). There is strong evidence to suggest that CH_4 production is fueled by recent plant photosynthate in the form of root exudates in the rhizosphere as confirmed by ^{14}C-labeling studies (Megonigal *et al.*, 1999; King *et al.*, 2002; Dorodnikov *et al.*, 2011). In addition to directly fueling methanogenesis, there is also evidence that root exudates can stimulate the decomposition of more recalcitrant soil organic matter through priming effects (Guenet *et al.*, 2010; Basiliko *et al.*, 2012).

The relative contribution of recent plant photosynthate and older peat to anaerobic carbon respiration, however, can be relatively nuanced among different types of peatlands, reflecting differences in their plant community composition. Dissolved organic matter (DOM) appears to be relatively young compared to bulk soil in all peatlands even at great depth in the soil profile (Chanton *et al.*, 2008), reinforcing the importance of recent plant carbon in these systems. However, the DOM from sedge-dominated peatlands (i.e. fens) appears to be substantially more labile than the DOM from *Sphagnum* moss and woody plant-dominated peatlands (i.e. bogs),

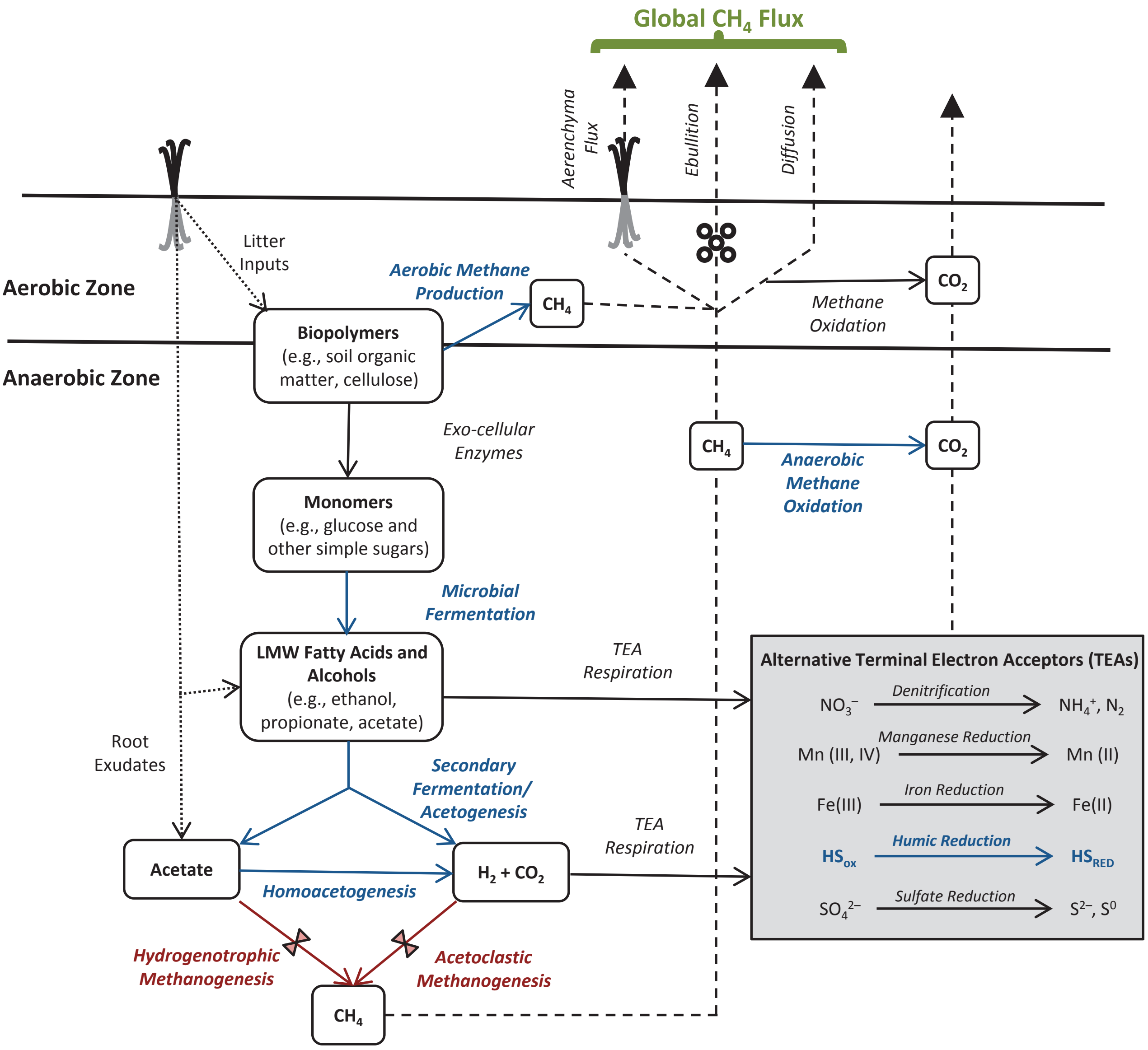

Fig. 4 Methane cycling in wetland ecosystems. Pools of carbon are shown in white boxes and solid arrows show the progressive mineralization of these carbon pools by the identified microbial processes or groups. Dotted lines illustrate carbon inputs from the plant community. Dashed lines represent the flux of the gaseous end products of these processes (CH_4 and CO_2) to the atmosphere. New advances discussed in greater detail in this manuscript are highlighted in color. Novel biogeochemical processes (in blue) are discussed in *New frontiers in* CH_4 *biogeochemistry*; methanogen community structure (in red) is discussed in *Methanogen community dynamics*; and the process and result of modeling global CH_4 fluxes (in green) are discussed in *Modeling biogenic* CH_4 *emissions from wetlands* and *A global accounting of wetland (and other) atmospheric* CH_4 *sources*.

and thus it appears that CO_2 and CH_4 from anaerobic respiration in fens is primarily from DOM whereas in bogs CO_2 and CH_4 is derived from a combination of DOM and the bulk peat (Chanton *et al.*, 2008). This may be one of several reasons that bogs typically produce low amounts of CH_4.

Organic carbon needs to be broken down to simple substrates before it can be utilized by methanogens. Depending on its initial complexity, this processing may involve several steps, starting with degradation of complex polymers by microbial exoenzymes followed by subsequent degradation steps by fermenting bacteria (Drake *et al.*, 2009). In freshwater ecosystems, it is generally assumed that the sole fermentation products utilized by methanogens are H_2, which is oxidized to CH_4 using CO_2 as an electron acceptor in the process of hydrogenotrophic methanogenesis, and acetate which is split to form CO_2 and CH_4 in the process of acetoclastic methanogenesis. In reality, methanogens are known to use additional substrates (e.g. carbon monoxide, formate, some alcohols, and methylated compounds such as trimethylamine, dimethyl sulfate, and methanol) under laboratory conditions (Zinder, 1993). Under hypersaline conditions, methylated compounds appear to be the main methanogen substrates because sulfate reducers (see next paragraph) have low affinity for them (Oremland, 1988; Sowers & Ferry, 2003; Potter *et al.*, 2009).

The fermentation end products (e.g. H_2/CO_2 and acetate) used by methanogens in the final step of anaerobic decomposition can also be used by microbial groups that utilize a variety of inorganic terminal electron acceptors (TEAs) in their metabolism (Megonigal *et al.*, 2004). The competitiveness, and thus relative importance, of these TEAs is thought to be controlled primarily by their thermodynamic favorability in the following order: NO_3^- (denitrification), Fe(III) (iron reduction), Mn(III, IV) (manganese reduction), and SO_4^{2-} (sulfate reduction). There is also mounting evidence that humic substances may act as organic TEAs in wetland ecosystems (described in more detail below). Based on thermodynamic theory, CH_4 production will be competitively suppressed by more favorable TEA-reducing processes until those TEAs have been consumed. While this theory generally holds, particularly in homogeneous sediment and aquifer environments, there is evidence that many of these competing processes occur simultaneously *in situ* and in laboratory incubations of even well-mixed wetland soils. Recent work has suggested that ecological and physiological factors may be as important as thermodynamics in regulating microbial competition (Bethke *et al.*, 2011).

The availability of TEAs, and thus the importance of competitive suppression of CH_4 production, is regulated by a complex set of factors. Many inorganic TEAs are present in low concentrations in highly organic wetland soils and increase in concentration in more mineral systems. The reduction in metallic TEAs (e.g. Fe (III) and Mn(III, IV)) contributes to anaerobic decomposition in many mineral wetland soils (e.g. Lovley & Phillips, 1986, 1988; Roden & Wetzel, 1996, 2003; Roden, 2003). Sulfate reduction generally dominates anaerobic decomposition and suppresses methanogenesis in brackish and salt water wetlands due to a constant supply of SO_4^{2-} as a TEA by tidal exchange in these systems (Bartlett *et al.*, 1987; Poffenbarger *et al.*, 2011). Sulfate reduction can also be an important microbial pathway in freshwater systems, despite low sulfate availability, as a result of rapid sulfur cycling in these systems (Vile *et al.*, 2003a). High rates of atmospheric deposition of sulfate can also cause lower rates of CH_4 production in freshwater wetlands (Vile *et al.*, 2003b; Gauci *et al.*, 2004). TEA availability also changes seasonally within a wetland due to the reduction and reoxidation of TEAs driven by the aerobic status of soils. Drops in water table levels have been shown to reoxidize reduced forms of TEAs (e.g. Deppe *et al.*, 2010) and explain why rates of CH_4 production remain low even after an increased water table level in many systems. Oxygen input via the rhizosphere of plants (i.e. ROL or radial oxygen loss) into otherwise anaerobic soil can also reoxidize reduced TEAs and result in the suppression of CH_4 production (Laanbroek, 2010 and references cited therein).

CH_4 emissions

Methane can leave a wetland via diffusion, ebullition (i.e. bubble release), and/or plant-mediated transport, and the relative importance of these various routes is an important control on wetland CH_4 emissions. When CH_4 exits a system through diffusion when the water table is below the soil surface, chemoautotrophic methanotrophs can oxidize it to CO_2 (Hanson & Hanson, 1996). Aerobic methanotrophy can dominate wetland CH_4 cycling, and the global wetland CH_4 oxidation sink has been estimated to be between 40 and 70% of gross CH_4 production (Megonigal *et al.*, 2004). Water table level is perhaps the most dramatic control on the relative importance of CH_4 oxidation, and numerous studies have documented the expected decline in net CH_4 flux accompanying a lowering of the water table (e.g. Updegraff *et al.*, 2001; Turetsky *et al.*, 2008; Meijide *et al.*, 2011; Moore *et al.*, 2011). In addition, ROL can create aerobic volumes where CH_4 oxidation can occur in saturated wetland soils. Rhizosphere-associated methanotrophy is likely linked to plant type (Laanbroek, 2010) and diversity (Bouchard *et al.*, 2007), and can consume virtually 100% of gross CH_4 production (Fritz *et al.*, 2011). There is also a growing appreciation for a symbiotic relationship between methanotrophs and *Sphagnum* mosses (Raghoebarsing *et al.*, 2005), which appears to be nearly ubiquitous in peatland ecosystems, especially in frequently flooded pools (Kip *et al.*, 2010).

Flux of CH_4 through plant aerenchyma can also be an important component of net CH_4 flux from wetlands and allows CH_4 to bypass zones of aerobic methanotrophy. The contribution of plant-mediated CH_4 flux varies dramatically between systems and ranges from ca. 30–100% of total CH_4 flux (e.g. Whiting & Chanton, 1992; Shannon *et al.*, 1996; van der Nat & Middelburg, 1998; Cheng *et al.*, 2006; Dorodnikov *et al.*, 2011). While much of this work has focused on emergent wetland vegetation, there is also evidence that woody species can serve as a conduit for CH_4 flux to the atmosphere (e.g. Vann & Megonigal, 2002; Gauci *et al.*, 2010; Rice *et al.*, 2010).

Ebullition also allows CH_4 leaving a wetland to bypass zones of aerobic oxidation. Historically, ebullition has been thought to be primarily episodic following supersaturation of pore water CH_4. These spatially and temporally variable CH_4 release events are particularly challenging to measure, although the limited work on this topic suggests that ebullition events can release significant amounts of CH_4 from wetlands (Glaser *et al.*, 2004; Tokida *et al.*, 2007a,b). Recent methodological advances have allowed for high-resolution sampling of ebullition dynamics both spatially and temporally (e.g. Walter *et al.*, 2006; Gogo *et al.*, 2011; Goodrich *et al.*, 2011; Kettridge *et al.*, 2011). Goodrich *et al.* (2011) suggested that ebullition can occur not just as rare releases of accumulated CH_4, but as a regular transport pathway of CH_4 as typical as diffusion and plant transport. These approaches have also suggested that ebullition events may exhibit diel patterns and that these patterns may vary seasonally (Gogo *et al.*, 2011; Goodrich *et al.*, 2011).

New frontiers in CH_4 biogeochemistry

Rethinking anaerobic and aerobic CH_4 dynamics

Much of our current understanding of CH_4 dynamics in wetland soils centers around the premise that the production of CH_4 is restricted to anaerobic soil volumes whereas the oxidation of CH_4 occurs in aerobic environments. Both of these central tenants of CH_4 biogeochemistry may need to be revisited in light of recent evidence. Keppler *et al.* (2006) suggested that CH_4 production may occur through nonmicrobially mediated aerobic pathways in living plant tissue, and that these pathways could be responsible for 30–40% of the global CH_4 flux. While this finding was initially highly controversial (e.g. Dueck *et al.*, 2007), aerobic CH_4 production from vegetation has been subsequently reported multiple times (Keppler *et al.*, 2009 and references therein). There is a growing consensus that this novel process is linked to photodegradation of pectin by UV-B radiation (Keppler *et al.*, 2008; McLeod *et al.*, 2008). However, recent estimates suggest that this process contributes to less than 1% of the global CH_4 flux (summarized in Megonigal & Guenther, 2008; Bloom *et al.*, 2010a).

The potential for significant rates of CH_4 production in oxic soils has also been demonstrated by estimating gross CH_4 production using ^{14}C (Andersen *et al.*, 1998) and ^{13}C stable isotope dilution techniques (Teh *et al.*, 2005; von Fisher & Hedin, 2007), and chemical inhibitors of CH_4 oxidation (Yavitt *et al.*, 1995; Kammann *et al.*, 2009). These studies generally suggest that such production is limited to anaerobic microsites in the soils, although Kammann *et al.* (2009) identified soil macrofauna as a significant source of CH_4 production. As discussed below (*Methanogen community composition within a single ecosystem type*), recent evidence suggests that methanogens are ubiquitous in aerobic soil and their activity can be activated upon flooding. While the presence of anaerobic microsites (and potentially soil fauna) may explain these observations of CH_4 production in otherwise oxic soil, there is also evidence that aerobic CH_4 production by a nonmicrobially mediated mechanism similar to those observed in plant tissues may be possible in soil environments (Hurkuck *et al.*, 2012). A recent modeling study suggested that wet (but oxic) mineral soils can be a globally significant source of CH_4, emitting ca. 60 Tg CH_4 yr^{-1}, reflecting their large areal extent (Spahni *et al.*, 2011).

Methane production has also been observed in aerobic aquatic environments. Significant rates of CH_4 production and transport have been attributed to anaerobic microsites within particulate organic matter in oxygenated surface ocean waters (Karl & Tilbrook, 1994). Grossart *et al.* (2011) also reported CH_4 production in the oxygenated water column of a freshwater lake and detected archaea attached to photoautotrophs, suggesting a transfer of carbon substrate to methanogens and the possibility of anaerobic microsites in this system. Furthermore, recent evidence suggests that CH_4 can be produced aerobically as a byproduct of the decomposition of organic phosphorus compounds in nutrient-limited marine ecosystems (Karl *et al.*, 2008; Damm *et al.*, 2010).

Concomitant with our expanded understanding of the potential for CH_4 production in the presence of oxygen, there is a growing body of evidence demonstrating that CH_4 oxidation can occur under anaerobic conditions, using alternative electron acceptors in place of oxygen. The likelihood for anaerobic methane oxidation (AOM) in marine systems has been accepted since the mid-1970s (e.g. Martens & Berner, 1974; Barnes & Goldberg, 1976). The mechanism, biogeochemistry, and microbiology of AOM remain important questions in marine CH_4 cycling (see reviews by Valentine & Reeburgh, 2000; Hinrichs & Boetius, 2002; Caldwell *et al.*, 2008; Knittel & Boetius, 2009), especially considering that this process is thought to consume >90% of the CH_4 produced by marine systems (Hinrichs & Boetius, 2002; Reeburgh, 2007). Hoehler *et al.* (1994) hypothesized that anaerobic CH_4 oxidation was likely driven by a syntrophic relationship between methanogenic archaea undergoing 'reverse methanogenesis' and sulfate-reducing bacteria, despite the low thermodynamic energy yield of this process. Subsequent work revealed the presence of methanogen-sulfate-reducing aggregates in a number of marine sediments (e.g. Boetius *et al.*, 2000; Orphan *et al.*, 2001; Michaelis *et al.*, 2002) in support of this hypothesis. While the archaea capable of AOM have yet to be cultured, molecular approaches suggest that there are three distinct clusters of Euryarchaeota responsible for this process (Knittel & Boetius, 2009).

While AOM has been known to occur in freshwater systems for some time (e.g. Hallam *et al.*, 2004), comparatively little work on AOM has taken place in freshwater ecosystems compared to marine environments. One possible reason for this discrepancy is that sulfate is the electron acceptor that drives this process in marine systems, but its concentration is typically too low in freshwater environments for it to play a comparable role in AOM (Caldwell *et al.*, 2008). However, a growing realization that AOM can be linked to additional electron acceptors, including manganese and iron (Beal *et al.*, 2009; Sivan *et al.*, 2011), denitrification of nitrate (Smith *et al.*, 1991; Raghoebarsing *et al.*, 2006), and possibly organic TEAs (Smemo & Yavitt, 2011), has led to additional work on the importance of AOM in freshwater ecosystems. Recent evidence from freshwater lakes suggests that AOM coupled to both sulfate reduction and iron reduction is possible, and molecular evidence points to a possible role of AOM coupled to denitrification (Borrel *et al.*, 2011 and references therein). Smemo & Yavitt (2007) also demonstrated that AOM can consume a significant fraction of gross CH_4 production in freshwater peatland soils, although the electron acceptor used was not clear. Using a ^{13}C-CH_4 isotope tracer, Blazewicz *et al.* (2012) recently demonstrated the occurrence of AOM in soils from both an Alaskan peatland and a mineral soil from Puerto Rico, although AOM consumed less than 1% of gross CH_4 production in both soils. In these experiments, rates of AOM were strongly correlated with rates of CH_4 production and both processes were inhibited by the addition of TEAs, suggesting that AOM in natural ecosystems can be mediated by archaea in reverse methanogenesis that is not coupled to TEA reduction (Blazewicz *et al.*, 2012).

The importance of humic substances in CH_4 cycling

Humic substances have been traditionally described as a heterogeneous group of high-molecular weight, aromatic, refractory organic compounds of secondary origin in soils (Sposito, 2008). Humic substances in both the dissolved and solid phases are typically considered to be at very high concentrations in wetlands (Kracht & Gleixner, 2000; Collins & Kuehl, 2001). However, recent research, albeit primarily in a terrestrial soil context, has challenged this traditional view of humic substances and suggested that it may be an artifact of the alkali extractions that have operationally defined this soil organic fraction (Kleber & Johnson, 2010; Schmidt *et al.*, 2011). Recent work using cutting-edge technologies indicate that soil ‘humus’ is composed of ‘supramolecules’ of identifiable, low-molecular weight biopolymers held together by hydrophobic interactions and hydrogen bonds (Sutton & Sposito, 2005; Kelleher & Simpson, 2006; Lehmann *et al.*, 2008). The consequences of this new view of humic substances have yet to be integrated into a modern synthesis of carbon dynamics in wetlands. However, whatever their exact chemical nature and origin, abundant phenolic-containing polymers appear to exist in peatlands in both the solid and dissolved phases (Kracht & Gleixner, 2000; D’Andrilli *et al.*, 2010; McClymont *et al.*, 2011).

In parallel with this revision in the definition of humic substances, research in the last two decades strongly suggests that electron transfers mediated by organic matter are important processes in many wetland soils (Sposito, 2011). The veracity of this research is not dependent on the revised understanding of humic chemical structure described above, as much of it has used natural organic matter rather than alkali-extracted humic and fulvic acids. Furthermore, the new view of humic substances as supramolecules of identifiable biopolymers in no way precludes the possibility of electron transfers. Lovley *et al.* (1996) were the first to demonstrate that humic substances can serve as organic TEAs. In their model, the microbially mediated reduction in an oxidized humic substance (HS_{OX}) is coupled to the oxidization of an organic electron donor such as acetate. The reduced humic substance (HS_{RD}) could subsequently serve as an electron shuttle for the reduction in Fe(III) (Fig. 5). Subsequently, microbes capable of this process have been isolated from a number of anaerobic environments, including wetlands (Coates *et al.*, 1998, 2002). It also seems that this respiratory pathway can be found in numerous microbial groups in addition to the metal reducers, including fermenters (Benz *et al.*, 1998), sulfate reducers, and methanogens (Cervantes *et al.*, 2002). Humic substances can also be reduced abiotically coupled to the oxidation of sulfide (Heitmann & Blodau, 2006), which may play a role in the rapid sulfur cycling observed in many freshwater peatlands (Fig. 5). As mentioned above, a similar abiotic reduction in oxidized humics coupled to the anaerobic oxidation of CH_4 has also been proposed (Smemo & Yavitt, 2011).

Quinone moieties have a dominant role in electron transfer in organic matter (Scott *et al.*, 1998; Nurmi & Tratnyek, 2002; Wolf *et al.*, 2009), although additional chemical structures likely have the ability to accept or donate electrons as well (Struyk & Sposito, 2001; Ratasuk & Nanny, 2007; Hernández-Montoya *et al.*, 2012).

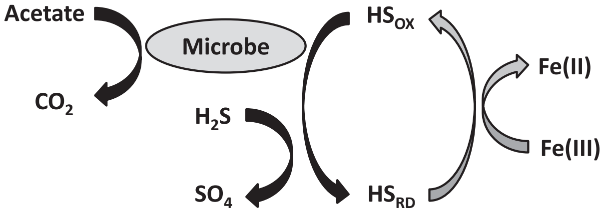

Fig. 5 Conceptual diagram of humic substance reduction. Microbes reduce oxidized humic substances (HS_{OX}) as an organic terminal electron acceptor coupled to the oxidation of simple organic electron donors (e.g. acetate). This humic reduction can also occur abiotically resulting in the oxidation of reduced sulfur species. Reduced humic substances (HS_{RD}) can also shuttle electrons to oxidized forms of Fe(III) driving subsequent iron reduction.

Thermodynamic calculations using anthraquinone-2,6-disulfonate (AQDS), a quinone molecule often used as a homologue for humic chemistry, suggest that the thermodynamic favorability of humic reduction is intermediate between Fe(III) and sulfate reduction (Cervantes *et al.*, 2000). Thus, the presence of oxidized humics as TEAs should competitively suppress CH_4 production based on thermodynamics (Fig. 4), and a number of researchers have hypothesized that the microbial reduction in humics may contribute to unexplained high CO_2 and low CH_4 production in wetland soils (Segers, 1998; Neubauer *et al.*, 2005; Heitmann *et al.*, 2007; Keller & Bridgham, 2007).

In support of this hypothesis, there is a growing body of experimental evidence suggesting that humic reduction may play a key role in regulating anaerobic carbon cycling and CH_4 dynamics in wetland environments. For example, the addition of the humic analog AQDS to an arctic peat soil stimulated microbial CO_2 production (Lipson *et al.*, 2010). Research in a Canadian peatland demonstrated that dissolved humic substances contributed either directly (through microbial humic reduction) or indirectly (through the reoxidation of dissolved sulfur) to high $CO_2 : CH_4$ production ratios (Heitmann & Blodau, 2006; Heitmann *et al.*, 2007; Blodau & Deppe, 2012). AOM coupled to humic reduction could also help explain this pattern. However, most humic substances in wetlands are found in the solid-phase rather than the dissolved pool (Stevenson, 1994), and it has been hypothesized that the reduction in solid-phase, soil-associated humics may play a more important role in anaerobic carbon cycling. Substantial recent evidence supports this hypothesis. Roden *et al.* (2010) experimentally demonstrated that bacteria can transfer electrons to solid-phase humic substances in a wetland soil, and Scott *et al.* (1998) demonstrated that the electron accepting capacity of humics extracted from soils is greater than that of dissolved humics in a number of systems. Humic acids extracted from wetland soils were capable of altering the $CO_2 : CH_4$ production ratios in anaerobic incubations (Keller *et al.*, 2009), although, to date, CO_2 production by the use of organic TEAs has not been demonstrated conclusively.

Important research questions remain to be answered on this topic, such as: How important are organic TEAs in driving anaerobic mineralization and CH_4 dynamics under *in situ* conditions in the diversity of types of wetlands that exist on the landscape (e.g. fen vs. bog vs. mineral soil wetlands)? What are the organic moieties responsible for electron transfer in wetlands and what are their source(s)? Do organic molecules also play a crucial inhibitory role in anaerobic carbon cycling and CH_4 production beyond their role as TEAs in wetlands? The next section addresses this last critical question.

Why do some wetlands produce so little CH_4?

The fraction of mineralized carbon that is CH_4, and the controls over that efficiency, in wetlands are important questions given the importance of these systems as a global source of atmospheric CH_4 and their potential sensitivity to future global change. In an exclusively fermentative and methanogenic system (i.e. without respiration via TEAs), the $CO_2 : CH_4$ ratio of the end products of anaerobic carbon mineralization should be ca. 1 : 1 (Conrad, 1999). However, this ratio is typically much greater than 1 : 1 in wetland soils and varies by several orders of magnitude among different types of wetlands, with anaerobic incubations of bog soils often resulting in particularly high $CO_2 : CH_4$ ratios despite their low concentrations of inorganic TEAs (Updegraff *et al.*, 1995; Bridgham *et al.*, 1998; van Hulzen *et al.*, 1999; Vile *et al.*, 2003b; Yavitt & Seidman-Zager, 2006; Keller & Bridgham, 2007; Galand *et al.*, 2010). A likely partial reason for this phenomenon is the importance of organic TEAs in anaerobic respiration, as discussed above. However, the use of organic TEAs is insufficient to explain these high $CO_2 : CH_4$ ratios which persist even after prolonged anaerobic incubations when all organic TEAs would have been consumed (e.g. Bridgham *et al.*, 1998; Yavitt & Seidman-Zager, 2006; Ye *et al.*, 2012).

Another potential explanation for high $CO_2 : CH_4$ ratios is the buildup of fermentation byproducts (Vile *et al.*, 2003b; Galand *et al.*, 2010) if they are not eventually converted into CH_4, and acetate in particular has often been observed to accumulate in peatlands, particularly in bogs (Shannon & White, 1996; Duddleston *et al.*, 2002; Keller & Bridgham, 2007; Ye *et al.*, 2012). This obviously begs the questions of why acetoclastic methanogens do not quickly consume this acetate. The acetoclastic pathway of methanogenesis is typically dominant in most aquatic ecosystems (Conrad, 1999), including minerotrophic peatlands (e.g. fens), but the hydrogenotrophic pathway dominates in many ombrotrophic bogs (Duddleston *et al.*, 2002; Galand *et al.*, 2005; Keller & Bridgham, 2007). It has thus been suggested that the low pH of bogs causes a fundamental disconnect between acetogenesis and acetoclastic methanogenesis (Duddleston *et al.*, 2002; Yavitt & Seidman-Zager, 2006; Keller & Bridgham, 2007; Kotsyurbenko *et al.*, 2007). We recently demonstrated that while pH is the predominant control over acetogenesis and CO_2 production across a wide variety of peatlands, low pH was insufficient to explain the low CH_4 production efficiency in more ombrotrophic sites even though the acetoclastic pathway of methanogenesis was dominant in all sites (Ye *et al.*, 2012). After eliminating other possibilities, Ye *et al.* (2012) hypothesized that there is some fundamental inhibitory substance in ombrotrophic peatlands that inhibits methanogenesis in these sites, and suggested that phenolic/aromatic substances are the most likely candidate.

In addition to the effects of these substances in their role as organic TEAs, they also appear to have a direct toxic effect on many microbes. For example, the addition of a 'humic'-rich peat extract was found to be inhibitory to CO_2 production, sulfate reduction, and methanogenesis, but not to acetogenesis in a bog soil (Minderlein & Blodau, 2010). Cervantes *et al.* (2000) suggested methanogens may be particularly sensitive to this toxic effect.

There is suggestive evidence that the toxic effects observed in many peatlands may result from organic chemicals derived from *Sphagnum* mosses. This genus is a dominant component of the plant community in many peatlands, and particularly in more ombrotrophic peatlands. While these plants contain no lignin, they have high concentrations of unique polyphenolic compounds including sphagnum acid (*p*-hydroxy-*β*[carboxymethyl]-cinnamic acid) (Rasmussen *et al.*, 1995; McClymont *et al.*, 2011), as well as the cell wall polysaccharide sphagnan which acidifies its environment (Stalheim *et al.*, 2009). *Sphagnum* has long been known to have important antibiotic properties (van Breemen, 1995; Verhoeven & Toth, 1995; Stalheim *et al.*, 2009). Moreover, Alaskan peatlands that contain *Sphagnum* have lower rates of methanogenesis, methanogenesis occurs primarily through the hydrogenotrophic pathway, there are very few acetoclastic methanogens present, and acetate accumulates in porewater (Rooney-Varga *et al.*, 2007; Hines *et al.*, 2008). These observations have far reaching implications. *Sphagnum*-dominated peatlands may have limited ability to increase CH_4 emissions in a warmer climate if methanogenesis is fundamentally constrained by inhibitory organic compounds. However, experimental climate manipulations have shown that there are increases in vascular plant cover and decreases in moss cover with warming in the arctic (Elmendorf *et al.*, 2012) and with warming and drying in boreal peatlands (Weltzin *et al.*, 2003), which may eventually eliminate the toxicity constraint of methanogenesis and lead to a very large indirect positive temperature response.

Finally, it is important to emphasize how poorly studied fermentation processes are in natural wetlands (e.g. Bräuer *et al.*, 2004; Drake *et al.*, 2009; Galand *et al.*, 2010; Ye *et al.*, 2012), despite their central importance in anaerobic mineralization and methanogenesis. In addition, other processes may be of greater importance than previously thought. For example, homoacetogenesis (i.e. the conversion of $CO_2 + H_2 \rightarrow$ acetate; Fig. 4) has been rarely studied in peatlands because it is thought to be thermodynamically unfavorable, but it may be more important than previously thought (Drake *et al.*, 2009; Hädrich *et al.*, 2012). This process should favor the acetoclastic pathway of methanogenesis over the hydrogenotrophic pathway to the extent that it is found to important in other peatlands. Given the evidence presented above that acetoclastic methanogenesis appears to be severely inhibited in many wetlands, these findings can have important implications for global CH_4 production.

Methanogen community dynamics

As discussed above, CH_4 emissions from wetlands represent the balance between methanogenesis and methanotrophy. While the microbial community dynamics of both processes are important for understanding CH_4 fluxes, others have reviewed the ecology and biology of aerobic methanotrophs (Le Mer & Roger, 2001; Trotsenko & Murrell, 2008; Semrau *et al.*, 2010; Borrel *et al.*, 2011). As several aspects of the phylogeny, biochemistry, and ecology of methanogens have been reviewed elsewhere (Liu & Whitman, 2008), we focus here on recent advances in the understanding of methanogen community dynamics in freshwater ecosystems.

Methanogens are a phylogenetically cohesive group of microbes from the domain Archaea. They exhibit a somewhat close congruency between phylogeny and the presence of the hydrogenotrophic or acetoclastic metabolic pathways in cultured species, and putatively in related uncultured taxa. Only members of the Methanosaetaceae and Methanosarcinaceae families are acetoclastic, whereas all other methanogen families are hydrogenotrophic (Fig. 6), although some

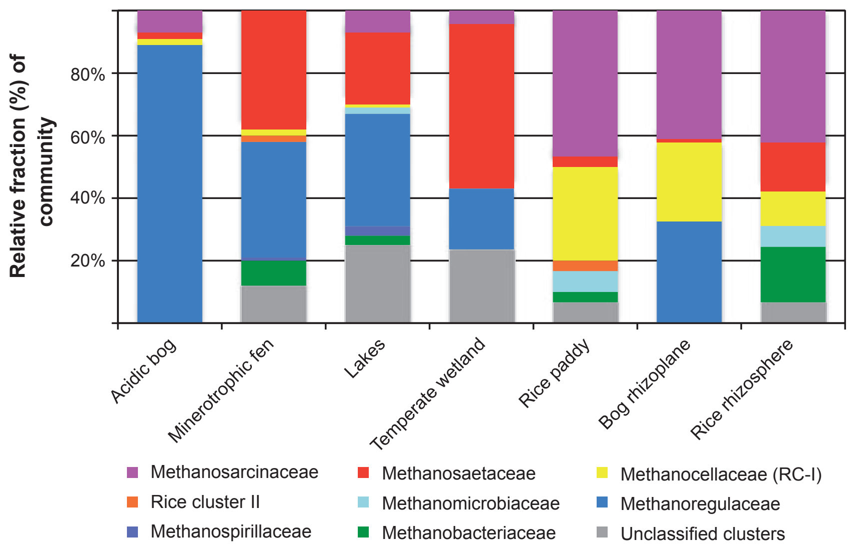

Fig. 6 Methanogenic community structure among different ecosystems or root-associated niches within an ecosystem. *Y*-axis represents the fraction (%) of each group in 16S rRNA gene-derived clone libraries. Methanogenic groups were classified at the family level plus uncultured clusters. Data were summarized from previous reports taken as representative samples of: acidic bog (Cadillo-Quiroz *et al.*, 2006), minerotrophic fen (Cadillo-Quiroz *et al.*, 2008), rice paddy soil (Lueders & Friedrich, 2000), temperate wetland (Castro *et al.*, 2004), lakes (Borrel *et al.*, 2011), root surface (rhizoplane) in acidic bog (Cadillo-Quiroz *et al.*, 2010), and root-associated soil (rhizosphere) in rice paddy (Chin *et al.*, 2004).

hydrogenotrophic methanogens require acetate for growth but do not make it into CH_4 (Bräuer *et al.*, 2006; Liu & Whitman, 2008; Sakai *et al.*, 2012). Methanosarcinaceae are the most metabolically versatile group of methanogens, consuming acetate and capable of using methanol, methylamines, and for some terrestrial species also H_2 (Galagan *et al.*, 2002; Liu & Whitman, 2008). However, there is no evidence that Methanosarcinaceae play a quantitatively important role in hydrogenotrophic methanogenesis in wetlands.

The composition and dynamics of methanogenic communities are an important yet often overlooked potential control of CH_4 production. How community composition affects the response to fine and large-scale ecosystem controls needs to be considered to better understand the spatial and temporal variability in CH_4 production. Do the same methanogens inhabit different types of aquatic systems? Does methanogen composition vary among different niches within an ecosystem? Are all methanogenic groups similarly susceptible to the same ecosystem-level controls? In this section, we review studies on community composition within and between sites, distribution of methanogenic groups, community dynamics, and recent reports on the relationship between gene transcription and methanogenesis. In all cases, there is a need for further research to evaluate the role of methanogen composition and dynamics as a control of ecosystem CH_4 dynamics.

Methanogen diversity and community composition among ecosystems

Molecular surveys using phylogenetic or functional gene markers (i.e. 16S rRNA or Methyl Coenzyme M Reductase A [*mcrA*] gene, respectively) have provided *in situ* community composition data from a variety of environments, including lake sediments (Borrel *et al.*, 2011; Grossart *et al.*, 2011), temperate wetlands (Castro *et al.*, 2004), peatlands (Juottonen *et al.*, 2005; Cadillo-Quiroz *et al.*, 2006, 2008), tundra and permafrost (Ganzert *et al.*, 2007; Metje & Frenzel, 2007), estuarine and marine sediments (Purdy *et al.*, 2002), and rice paddies (Krüger *et al.*, 2005). Community composition is generally distinct among ecosystems (Fig. 6). Other studies not included in Fig. 6 because they used different molecular approaches also support this observation (Kemnitz *et al.*, 2004; Juottonen *et al.*, 2005; Clementino *et al.*, 2007; Kim *et al.*, 2008; Steinberg & Regan, 2008).

Acidic bogs contain the most uneven, least diverse community dominated by the novel family of hydrogenotrophic methanogens Methanoregulacea (Fig. 6; Galand *et al.*, 2005; Bräuer *et al.*, 2006; Sakai *et al.*, 2012). Community differences are also striking when comparing geographically close but ecologically contrasting sites, as in the case of studies looking at bogs vs. minerotrophic fens in upstate New York, USA in Fig. 6 (Cadillo-Quiroz *et al.*, 2006, 2008). In addition to members of Methanoregulaceae, acetoclastic methanogens from the Methanosaetacea are a codominant fraction in the fen. Acetoclastic methanogens increase in relative abundance from less than 10% in bogs to 40% or more in the fen. This supports the observed functional shift in metabolic pathways, with hydrogenotrophic methanogenesis often being dominant in bogs and acetoclastic methanogenesis being dominant in fens, as discussed above (*Why do some wetlands produce so little* CH_4*?*). A study of archael diversity of peatlands in Alaska and Massachusetts, USA not only supports this trend across the ombrotrophic-minerotrophic gradient, but also suggested that temperature is an important control over methanogenesis pathways and methanogen community structure (Rooney-Varga *et al.*, 2007). Importantly, the two acetoclastic families were either not detected (Methanosarcinaceae) or were at very low abundance (Methanosaetaceae) in the Alaskan sites, and no CH_4 was produced by the acetoclastic pathway in the Alaskan bog sites despite significant rates of acetate production and accumulation (Rooney-Varga *et al.*, 2007; Hines *et al.*, 2008).

In general, current studies suggest the communities from lakes and other wetlands are more similar to minerotrophic fens (Fig. 6) with acetoclastic methanogens as an important or dominant fraction. However, lakes and wetlands differ in the relative proportions of Methanoregulaceae, Methanosaetacea, and uncultured putative methanogens.

Unique sequence clusters are commonly reported in freshwater ecosystems (Auguet *et al.*, 2009; Borrel *et al.*, 2011), and their putative methanogen classification and role in ecosystems needs to be further explored. A recent report from Alaska's permafrost exemplifies this point. A novel putative methanogen group was dominant in melting permafrost samples and a nearly complete genome reconstruction of the uncultured group was achieved (Mackelprang *et al.*, 2011); nevertheless, the CH_4 contribution, physiology, and basis for its dominance in frozen soil remain to be established.

Even though both hydrogenotrophic and acetoclastic methanogens are present in rice fields, the dominant groups differ from those observed in natural sites. Roughly a third of the community in rice soils can be made up of Methanocellacea, formerly known as Rice Cluster I, a hydrogenotrophic group isolated from rice soils (Sakai *et al.*, 2012). The metabolically diverse Methanosarcinacea are the other codominant methanogens in rice paddies. Drying-flooding dynamics and high nutrient levels in rice fields likely select for methanogens with particular features (e.g. desiccation and oxygen resistance) and substrate affinities. For instance, Methanocellaceae harbors genes for resistance to oxygen, antioxidant systems, as well as putative genes for sulfate reduction to sulfide (Sakai *et al.*, 2012). Moreover, affinity for substrate transport varies among methanogens with acetate representing a well-known example. For example, Methanosarcinaceae isolates require minimum acetate levels near 1 mM and thus should be abundant in environments with high acetate availability (Liu & Whitman, 2008). However, Methanosarcinaceae are outcompeted in low acetate conditions by the other known acetoclastic group, Methanosaetaceae, which can use acetate at concentrations as low as 5–20 μM (Liu & Whitman, 2008). In fens, lakes, and wetlands, Methanosaetaceae are commonly dominant over Methanosarcinaceae, while the opposite is true in rice paddies. Hence, variations in the ecophysiology of methanogens are likely factors accounting for differences in CH_4 production. The potential control on CH_4 production by community composition, however, has not been systematically addressed beyond broad observations on the kinetic properties of a few isolates.

As discussed above (*Rethinking anaerobic and aerobic* CH_4 *dynamics*), CH_4 activity has been found in unsaturated ecosystems. Recent findings demonstrate that methanogens persist in aerobic environments such as upland soils and phototrophic desert crusts and are readily activated when provided with anaerobic conditions *in vivo* or *in vitro* (Angel *et al.*, 2011, 2012; Frey *et al.*, 2011). Different groups of methanogens seem to inhabit oxic soils, and Methanosarcinacea has been proposed to play a major role in temporary anaerobic soils (Angel *et al.*, 2011, 2012). Oxic water columns in lakes have been found to also host a variety of active methanogens (Grossart *et al.*, 2011).

Methanogen community composition within a single ecosystem type

Multiple ecological niches harboring different methanogen communities exist within an ecosystem. The association of methanogens and plants through root surfaces or soil influenced by root activity (i.e. rhizoplane and rhizosphere) is an important control over the composition and activity of methanogens. Root surfaces exert strong effects on heterotrophic and methanogenic communities by releasing nutrient rich and highly biodegradable substrates, including organic acids such as acetate (Chin *et al.*, 2004). Differences in community structure between bulk soil and root surface in rice paddies and bogs shown in Fig. 6 exemplify this influence. The methanogenic community in the bog is dominated by hydrogenotrophic Methanoregulaceae in bulk soil, but along root surfaces the community has similar fractions of acetoclastic Methanosarcinacea and hydrogenotrophic Methanocellaceae and Methanoregulaceae (Cadillo-Quiroz *et al.*, 2010). The presence of methanogens on root surfaces is likely the norm rather than the exception in terrestrial and vegetated freshwater ecosystems. For instance, greenhouse studies with wetland plants have shown the occurrence of both hydrogenotrophic and acetoclastic methanogens in all roots tested, with the community composition being variable among plant species (Kao-Kniffin *et al.*, 2010). Thus, the many effects of roots on CH_4 dynamics described above (*Mechanisms controlling CH_4 production and emissions – the current paradigm*) are substantially mediated through microbial community controls.

Spatial variability and disturbance in ecosystems provide several niches with variable methanogenic composition and activity. For instance, a trend of lower methanogenic activity as depth increases in peatlands has been observed across sites (Galand *et al.*, 2003; Cadillo-Quiroz *et al.*, 2006; Kotiaho *et al.*, 2010). The variation in methanogenic composition along vertical profiles, however, seems to be site specific (Kotiaho *et al.*, 2010) or related to the ecological succession in a site (Cadillo-Quiroz *et al.*, 2006).

The above examples demonstrate that different methanogenic communities with different functional attributes exist within a single ecosystem. Whether this intra-site variation plays a quantitative role in regulating CH_4 production has not been systematically addressed and deserves further attention.

Temporal dynamics of methanogen composition and activity

Many studies have evaluated the temporal dynamics of CH_4 emissions, but few have evaluated temporal methanogen community dynamics. Seasonal fluctuations in temperature, moisture, substrate availability, and flooding-drying cycles are expected to drive changes in methanogenic communities. However, major community changes have not been observed when using DNA-based molecular techniques in temporal studies. Nearly constant community composition has been observed *in situ* along seasonal or flooding-drying cycles in peatlands and rice soils, respectively (Krüger *et al.*, 2005; Juottonen *et al.*, 2008; Sun *et al.*, 2012). Even long-term perturbations such as 15 years of drying in rice fields do not seem to produce major DNA community shifts (Watanabe *et al.*, 2007). This pattern can arise from the high stability of DNA even in non viable cells, high resilience and persistence of methanogens due to minimal metabolic activity under adverse conditions, or a combination of these factors. Evidence for high resilience to ecosystem fluctuations is provided by experiments where samples with low to no-methanogenic fluxes were capable of quickly producing CH_4 upon incubation (Watanabe *et al.*, 2007). Resilience and long residence are also supported by reports of methanogens inhabiting aerobic environments such as water columns and aerated soils, as discussed above. Molecular analysis through DNA provides a picture of the extant methanogenic community, but the few available temporal studies indicate it does not reflect the patterns of CH_4 flux (Watanabe *et al.*, 2007; Juottonen *et al.*, 2008).

Molecular evaluations of rRNA (ribosomal content) and messenger mRNA (transcriptional content) have the potential to better link microbial composition and function. Only a few studies have targeted rRNA or mRNA of the *mcr*A gene. In peatlands, evaluations of rRNA demonstrated shifts in the methanogenic community in contrast to the nearly invariable community structure based on DNA (Juottonen *et al.*, 2008). Also, a weak correlation between rates of methanogenesis and mRNA/DNA ratios of the mcrA gene has been found in peatland soils (Freitag & Prosser, 2009), demonstrating that it is indeed possible to use transcriptomic data as an indicator of *in situ* activity in a complex microbial community. In rice soils it has been shown that brief exposure to oxygen quickly inhibits methanogenic activity, decreasing the magnitude and abundance of *mcrA* transcripts without any alteration in the DNA community composition (Yuan *et al.*, 2011). Also, continuous dry/wet cycles in rice soils reduce methanogenic activity and methanogenic transcript levels (Ma *et al.*, 2012). Hence, evaluating methanogen communities and their activity through changes in mRNA has been shown to correlate with CH_4 production, unlike DNA-based results. The relationship between transcript levels and *in situ* activities needs to be systematically evaluated, however, for more generalized interpretations and quantitative predictions. We suggest that new research efforts should evaluate the nature and variation in the transcript/activity relationship, as well as the transcript/enzyme content relationship, in methanogen isolates as well as mixed communities.

The methanogenic community composition is variable among ecosystems, is variable among niches within ecosystems, and is seasonally variable among different environmental conditions at the transcriptional (mRNA) and activity level. The role of such variability as a control for methanogenic activity remains largely unknown and needs further evaluation. One of the frontiers in microbial ecology is to determine the extent to which knowledge of microbial community structure, or measurements of their cellular activity, is necessary to predict the variability in ecosystem function, vs. microbial communities being merely a passive reflection of larger ecosystem physicochemical controls. This is true of methanogens and methanotrophs for CH_4 dynamics, as well as other microbially mediated biogeochemical processes.

Modeling biogenic CH_4 emissions from wetlands

State-of-the-art modeling

To quantify global wetland CH_4 emissions, process-based biogeochemistry models with different complexities have been developed and applied at regional and global scales (e.g. Cao *et al.*, 1995; Potter, 1997; Walter & Heimann, 2000; Zhuang *et al.*, 2004, 2006; Wania *et al.*, 2010; Riley *et al.*, 2011; Melton *et al.*, 2012). Another set of process-based models designed for the heuristic understanding CH_4 cycling with detailed processes and mechanisms are often parameterized and applied at a site-level based upon extensive physical, chemical, and biological empirical data (e.g. Segers & Leffelaar, 2001a, b; Segers *et al.*, 2001; Grant & Roulet, 2002; Zhang *et al.*, 2002). Applying the latter set of models to quantify highly heterogeneous wetland ecosystems at regional and global scales is often limited by the lack of spatially explicit information for model input.

As discussed above (*A global accounting of wetland [and other] atmospheric CH_4 sources*), the boreal and arctic zones, the tropics, and rice paddies have been identified as major CH_4 sources. However, the processes of and controls on CH_4 cycling differ among these ecosystems, which provide both challenges and opportunities for modeling efforts (Zhuang *et al.*, 2009; Melton *et al.*, 2012). Recently developed process-based CH_4 models have become more specialized to adequately represent CH_4 production, oxidation, and transport by considering various factors and controls unique to those processes in various ecosystem types. For example, Lu & Zhuang (2012) considered more detailed freeze-thawing dynamics and highly heterogeneous water table depth distribution on CH_4 production and emissions from arctic wetlands. With the recognition that both bubbling and diffusion of CH_4 between soils and the atmosphere are affected by atmospheric and soil column pressure, Tang *et al.* (2010) incorporated pressure effects with more physical and chemical processes-oriented algorithms into an extant CH_4 model (Zhuang *et al.*, 2004). While most existing CH_4 models have not considered dynamic vegetation effects (e.g. the effects on plant-aided transport), Wania *et al.* (2010) made a significant advancement by linking a dynamical vegetation model with a CH_4 model. Lakes are another major CH_4 emission source (Fig. 1). To quantify emissions from aquatic ecosystems, a few lake physical and biogeochemistry models have also been developed (e.g. Kessler *et al.*, 2012; Subin *et al.*, 2012).

Biogeochemistry models generally predict that future CH_4 emissions from wetlands will increase. For instance, using a simple hydrological model and a CH_4 emission model, Gedney *et al.* (2004) predicted that the global wetland emissions would be 500–600 Tg yr^{-1} by 2100. Similarly, Zhuang *et al.* (2006) estimated that emissions from northern high latitudes would double in response to climate change in the 21st century. In comparison, Shindell *et al.* (2004) estimated an increase in annual average wetland CH_4 emissions from 156 to 277 Tg yr^{-1}, a rise of 78%, under doubled atmospheric CO_2 condition, incorporating a simple wetland distribution and CH_4 emissions model into a general circulation model. A recent study indicated that the annual CH_4 emissions will increase by 6–51% relative to present conditions in northern Eurasia under various wetland extent datasets and climate scenarios by the end of the 21st century (Zhu *et al.*, 2011). All of the models examined in the inter-model comparison by Melton *et al.* (2012) showed large increases in CH_4 emissions due to increased atmospheric CO_2 concentrations, but effects of increased temperature and precipitation were more variable.

Limitations of existing modeling and future challenges

The large uncertainty of CH_4 emissions from global aquatic ecosystems is due to several factors. First, there are a number of important controls over CH_4 production, consumption, and transport that have not been, or are inadequately, incorporated into existing CH_4 biogeochemistry models. Some of these controls are universal, whereas others are unique to different source regions. Second, significant errors in regional and global emission estimates are derived from large spatial-scale extrapolations from highly heterogeneous and, often poorly mapped, wetland complexes. Third, the limited number of observations of CH_4 fluxes and their associated environmental variables loosely constrains the parameterization of process-based biogeochemistry models.

One good example of an insufficiently modeled process is the effects of thawing permafrost on the complex dynamics of hydrology and carbon substrates in the Arctic, which significantly affect net CH_4 emissions (Walter *et al.*, 2006). The geomorphic effects of permafrost thaw on the dynamics of the area and biogeochemistry in lakes have just been modeled at a site level (Walter *et al.*, 2006; Khvorostyanov *et al.*, 2008; Kessler *et al.*, 2012). Similarly, the observed effects of thawing and freezing of soils and snow melting on CH_4 production and diffusion should also be considered in process-based modeling (e.g. Tokida *et al.*, 2007b; Mastepanov *et al.*, 2008).

A number of critical chemical controls of CH_4 production and consumption, including the dynamics of redox potential, soil pH, and carbon substrates in the soil profile, are inadequately represented in current models (e.g. Zhuang *et al.*, 2004). This is due to the fact that these chemical dynamics are difficult to model as each is determined by a series of chemical reactions. As a result, most current models might treat those chemical controls as constant (e.g. soil pH) or model them with relatively simple functions with only a few factors considered (e.g. redox potential). Most models use net primary production as an index to represent substrate availability for CH_4 production, thus they do not consider recalcitrant carbon in deep soils or in permafrost. Moreover, substrate quality within a soil profile can also vary in wetlands. In addition to the effect of this on the production of substrates for methanogenesis (Fig. 4), these variations can result in soils having different temperature responses (Davidson & Janssens, 2006), with the Q_{10} of CH_4 production ranging widely from 1 to 28 (van Hulzen *et al.*, 1999). To accurately quantify the temperature response requires field experimentalists and modelers to develop more precise Q_{10} values for different wetland ecosystems.

In addition, the effects of atmospheric deposition of nitrogen and sulfur on both methanogenesis and methanotrophy (e.g. Eriksson *et al.*, 2010; Pancotto *et al.*, 2010) should also be considered in future CH_4 modeling. For example, Gauci *et al.* (2004) found that the inhibitive effects of atmospheric sulfur deposition may counteract a climate-induced growth in CH_4 production from wetlands, reducing current CH_4 emissions by 8% and emissions in 2030 by 15%.

Current biogeochemistry models have not incorporated microbial community dynamics, and to do so will be a formidable task for at least two reasons. First, it is not yet clear how to relate the community dynamics (types and abundance) and rates of cell activity (transcriptomics and possibly proteomics) of methanogens and methanotrophs into improved predictions of *in situ* rates of methanogenesis and methanotrophy. It is also not clear to what extent the community dynamics of other groups of microbes with their many complex interactions (e.g. Bethke *et al.*, 2011) need to be incorporated into models. This obstacle is significant but tractable, and we discuss the current state of knowledge on this topic above (*Methanogen community dynamics*). Second, it is very unclear how, or if it is even possible, to incorporate the fine-scale spatial and temporal variability in microbial dynamics into regional and global models.

In addition, better modeling and characterization of plant community structure will improve predictions of CH_4 emissions as different plant species have different substrate quality, above- and belowground production dynamics, rhizosphere effects, and plant-mediated transport. For instance, better characterizing differences between vascular (e.g. sedge) and nonvascular (e.g. mosses) plants is important to modeling plant-mediated transport emissions. Moreover, *Sphagnum* mosses may also have important effects on organic TEAs and inhibitory substances (see *Why do some wetlands produce so little CH_4?*).

When biogeochemistry models are applied to regional and global scales, large errors can arise due to highly heterogeneous landscapes. This is true, in particular, of the vast area of northern high latitude wetlands, which are often characterized by fine-scale hummock and hollow microtopography. Current models generally lack the capability to account for the effects of microtopography on hydrological, chemical, and biological dynamics that are essential to CH_4 cycling (e.g. Bubier *et al.*, 1993). Another challenge is modeling the dynamic spatial extent of wetlands and lakes due to changing climate and thawing permafrost. Recent progress in modeling water table fluctuations that incorporate groundwater dynamics, climate, and connections with rivers and ocean systems at a relatively high resolution (e.g. 1 km) is promising for better CH_4 modeling (e.g. Miguez-Macho *et al.*, 2008).

As discussed above (*A global accounting of wetland (and other) atmospheric CH_4 sources*), poorly constrained estimates of wetland and lake area are a major uncertainty in estimating current and future CH_4 emissions. However, a recent advancement in CH_4 modeling is the ability to use satellite data to characterize seasonal variation in wetland inundation (e.g. Ringeval *et al.*, 2010; Melton *et al.*, 2012). However, many wetlands still emit large amounts of CH_4 when the water table is below the surface, especially those wetlands with a high vascular plant component and thus a domination of plant-mediated CH_4 transport from the soil to the atmosphere. Some models have internal hydrological routines to estimate wetland area and so are not dependent on (poorly defined) external inputs of wetland area, but these models seem to vastly overestimate wetland area (Melton *et al.*, 2012). To characterize the distribution and extent of the global wetlands and lakes, including the seasonality of their water table levels, at sufficiently high resolution should be a modeling priority.

Finally, the observational data related to processes of and controls on CH_4 production, consumption, and transport are still limited. Measurements of net CH_4 emissions are only useful to constrain a few model parameters. Ideally, both measurement of fluxes and the factors that control the various processes of CH_4 cycling are needed to better constrain the uncertainty of the parameters related to the particular process. For instance, current biogeochemistry models are not able to partition well the fluxes due to diffusion, bubbling, and plant-mediated transport pathways. Lack of knowledge of the importance of these transport pathways can contribute to a large error in total CH_4 emissions.

Summary

Our ability to adequately include wetlands in earth systems models in large part hinges on our understanding of CH_4 dynamics in the context of environmental change. We have demonstrated above that CH_4 cycling in natural ecosystems and rice fields is regulated by a complex set of microbial, plant, and physicochemical controls, some of which are reasonably well understood and some of which are very poorly known. There have been substantial advancements in recent years in the estimation of global and regional atmospheric CH_4 fluxes, understanding the biogeochemical controls of CH_4 dynamics, and in the modeling of CH_4 dynamics. However, much research remains to be carried out, and we have attempted to highlight these gaps in our knowledge in this review. Given the potential importance of CH_4 as a feedback to anthropogenic climate change and other global perturbations, it is of paramount importance that researchers continue to address these knowledge gaps.

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References

Andersen BL, Bidoglio G, Leip A, Rembges D (1998) A new method to study simultaneous methane oxidation and methane production in soils. *Global Biogeochemical Cycles*, **12**, 587–594.

Angel R, Matthies D, Conrad R (2011) Activation of methanogenesis in arid biological soil crusts despite the presence of oxygen. *PLoS ONE*, **6**, e20453. doi: 10.1371/journal.pone.0020453

Angel R, Claus P, Conrad R (2012) Methanogenic archaea are globally ubiquitous in aerated soils and become active under wet anoxic conditions. *The ISME Journal*, **6**, 847–862.

Aselmann I, Crutzen PJ (1989) Global distribution of natural freshwater wetlands and rice paddies, their net primary productivity, seasonality and possible methane emissions. *Journal of Atmospheric Chemistry*, **8**, 307–359.

Auguet J-C, Barberan A, Casamayor EO (2009) Global ecological patterns in uncultured Archaea. *The ISME Journal*, **4**, 182–190.

Aydin M, Verhulst KR, Saltzman ES *et al.* (2011) Recent decreases in fossil-fuel emissions of ethane and methane derived from firn air. *Nature*, **476**, 198–201.

Barnes RO, Goldberg ED (1976) Methane production and consumption in anoxic marine sediment. *Geology*, **4**, 297–300.

Bartlett KB, Bartlett DS, Harriss RC, Sebacher DI (1987) Methane emissions along a salt marsh salinity gradient. *Biogeochemistry*, **4**, 183–202.

Basiliko N, Stewart H, Roulet N, Moore T (2012) Do root exudates enhance peat decomposition? *Geomicrobiology Journal*, **29**, 374–378.

Bastviken D, Tranvik LJ, Downing JA, Crill PM, Enrich-Prast A (2011) Freshwater methane emissions offset the continental carbon sink. *Science*, **331**, 50.

Beal EJ, House CH, Orphan VJ (2009) Manganese- and iron-dependent marine methane oxidation. *Science*, **325**, 184–187.

Benz M, Schink B, Brune A (1998) Humic acid reduction by *Propionibacterium freudenreichii* and other fermenting bacteria. *Environmental Microbiology*, **64**, 4507–4512.

Bethke CM, Sanford RA, Kirk MF, Jin QS, Flynn TM (2011) The thermodynamic ladder in geomicrobiology. *American Journal of Science*, **311**, 183–210.

Blazewicz SJ, Petersen DG, Waldrop MP, Firestone MK (2012) Anaerobic oxidation of methane in tropical and boreal soils: ecological significance in terrestrial methane cycling. *Journal of Geophysical Research*, **117**, G02033. doi: 10.1029/2011jg001864

Blodau C (2002) Carbon cycling in peatlands – a review of processes and controls. *Environmental Reviews*, **10**, 111–134.

Blodau C, Deppe M (2012) Humic acid addition lowers methane release in peats of the Mer Bleue bog, Canada. *Soil Biology and Biochemistry*, **52**, 96–98.

Bloom AA, Lee-Taylor J, Madronich S, Messenger DJ, Palmer PI, Reay DS, McLeod AR (2010a) Global methane emission estimate from ultraviolet irradiation of terrestrial plant foliage. *New Phytologist*, **187**, 417–425.

Bloom AA, Palmer PI, Fraser A, Reay DS, Frankenberg C (2010b) Large-scale controls of methanogenesis inferred from methane and gravity spaceborne data. *Science*, **327**, 322–325.

Blunier T, Chappellaz J, Schwander J, Stauffer B, Raynaud D (1995) Variations in atmospheric methane concentration during the Holocene epoch. *Nature*, **374**, 46–49.

Boetius A, Ravenschlag K, Schubert CJ *et al.* (2000) A marine microbial consortium apparently mediating anaerobic oxidation of methane. *Nature*, **407**, 623–626.

Borrel G, Jézéquel D, Biderre-Petit C *et al.* (2011) Production and consumption of methane in freshwater lake ecosystems. *Research in Microbiology*, **162**, 832–847.

Bouchard V, Frey SD, Gilbert JM, Reed SE (2007) Effects of macrophyte functional group richness on emergent freshwater wetland functions. *Ecology*, **88**, 2903–2914.

Bousquet P, Ciais P, Miller JB *et al.* (2006) Contribution of anthropogenic and natural sources to atmospheric methane variability. *Nature*, **443**, 439–443.

Bousquet P, Ringeval B, Pison I *et al.* (2011) Source attribution of the changes in atmospheric methane for 2006–2008. *Atmospheric Chemistry and Physics*, **11**, 3689–3700.

Bräuer SL, Yavitt JB, Zinder SH (2004) Methanogenesis in McLean Bog, an acidic peat bog in upstate New York: stimulation by H_2/CO_2 in the presence of rifampicin, or by low concentrations of acetate. *Geomicrobiology Journal*, **21**, 433–443.

Bräuer SL, Cadillo-Quiroz H, Yashiro E, Yavitt JB, Zinder SH (2006) Isolation of a novel acidiphilic methanogen from an acidic peat bog. *Nature*, **442**, 192–194.

van Breemen N (1995) How *Sphagnum* bogs down other plants. *Trends in Ecology and Evolution*, **10**, 270–275.

Bridgham SD, Updegraff K, Pastor J (1998) Carbon, nitrogen, and phosphorus mineralization in northern wetlands. *Ecology*, **79**, 1545–1561.

Bridgham SD, Megonigal JP, Keller JK, Bliss NB, Trettin C (2006) The carbon balance of North American wetlands. *Wetlands*, **26**, 889–916.

Bubier JL, Costello A, Moore TR, Roulet NT, Savage K (1993) Microtopography and methane flux in boreal peatlands, northern Ontario, Canada. *Canadian Journal of Botany*, **71**, 1056–1063.

Cadillo-Quiroz H, Bräuer S, Yashiro E, Sun C, Yavitt J, Zinder S (2006) Vertical profiles of methanogenesis and methanogens in two contrasting acidic peatlands in central New York State, USA. *Environmental Microbiology*, **8**, 1428–1440.

Cadillo-Quiroz H, Yashiro E, Yavitt JB, Zinder SH (2008) Characterization of the archaeal community in a minerotrophic fen and terminal restriction fragment length polymorphism-directed isolation of a novel hydrogenotrophic methanogen. *Applied and Environmental Microbiology*, **74**, 2059–2068.

Cadillo-Quiroz H, Yavitt J, Zinder S, Thies J (2010) Diversity and community structure of *Archaea* inhabiting the rhizoplane of two contrasting plants from an acidic bog. *Microbial Ecology*, **59**, 757–767.

Caldwell SL, Laidler JR, Brewer EA, Eberly JO, Sandborgh SC, Colwell FS (2008) Anaerobic oxidation of methane: mechanisms, bioenergetics, and the ecology of associated microorganisms. *Environmental Science and Technology*, **42**, 6791–6799.

Cao M, Dent J, Heal O (1995) Modeling methane emissions from rice paddies. *Global Biogeochemical Cycles*, **9**, 183–195.

Castro H, Ogram A, Reddy KR (2004) Phylogenetic characterization of methanogenic assemblages in eutrophic and oligotrophic areas of the Florida Everglades. *Applied and Environmental Microbiology*, **70**, 6559–6568.

Cervantes FJ, van der Velde S, Lettinga G, Field JA (2000) Competition between methanogenesis and quinone respiration for ecologically important substrates in anaerobic consortia. *FEMS Microbiology Ecology*, **34**, 161–171.

Cervantes FJ, de Bok FAM, Duong-Dac T, Stams AJM, Lettinga G, Field JA (2002) Reduction of humic substances by halorespiring, sulphate-reducing and methanogenic microorganisms. *Environmental Microbiology*, **4**, 51–57.

Chanton JP, Glaser PH, Chasar LS *et al.* (2008) Radiocarbon evidence for the importance of surface vegetation on fermentation and methanogenesis in contrasting types of boreal peatlands. *Global Biogeochemical Cycles*, **22**, GB4022. doi: 10.1029/2008gb003274

Chappellaz J, Bluniert T, Raynaud D, Barnola JM, Schwander J, Stauffert B (1993a) Synchronous changes in atmospheric CH_4 and Greenland climate between 40 and 8 kyr BP. *Nature*, **366**, 443–445.

Chappellaz JA, Fung IY, Thompson AM (1993b) The atmospheric CH_4 increase since the Last Glacial Maximum. *Tellus B*, **45**, 228–241.

Cheng W, Yagi K, Sakai H, Kobayashi K (2006) Effects of elevated atmospheric CO_2 concentrations on CH_4 and N_2O emission from rice soil: an experiment in controlled-environment chambers. *Biogeochemistry*, **77**, 351–373.

Chin KJ, Lueders T, Friedrich M, Klose M, Conrad R (2004) Archaeal community structure and pathway of methane formation on rice roots. *Microbial Ecology*, **47**, 59–67.

Clementino MM, Fernandes CC, Vieira RP, Cardoso AM, Polycarpo CR, Martins OB (2007) Archaeal diversity in naturally occurring and impacted environments from a tropical region. *Journal of Applied Microbiology*, **103**, 141–151.

Coates JD, Ellis DJ, Blunt-Harris EL, Gaw CV, Roden EE, Lovley DR (1998) Recovery of humic-reducing bacteria from a diversity of environments. *Applied and Environmental Microbiology*, **64**, 1504–1509.

Coates JD, Cole KA, Chakraborty R, O'Connor SM, Achenbach LA (2002) Diversity and ubiquity of bacteria capable of utilizing humic substances as electron donors for anaerobic respiration. *Applied and Environmental Microbiology*, **68**, 2445–2452.

Collins ME, Kuehl RJ (2001) Organic matter accumulation and organic soils. In: *Wetland Soils: Genesis, Hydrology, Landscapes, and Classification* (eds Richardson JL, Vepraskas MJ), pp. 137–162. CRC Press, LLC, Boca Raton, FL.

Conrad R (1999) Contribution of hydrogen to methane production and control of hydrogen concentrations in methanogenic soils and sediments. *FEMS Microbiology Ecology*, **28**, 193–202.

Damm E, Helmke E, Thoms S, Schauer U, Nöthing E, Bakker K, Kiene RP (2010) Methane production in aerobic oligotrophic surface waters in the central Arctic Ocean. *Biogeosciences*, **7**, 1099–1108.

D'Andrilli J, Chanton JP, Glaser PH, Cooper WT (2010) Characterization of dissolved organic matter in northern peatland soil porewaters by ultra high resolution mass spectrometry. *Organic Geochemistry*, **41**, 791–799.

Davidson EA, Janssens IA (2006) Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. *Nature*, **440**, 165–173.

Denman KL, Brasseur G, Chidthaisong A *et al.* (2007) Couplings between changes in the climate system and biogeochemistry. In: *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* (eds Solomon S, Qin D, Manning M, Chen Z, Marquis M, Averyt KB, Tignor M, Miller HL), pp. 499–587. Cambridge University Press, Cambridge, UK.

Deppe M, McKnight DM, Blodau C (2010) Effects of short-term drying and irrigation on electron flow in mesocosms of a northern bog and an alpine fen. *Environmental Science and Technology*, **44**, 80–86.

Dlugokencky EJ, Bruhwiler L, White JWC *et al.* (2009) Observational constraints on recent increases in the atmospheric CH_4 burden. *Geophysical Research Letters*, **36**, L18803. doi: 10.1029/2009gl039780

Dlugokencky EJ, Nisbet EG, Fisher R, Lowry D (2011) Global atmospheric methane: budget, changes and dangers. *Philosophical Transactions of the Royal Society A-Mathematical Physical and Engineering Sciences*, **369**, 2058–2072.

Dorodnikov M, Knorr K-H, Kuzyakov Y, Wilmking M (2011) Plant-mediated CH_4 transport and contribution of photosynthates to methanogenesis at a boreal mire: a ^{14}C pulse-labeling study. *Biogeosciences*, **8**, 2365–2375.

Drake HL, Horn MA, Wust PK (2009) Intermediary ecosystem metabolism as a main driver of methanogenesis in acidic wetland soil. *Environmental Microbiology Reports*, **1**, 307–318.

Duddleston KN, Kinney MA, Kiene RP, Hines ME (2002) Anaerobic microbial biogeochemistry in a northern bog: acetate as a dominant metabolic end product. *Global Biogeochemical Cycles*, **16**, 1063–1064. doi: 10.1029/2001GB001402,2002

Dueck TA, de Visser R, Poorter H *et al.* (2007) No evidence for substantial aerobic methane emission by terrestrial plants: a ^{13}C-labelling approach. *New Phytologist*, **175**, 29–35.

Elmendorf SC, Henry GH, Hollister RD *et al.* (2012) Global assessment of experimental climate warming on tundra vegetation: heterogeneity over space and time. *Ecology Letters*, **15**, 164–175.

Eriksson T, Öquist MG, Nilsson MB (2010) Production and oxidation of methane in a boreal mire after a decade of increased temperature and nitrogen and sulfur deposition. *Global Change Biology*, **16**, 2130–2144.

Finlayson CM, Davidson NC, Spiers AG, Stevenson NJ (1999) Global wetland inventory–current status and future priorities. *Marine Freshwater Research*, **50**, 717–727.

von Fisher JC, Hedin LO (2007) Controls on soil methane fluxes: tests of biophysical mechanisms using stable isotope tracers. *Global Biogeochemical Cycles*, **21**, GB2007.

Forster P, Ramaswamy P, Artaxo P *et al.* (2007) Changes in atmospheric constituents and in radiative forcing. In: *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* (eds Solomon S, Qin D, Manning M, Chen Z, Marquis M, Averyt KB, Tignor M, Miller HL), pp. 129–234. Cambridge University Press, Cambridge, UK.

Frankenberg C, Aben I, Bergamaschi P *et al.* (2011) Global column-averaged methane mixing ratios from 2003 to 2009 as derived from SCIAMACHY: trends and variability. *Journal of Geophysical Research*, **116**, D04302. doi: 04310.01029/02010jd014849

Freitag TE, Prosser JI (2009) Correlation of methane production and functional gene transcriptional activity in a peat soil. *Applied and Environmental Microbiology*, **75**, 6679–6687.

Frey B, Niklaus PA, Kremer J, Lüscher P, Zimmermann S (2011) Heavy-machinery traffic impacts methane emissions as well as methanogen abundance and community structure in oxic forest soils. *Applied and Environmental Microbiology*, **77**, 6060–6068.

Fritz C, Pancotto VA, Elzenga JTM *et al.* (2011) Zero methane emission bogs: extreme rhizosphere oxygenation by cushion plants in Patagonia. *New Phytologist*, **190**, 398–408.

Galagan JE, Nusbaum C, Roy A *et al.* (2002) The genome of *M. acetivorans* reveals extensive metabolic and physiological diversity. *Genome Research*, **12**, 532–542.

Galand PE, Fritze H, Yrjala K (2003) Microsite-dependent changes in methanogenic populations in a boreal oligotrophic fen. *Environmental Microbiology*, **5**, 1133–1143.

Galand PE, Fritze H, Conrad R, Yrjala K (2005) Pathways for methanogenesis and diversity of methanogenic archaea in three boreal peatland ecosystems. *Applied and Environmental Microbiology*, **71**, 2195–2198.

Galand PE, Conrad R, Yrjälä K (2010) Stable carbon isotope fractionation during methanogenesis in three boreal peatland ecosystems. *Biogeosciences*, **7**, 3893–3900.

Ganzert L, Jurgens G, Munster U, Wagner D (2007) Methanogenic communities in permafrost-affected soils of the Laptev Sea coast, Siberian Arctic, characterized by 16S rRNA gene fingerprints. *FEMS Microbiology Ecology*, **59**, 476–488.

Gauci V, Matthews E, Dise N, Walter B, Koch D, Granberg G, Vile M (2004) Sulfur pollution suppression of the wetland methane source in the 20th and 21st centuries. *Proceedings of the National Academy of Sciences of the United States of America*, **101**, 12583–12587.

Gauci V, Gowing DJG, Hornibrook ERC, Davis JM, Dise NB (2010) Woody stem methane emission in mature wetland alder trees. *Atmospheric Environment*, **44**, 2157–2160.

Gedney N, Cox PM, Huntingford C (2004) Climate feedbacks from methane emissions. *Geophysical Research Letters*, **31**, L20503. doi: 20510.21029/22004GL020919

Glaser PH, Chanton JP, Morin P *et al.* (2004) Surface deformations as indicators of deep ebullition fluxes in a large northern peatland. *Global Biogeochemical Cycles*, **18**, GB1003. doi: 10.1029/2003GB002069

Gogo S, Guimbaud C, Laggoun-Défarge F, Catoire V, Robert C (2011) In situ quantification of CH_4 bubbling events from a peat soil using a new infrared laser spectometer. *Journal of Soils and Sediments*, **11**, 545–551.

Goodrich JP, Varner RK, Frolking S, Duncan BN, Crill PM (2011) High-frequency measurements of methane ebullition over a growing season at a temperature peatland site. *Geophysical Research Letters*, **38**, L07404. doi: 07410.01029/02011GL046915

Grant RF, Roulet NT (2002) Methane efflux from boreal wetlands: theory and testing of the ecosystem model Ecosys with chamber and tower flux measurements. *Global Biogeochemical Cycles*, **16**, 1054.

Grossart H-P, Frindte K, Dziallas C, Eckert W, Tang KW (2011) Microbial methane production in oxygenated water column of an oligotrophic lake. *Proceedings of the National Academy of Sciences of USA*, **108**, 19657–19661.

Guenet B, Danger M, Abbadie L, Lacroix G (2010) Priming effect: bridging the gap between terrestrial and aquatic ecology. *Ecology*, **91**, 2850–2861.

Hädrich A, Heuer VB, Herrmann M, Hinrichs K-U, Küsel K (2012) Origin and fate of acetate in an acidic fen. *FEMS Microbiology Ecology*, **81**, 339–354.

Hallam SJ, Putnam N, Preston CM, Detter JC, Rokhsar D, Richardson PM, DeLong EF (2004) Reverse methanogenesis: testing the hypothesis with environmental genomics. *Science*, **305**, 1457–1462.

Hanson RS, Hanson TE (1996) Methanotrophic bacteria. *Microbiological Reviews*, **60**, 439–476.

Heitmann T, Blodau C (2006) Oxidation and incorporation of hydrogen sulfide by dissolved organic matter. *Chemical Geology*, **235**, 12–20.

Heitmann T, Goldhammer T, Beer J, Blodau C (2007) Electron transfer of dissolved organic matter and its potential significance for anaerobic respiration in a northern bog. *Global Change Biology*, **13**, 1771–1785.

Hernández-Montoya V, Alvarez LH, Montes-Morán MA, Cervantes FJ (2012) Reduction of quinone and non-quinone redox functional groups in different humic acid samples by *Geobacter sulfurreducens*. *Geoderma*, **183**, 25–31.

Hines ME, Duddleston KN, Rooney-Varga JN, Fields D, Chanton JP (2008) Uncoupling of acetate degradation from methane formation in Alaskan wetlands: connections to vegetation distribution. *Global Biogeochemical Cycles*, **22**, GB2017. doi: 10.1029/2006GB002903

Hinrichs K-U, Boetius A (2002) The anaerobic oxidation of methane: new insights in microbial ecology and biogeochemistry. In: *Ocean Marine Systems* (eds Wefer G, Billett D, Hebbeln D, Jørgensen BB, Schlüter M, Van Weering TCE), pp. 457–477. Springer-Verlag, Berlin.

Hodson EL, Poulter B, Zimmermann NE, Prigent C, Kaplan JO (2011) The El Niño-Southern Oscillation and wetland methane interannual variability. *Geophysical Research Letters*, **38**, L08810. doi: 10.1029/2011gl046861

Hoehler TM, Alperin MJ, Albert DB, Martens CS (1994) Field and laboratory studies of methane oxidation in an anoxic marine sediment: evidence for a methanogen-sulfate reducer consortium. *Global Biogeochemical Cycles*, **8**, 451–463.

van Hulzen JB, Segers R, van Bodegom PM, Leffelaar PA (1999) Temperature effects on soil methane production: an explanation for observed variability. *Soil Biology and Biochemistry*, **31**, 1919–1929.

Hurkuck M, Althoff F, Jungkunst HF, Jugold A, Keppler F (2012) Release of methane from aeroibc soil: an indication of a novel chemical natural process? *Chemosphere*, **86**, 684–689.

Juottonen H, Galand PE, Tuittila ES, Laine J, Fritze H, Yrjala K (2005) Methanogen communities and Bacteria along an ecohydrological gradient in a northern raised bog complex. *Environmental Microbiology*, **7**, 1547–1557.

Juottonen H, Tuittila E-S, Juutinen S, Fritze H, Yrjala K (2008) Seasonality of rDNA- and rRNA-derived archaeal communities and methanogenic potential in a boreal mire. *The ISME Journal*, **2**, 1157–1168.

Kai FM, Tyler SC, Randerson JT, Blake DR (2011) Reduced methane growth rate explained by decreased Northern Hemisphere microbial sources. *Nature*, **476**, 194–197.

Kammann C, Hepp S, Lenhart K, Müller C (2009) Stimulation of methane consumption by endogenous CH_4 production in aerobic grassland soil. *Soil Biology and Biochemistry*, **41**, 622–629.

Kao-Kniffin J, Freyre DS, Balser TC (2010) Methane dynamics across wetland plant species. *Aquatic Botany*, **93**, 107–113.

Kaplan JO (2002) Wetlands at the last glacial maximum: distribution and methane emissions. *Geophysical Research Letters*, **29**, 1079. doi: 10.1029/2001gl013366

Karl DM, Tilbrook BD (1994) Production and transport of methane in oceanic particulate organic matter. *Nature*, **368**, 732–734.

Karl DM, Beversdorf L, Bjorkman KM, Church MJ, Martinez A, DeLong EF (2008) Aerobic production of methane in the sea. *Nature Geoscience*, **1**, 473–478.

Kelleher BP, Simpson AJ (2006) Humic substances in soils: are they really chemically distinct? *Environmental Science and Technology*, **40**, 4605–4611.

Keller JK, Bridgham SD (2007) Pathways of anaerobic carbon cycling across an ombrotrophic-minerotrophic peatland gradient. *Limnology and Oceanography*, **52**, 96–107.

Keller JK, Weisenhorn PB, Megonigal JP (2009) Humic acids as electron acceptors in wetland decomposition. *Soil Biology and Biochemistry*, **41**, 1518–1522.

Kemnitz D, Chin KJ, Bodelier P, Conrad R (2004) Community analysis of methanogenic archaea within a riparian flooding gradient. *Environmental Microbiology*, **6**, 449–461.

Keppler F, Hamilton JTG, Brass M, Rockmann T (2006) Methane emissions from terrestrial plants under aerobic conditions. *Nature*, **439**, 187–191.

Keppler F, Hamilton JTG, McRoberts WC, Vigano I, Brass M, Rockmann T (2008) Methoxyl groups of plant pectin as a precursor of atmospheric methane: evidence from deuterium labelling studies. *New Phytologist*, **178**, 808–814.

Keppler F, Boros M, Frankenberg C *et al.* (2009) Methane formation in aerobic environments. *Environmental Chemistry*, **6**, 459–465.

Kessler MA, Plug LJ, Anthony KMW (2012) Simulating the decadal- to millennial-scale dynamics of morphology and sequestered carbon mobilization of two thermokarst lakes in NW Alaska. *Journal of Geophysical Research-Biogeosciences*, **117**, G00M06. doi: 10.1029/2011jg001796

Kettridge N, Binley A, Green SM, Baird AJ (2011) Ebullition events monitored from northern peatlands using electrical imaging. *Journal of Geophysical Research*, **116**, G04004.

Khvorostyanov DV, Ciais P, Krinner G, Zimov SA (2008) Vulnerability of east Siberia's frozen carbon stores to future warming. *Geophysical Research Letters*, **35**, L10703. doi: 10.1029/2008gl033639

Kim SY, Lee SH, Freeman C, Fenner N, Kang H (2008) Comparative analysis of soil microbial communities and their responses to the short-term drought in bog, fen, and riparian wetlands. *Soil Biology and Biochemistry*, **40**, 2874–2880.

King JY, Reeburgh WS, Thieler KK, Kling GW, Loya WM, Johnson LC, Nadelhoffer KJ (2002) Pulse-labeling studies of carbon cycling in Arctic tundra ecosystems: the contribution of photosynthates to methane emission. *Global Biogeochemical Cycles*, **16**, 1062. doi: 10.1029/2001GB001456

Kip N, van Winden JF, Pan Y *et al.* (2010) Global prevalence of methane oxidation by symbiotic bacteria in peat-moss ecosystems. *Nature Geoscience*, **3**, 617–621.

Kleber M, Johnson MG (2010) Advances in understanding the molecular structure of soil organic matter: implications for interactions in the environment. *Advances in Agronomy*, **106**, 77–142.

Knittel K, Boetius A (2009) Anaerobic oxidation of methane: progress with an unknown process. *Annual Review of Microbiology*, **63**, 311–334.

Kotiaho M, Fritze H, Merilä P *et al.* (2010) Methanogen activity in relation to water table level in two boreal fens. *Biology and Fertility of Soils*, **46**, 567–575.

Kotsyurbenko OR, Friedrich MW, Simankova MV, Nozhevnikova AN, Golyshin PN, Timmis KN, Conrad R (2007) Shift from acetoclastic to H_2-dependent methanogenesis in a west Siberian peat bog at low pH values and isolation of an acidophilic Methanobacterium strain. *Applied and Environmental Microbiology*, **73**, 2344–2348.

Kracht O, Gleixner G (2000) Isotope analysis of pyrolysis products from *Sphagnum* peat and dissolved organic matter from bog water. *Organic Geochemistry*, **31**, 645–654.

Krüger M, Frenzel P, Kemnitz D, Conrad R (2005) Activity, structure and dynamics of the methanogenic archaeal community in a flooded Italian rice field. *FEMS Microbiology Ecology*, **51**, 323–331.

Laanbroek HJ (2010) Methane emission from natural wetlands: interplay between emergent macrophytes and soil microbial processes. A mini-review. *Annals of Botany*, **105**, 141–153.

Lai DYF (2009) Methane dynamics in northern peatlands: a review. *Pedosphere*, **19**, 409–421.

Le Mer J, Roger P (2001) Production, oxidation, emission and consumption of methane by soils: a review. *European Journal of Soil Biology*, **37**, 25–50.

Lehmann J, Solomon D, Kinyangi J, Dathe L, Wirick S, Jacobsen C (2008) Spatial complexity of soil organic matter forms at nanometre scales. *Nature Geoscience*, **1**, 238–242.

Lehner B, Döll P (2004) Development and validation of a global database of lakes, reservoirs and wetlands. *Journal of Hydrology*, **296**, 1–22.

Li S, Lu X (2011) Greenhouse gas emissions from reservoirs could double within 40 years. *Science*. Available at: www.sciencemag.org/content/331/6013/6050.short/reply#sci_el_14254 (accessed 28 June 2011)

Lipson DA, Jha M, Raab TK, Oechel WC (2010) Reduction of iron (III) and humic substances plays a major role in anaerobic respiration in an Arctic peat soil. *Journal of Geophysical Research-Biogeosciences*, **115**, G00I06. doi: 10.1029/2009jg001147

Liu Y, Whitman WB (2008) Metabolic, phylogenetic, and ecological diversity of the methanogenic Archaea. *Annals of the New York Academy of Sciences*, **1125**, 171–189.

Loulergue L, Schilt A, Spahni R *et al.* (2008) Orbital and millennial-scale features of atmospheric CH_4 over the past 800,000 years. *Nature*, **453**, 383–386.

Lovley DR, Phillips EJP (1986) Organic matter mineralization with reduction of ferric iron in anaerobic sediments. *Applied and Environmental Microbiology*, **51**, 683–689.

Lovley DR, Phillips EJP (1988) Novel mode of microbial energy metabolism: organic carbon oxidation coupled to dissimilatory reduction of iron or manganese. *Applied and Environmental Microbiology*, **54**, 1472–1480.

Lovley DR, Coates JD, Blunt-Harris EL, Phillips EJP, Woodward JC (1996) Humic substances as electron acceptors for microbial respiration. *Nature*, **382**, 445–448.

Lu X, Zhuang Q (2012) Modeling methane emissions from the Alaskan Yukon River basin, 1986–2005, by coupling a large-scale hydrological model and a process-based methane model. *Journal of Geophysical Research*, **G02010**. doi: 10.1029/2011jg001843

Lueders T, Friedrich M (2000) Archaeal population dynamics during sequential reduction processes in rice field soil. *Applied and Environmental Microbiology*, **66**, 2732–2742.

Ma K, Conrad R, Lu Y (2012) Responses of methanogen mcrA genes and their transcripts to an alternate dry/wet cycle of paddy field soil. *Applied and Environmental Microbiology*, **78**, 445–454.

Mackelprang R, Waldrop MP, DeAngelis KM *et al.* (2011) Metagenomic analysis of a permafrost microbial community reveals a rapid response to thaw. *Nature*, **480**, 368–371.

Maltby E, Immirzi P (1993) Carbon dynamics in peatlands and other wetland soils, regional and global perspectives. *Chemosphere*, **27**, 999–1023.

Martens CS, Berner RA (1974) Methane production in the interstitial waters of sulfate-depleted marine sediments. *Science*, **185**, 1167–1169.

Mastepanov M, Sigsgaard C, Dlugokencky EJ, Houweling S, Strom L, Tamstorf MP, Christensen TR (2008) Large tundra methane burst during onset of freezing. *Nature*, **456**, 628–630.

Matthews E, Fung I (1987) Methane emission from natural wetlands: global distribution, area, and environmental characteristics of sources. *Global Biogeochemical Cycles*, **1**, 61–86.

McClymont EL, Bingham EM, Nott CJ, Chambers FM, Pancost RD, Evershed RP (2011) Pyrolysis GC–MS as a rapid screening tool for determination of peat-forming plant composition in cores from ombrotrophic peat. *Organic Geochemistry*, **42**, 1420–1435.

McLeod AR, Fry SC, Loake GJ, Messenger DJ, Reay DS, Smith KA, Yun BW (2008) Ultraviolet radiation drives methane emissions from terrestrial plant pectins. *New Phytologist*, **180**, 124–132. doi: 10.1111/j.1469-8137.2008.02571.x

Meehl GA, Stocker TF, Collins WD *et al.* (2007) Global climate projections. In: *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* (eds Solomon S, Qin D, Manning M, Chen Z, Marquis M, Averyt KB, Tignor M, Miller HL), pp. 747–845. Cambridge University Press, Cambridge, UK.

Megonigal JP, Guenther AB (2008) Methane emissions from upland forest soils and vegetation. *Tree Physiology*, **28**, 491–498.

Megonigal JP, Whalen SC, Tissue DT, Bovard BD, Albert DB, Allen AS (1999) A plant-soil-atmosphere microcosm for tracing radiocarbon from photosynthesis through methanogenesis. *Soil Science Society of America Journal*, **63**, 665–671.

Megonigal JP, Hines ME, Visscher PT (2004) Anaerobic metabolism: linkages to trace gases and aerobic processes. In: *Biogeochemistry* (ed. Schlesinger WH), pp. 317–424. Oxford, UK, Elsevier-Pergamon.

Meijide A, Manca G, Goded I, Magliulo V, di Tommasi P, Seufert G, Cescatti A (2011) Seasonal trends and environmental controls of methane emissions in a rice paddy field in Northern Italy. *Biogeosciences*, **8**, 3809–3821.

Meirink JF, Eskes HJ, Goede APH (2006) Sensitivity analysis of methane emissions derived from SCIAMACHY observations through inverse modelling. *Atmospheric Chemistry and Physics*, **6**, 1275–1292.

Melton JR, Wania R, Hodson EL *et al.* (2012) Present state of global wetland extent and wetland methane modelling: conclusions from a model intercomparison project (WETCHIMP). *Biogeosciences Discussions*, **9**, 11577–11654.

Metje M, Frenzel P (2007) Methanogenesis and methanogenic pathways in a peat from subarctic permafrost. *Environmental Microbiology*, **9**, 954–964.

Michaelis W, Seifert R, Nauhaus K *et al.* (2002) Microbial reefs in the Black Sea fueled by anaerobic oxidation of methane. *Science*, **297**, 1013–1015.

Miguez-Macho G, Li H, Fan Y (2008) Simulated water table and soil moisture climatology over North America. *Bulletin of the American Meteorological Society*, **89**, 663–672.

Minderlein S, Blodau C (2010) Humic-rich peat extracts inhibit sulfate reduction, methanogenesis, and anaerobic respiration but not acetogenesis in peat soils of a temperate bog. *Soil Biology and Biochemistry*, **42**, 2078–2086.

Moore TR, DeYoung A, Bubier JL, Humphreys ER, Lafleur PM, Roulet NT (2011) A multi-year record of methane flux at the Mer Bleue Bog, southern Canada. *Ecosystems*, **14**, 646–657.

van der Nat F-J, Middelburg JJ (1998) Effects of two common macrophytes on methane dynamics in freshwater sediments. *Biogeochemistry*, **43**, 79–104.

Neef L, van Weele M, van Velthoven P (2010) Optimal estimation of the present-day global methane budget. *Global Biogeochemical Cycles*, **24**, GB4024. doi: 10.1029/2009gb003661

Neubauer SC, Givler K, Valentine SK, Megonigal JP (2005) Seasonal patterns and plant-mediated controls of subsurface wetland biogeochemistry. *Ecology*, **86**, 3334–3344.

Nurmi JT, Tratnyek PG (2002) Electrochemical properties of natural organic matter (NOM), fractions of NOM, and model biogeochemical electron shuttles. *Environmental Science and Technology*, **36**, 617–624.

Oremland RS (1988) Biogeochemistry of methanogenic bacteria. In: *Biology of Anaerobic Microorganisms* (eds Zehnder AJB, Tumm WS), pp. 641–705. John Wiley, New York.

Orphan VJ, House CH, Hinrichs K-U, McKeegan KD, DeLong EF (2001) Methane-consuming archaea revealed by directly coupled isotopic and phylogenetic analysis. *Science*, **293**, 484–487.

Pancotto VA, van Bodegom PM, van Hal J, van Logtestijn RSP, Blokker P, Toet S, Aerts R (2010) N deposition and elevated CO_2 on methane emissions: differential responses of indirect effects compared to direct effects through litter chemistry feedbacks. *Journal of Geophysical Research*, **115**, G02001. doi: 10.1029/2009jg001099

Petrescu AMR, van Beek LPH, van Huissteden J *et al.* (2010) Modeling regional to global CH_4 emissions of boreal and arctic wetlands. *Global Biogeochemical Cycles*, **24**, Gb4009. doi: 10.1029/2009gb003610

Poffenbarger HJ, Needelman BA, Megonigal JP (2011) Salinity influence on methane emissions from tidal marshes. *Wetlands*, **31**, 831–842.

Potter CS (1997) An ecosystem simulation model for methane production and emission from wetlands. *Global Biogeochemical Cycles*, **11**, 495–506.

Potter EG, Bebout BM, Kelley CA (2009) Isotopic composition of methane and inferred methanogenic substrates along a salinity gradient in a hypersaline microbial mat system. *Astrobiology*, **9**, 383–390.

Prigent C, Papa F, Aires F, Rossow WB, Matthews E (2007) Global inundation dynamics inferred from multiple satellite observations, 1993–2000. *Journal of Geophysical Research*, **112**, D12107. doi: 10.1029/2006jd007847

Purdy KJ, Munson MA, Nedwell DB, Embley TM (2002) Comparison of the molecular diversity of the methanogenic community at the brackish and marine ends of a UK estuary. *FEMS Microbiology Ecology*, **39**, 17–21.

Raghoebarsing AA, Smolders AJP, Schmid MC *et al.* (2005) Methanotrophic symbionts provide carbon for photosynthesis in peat bogs. *Nature*, **436**, 1153–1156.

Raghoebarsing AA, Pol A, van de Pas-Schoonen KT *et al.* (2006) A microbial consortium couples anaerobic methane oxidation to dentrification. *Nature*, **440**, 918–921.

Rasmussen S, Wolff C, Rudolph H (1995) Compartmentalization of phenolic constituents in *Sphagnum*. *Phytochemistry*, **38**, 35–39.

Ratasuk N, Nanny MA (2007) Characterization and quantification of reversible redox sites in humic substances. *Environmental Science & Technology*, **41**, 7844–7850.

Reeburgh WS (2007) Oceanic methane biogeochemistry. *Chemical Reviews*, **107**, 486–513.

Rice AL, Butenhoff CL, Shearer MJ, Teama D, Rosenstiel TN, Khalil MAK (2010) Emissions of anaerobically produced methane by trees. *Geophysical Research Letters*, **37**, L03807.

Riley WJ, Subin ZM, Lawrence DM *et al.* (2011) Barriers to predicting changes in global terrestrial methane fluxes: analyses using CLM4Me, a methane biogeochemistry model integrated in CESM. *Biogeosciences*, **8**, 1925–1953.

Ringeval B, de Noblet-Ducoudre N, Ciais P, Bousquet P, Prigent C, Papa F, Rossow WB (2010) An attempt to quantify the impact of changes in wetland extent on methane emissions on the seasonal and interannual time scales. *Global Biogeochemical Cycles*, **24**, Gb2003. doi: 10.1029/2008gb003354

Roden EE (2003) Diversion of electron flow from methanogenesis to crystalline Fe(III) oxide reduction in carbon-limited cultures of wetland sediment microorganisms. *Applied and Environmental Microbiology*, **69**, 5702–5706.

Roden EE, Wetzel RG (1996) Organic carbon oxidation and suppression of methane production by microbial Fe(III) oxide reduction in vegetated and unvegetated freshwater wetland sediments. *Limnology and Oceanography*, **41**, 1733–1748.

Roden EE, Wetzel RG (2003) Competition between Fe(III)-reducing and methanogenic bacteria for acetate in iron-rich freshwater sediments. *Microbial Ecology*, **45**, 252–258.

Roden EE, Kappler A, Bauer I *et al.* (2010) Extracellular electron transfer through microbial reduction of solid-phase humic substances. *Nature Geoscience*, **3**, 417–421.

Rooney-Varga JN, Giewat MW, Duddleston KN, Chanton JP, Hines ME (2007) Links between archaeal community structure, vegetation type and methanogenic pathway in Alaskan peatlands. *FEMS Microbiology Ecology*, **60**, 240–251.

Roulet NT (2000) Peatlands, carbon storage, greenhouse gases, and the Kyoto Protocol: prospects and significance for Canada. *Wetlands*, **20**, 605–615.

Sakai S, Ehara M, Tseng I-C *et al.* (2012) *Methanolinea mesophila*, sp. nov., a hydrogenotrophic methanogen isolated from a rice field in Taiwan, and proposal of the new archaeal family *Methanoregulaceae* fam. nov. within the order Methanomicrobiales. *International Journal of Systematic and Evolutionary Microbiology*, **62** (Pt 6), 1389–1395.

Schmidt MWI, Torn MS, Abiven S *et al.* (2011) Persistence of soil organic matter as an ecosystem property. *Nature*, **478**, 49–56.

Scott DT, McKnight DM, Blunt-Harris EL, Kolesar SE, Lovley DR (1998) Quinone moieties act as electron acceptors in the reduction of humic substances by humics-reducing microorganisms. *Environmental Science and Technology*, **32**, 2984–2989.

Segers R (1998) Methane production and methane consumption: a review of processes underlying wetland methane fluxes. *Biogeochemistry*, **41**, 23–51.

Segers R, Leffelaar PA (2001a) Modeling methane fluxes in wetlands with gas-transporting plants 1. Single-root scale. *Journal of Geophysical Research*, **106**, 3511–3528.

Segers R, Leffelaar PA (2001b) Modeling methane fluxes in wetlands with gas-transporting plants 3. Plot scale. *Journal of Geophysical Research*, **106**, 3541–3558.

Segers R, Rappoldt C, Leffelaar PA (2001) Modeling methane fluxes in wetlands with gas-transporting plants 2. Soil layer scale. *Journal of Geophysical Research*, **106**, 3529–3540.

Semrau JD, DiSpirito AA, Yoon S (2010) Methanotrophs and copper. *FEMS Microbiology Reviews*, **34**, 496–531.

Shannon RD, White JR (1996) The effects of spatial and temporal variations in acetate and sulfate on methane cycling in two Michigan peatlands. *Limnology and Oceaongraphy*, **41**, 435–443.

Shannon RD, White JR, Lawson JE, Gilmour BS (1996) Methane efflux from emergent vegetation in peatlands. *Journal of Ecology*, **84**, 239–246.

Shindell DT, Walter BP, Faluvegi G (2004) Impacts of climate change on methane emissions from wetlands. *Geophysical Research Letters*, **31**, L21202. doi: 10.1029/2004GL021009

Shindell DT, Faluvegi G, Koch DM, Schmidt GA, Unger N, Bauer SE (2009) Improved attribution of climate forcing to emissions. *Science*, **326**, 716–718.

Sivan O, Adler M, Pearson A, Gelman F, Bar-Or I, John SG, Eckert W (2011) Geochemical evidence for iron-mediated anaerobic oxidation of methane. *Limnology and Oceanography*, **56**, 1536–1544.

Smemo KA, Yavitt JB (2007) Evidence for anaerobic CH_4 oxidation in freshwater peatlands. *Geomicrobiology Journal*, **24**, 583–597.

Smemo KA, Yavitt JB (2011) Anaerobic oxidation of methane: an underappreciated aspect of methane cycling in peatland ecosystems? *Biogeosciences*, **8**, 779–793.

Smith RL, Howes BL, Garabedian SP (1991) In situ measurement of methane oxidation in groundwater by using natural-gradient tracer tests. *Applied and Environmental Microbiology*, **57**, 1997–2004.

Sowers KR, Ferry JG (2003) Methanogenesis in the marine environment. In: *Encyclopedia of Environmental Microbiology*. John Wiley & Sons, Inc., doi: 10.1002/0471263397.env226.

Spahni R, Wania R, Neef L *et al.* (2011) Constraining global methane emissions and uptake by ecosystems. *Biogeosciences*, **8**, 1643–1665.

Sposito G (2008) *The Chemistry of Soils*. Oxford University Press, Inc., New York.

Sposito G (2011) Electron shuttling by natural organic matter: twenty years after. In: *ACS Symposium Series 1071*. *Aquatic Redox Chemistry* (eds Tratnyek PG, Grundl TJ, Harderlein SB), pp. 113–127. American Chemical Society, Washington, DC.

Stalheim T, Ballance S, Christensen BE, Granum PE (2009) Sphagnan – a pectin-like polymer isolated from *Sphagnum* moss can inhibit the growth of some typical food spoilage and food poisoning bacteria by lowering the pH. *Journal of Applied Microbiology*, **106**, 967–976.

Steinberg LM, Regan JM (2008) Phylogenetic comparison of the methanogenic communities from an acidic, oligotrophic fen and an anaerobic digester treating municipal wastewater sludge. *Applied and Environmental Microbiology*, **74**, 6663–6671.

Stevenson FJ (1994) *Humus Chemistry: Genesis, Composition, Reaction*. John Wiley & Sons, Inc., New York, NY.

Struyk Z, Sposito G (2001) Redox properties of standard humic acids. *Geoderma*, **102**, 329–346.

Subin ZM, Riley WJ, Mironov D (2012) An improved lake model for climate simulations: model structure, evaluation, and sensitivity analyses in CESM1. *Journal of Advances in Modeling Earth Systems*, **4**, M02001. doi: 10.1029/2011 ms000072

Sun CL, Brauer SL, Cadillo Quiroz H, Zinder SH, Yavitt JB (2012) Seasonal changes in methanogenesis and methanogenic community in three peatlands. New York State. *Frontiers in Microbiology*, **3**. doi: 10.3389/fmicb.2012.00081

Sutton R, Sposito G (2005) Molecular structure in soil humic substances: the new view. *Environmental Science and Technology*, **39**, 9009–9015.

Tang J, Zhuang Q, Shannon RD, White JR (2010) Quantifying wetland methane emissions with process-based models of different complexities. *Biogeosciences*, **7**, 3817–3837.

Tarnocai C, Canadell JG, Schuur EAG, Kuhry P, Mazhitova G, Zimov S (2009) Soil organic carbon pools in the northern circumpolar permafrost region. *Global Biogeochemical Cycles*, **23**, GB2023. doi: 10.1029/2008GB003327,2009

Teh YA, Silver WL, Conrad ME (2005) Oxygen effects on methane production and oxidation in humic tropical forest soils. *Global Change Biology*, **11**, 1283–1297.

Tokida T, Miyazaki T, Mizoguchi M, Nagata O, Takakai F, Kagemoto A, Hatano R (2007a) Falling atmospheric pressue as a trigger for methane ebulltion from peatland. *Global Biogeochemical Cycles*, **21**, GB2003.

Tokida T, Mizoguchi M, Miyazaki T, Kagemoto A, Nagata O, Hatano R (2007b) Episodic release of methane bubbles from peatland during spring thaw. *Chemosphere*, **70**, 165–171.

Trotsenko YA, Murrell JC (2008) Metabolic aspects of aerobic obligate methanotrophy. *Advances in Applied Microbiology*, **63**, 183–229.

Turetsky MR, Treat CC, Waldrop MP, Waddington JM, Harden JW, McGuire AD (2008) Short-term response of methane fluxes and methanogen activity to water table and soil warming manipulations in an Alaskan peatland. *Journal of Geophysical Research*, **113**, G00A10. doi: 10.1029/2007jg000496

Updegraff K, Pastor J, Bridgham SD, Johnston CA (1995) Environmental and substrate controls over carbon and nitrogen mineralization in northern wetlands. *Ecological Applications*, **5**, 151–163.

Updegraff K, Bridgham SD, Pastor J, Weishampel P, Harth C (2001) Response of CO_2 and CH_4 emissions in peatlands to warming and water-table manipulation. *Ecological Applications*, **11**, 311–326.

Valentine DL, Reeburgh WS (2000) New perspectives on anaerobic methane oxidation. *Environmental Microbiology*, **2**, 477–484.

Valentine DW, Holland EA, Schimel DS (1994) Ecosystem and physiological controls over methane production in northern wetlands. *Journal of Geophysical Research*, **99**, 1563–1571.

Vann CD, Megonigal JP (2002) Productivity responses of *Acer rubrum* and *Taxodium distichum* seedlings to elevated CO_2 and flooding. *Environmental Pollution*, **116**, S31–S36.

Verhoeven JTA, Toth E (1995) Decomposition of *Carex* and *Sphagnum* litter in fens: effects of litter quality and inhibition by living tissue homogenates. *Soil Biology and Biochemistry*, **27**, 271–275.

Vile MA, Bridgham SD, Wieder RK (2003a) Response of anaerobic carbon mineralization rates to sulfate amendments in a boreal peatland. *Ecological Applications*, **13**, 720–734.

Vile MA, Bridgham SD, Wieder RK, Novák M (2003b) Atmospheric sulfur deposition alters pathways of gaseous carbon production in peatlands. *Global Biogeochemical Cycles*, **17**, 1058–1064.

Walter BP, Heimann M (2000) A process-based, climate-sensitive model to derive methane emissions from natural wetlands: application to five wetland sites, sensitivity to model parameters, and climate. *Global Biogeochemical Cycles*, **14**, 745–765.

Walter KM, Zimov SA, Chaton JP, Verbyla D, Chapin FS III (2006) Methane bubbling from Siberian thaw lakes as a positive feedback to climate warming. *Nature*, **443**, 71–75.

Walter KM, Smith LC, Chapin FS (2007) Methane bubbling from northern lakes: present and future contributions to the global methane budget. *Philosophical Transactions of the Royal Society A-Mathematical Physical and Engineering Sciences*, **365**, 1657–1676.

Wania R, Ross I, Prentice IC (2010) Implementation and evaluation of a new methane model within a dynamic global vegetation model: LPJ-WHyMe v1.3.1. *Geoscientific Model Development*, **3**, 565–584.

Watanabe T, Kimura M, Asakawa S (2007) Dynamics of methanogenic archaeal communities based on rRNA analysis and their relation to methanogenic activity in Japanese paddy field soils. *Soil Biology and Biochemistry*, **39**, 2877–2887.

Weltzin JF, Bridgham SD, Pastor J, Chen J, Harth C (2003) Potential effects of warming and drying on peatland plant community composition. *Global Change Biology*, **9**, 1–11.

Whiting GJ, Chanton JP (1992) Plant-dependent CH_4 emission in a subarctic Canadian fen. *Global Biogeochemical Cycles*, **6**, 225–231.

Whiting GJ, Chanton JP (1993) Primary production control of methane emissions from wetlands. *Nature*, **364**, 794–795.

Wolf M, Kappler A, Jian J, Meckenstock RU (2009) Effects of humic substances and quinones at low concentrations on ferrihydrite reduction by *Geobacter metallireducens*. *Environmental Science and Technology*, **43**, 5679–5685.

Yavitt JB, Lang GE (1990) Methane production in contrasting wetland sites: response to organic-chemical components of peat and to sulfate reduction. *Geomicrobiology Journal*, **8**, 27–46.

Yavitt JB, Seidman-Zager M (2006) Methanogenic conditions in northern peat soils. *Geomicrobiology Journal*, **23**, 119–127.

Yavitt JB, Fahey TJ, Simmons JA (1995) Methane and carbon dioxide dynamics in a northern hardwood ecosystem. *Soil Science Society of America Journal*, **59**, 796–804.

Ye R, Jin Q, Bohannan B, Keller JK, McAllister SA, Bridgham SD (2012) pH controls over anaerobic carbon mineralization, the efficiency of methane production, and methanogenic pathways in peatlands across an ombrotrophic-minerotrophic gradient. *Soil Biology and Biochemistry*, **54**, 36–47.

Yuan Y, Conrad R, Lu Y (2011) Transcriptional response of methanogen mcrA genes to oxygen exposure of rice field soil. *Environmental Microbiology Reports*, **3**, 320–328.

Zhang Y, Li CS, Trettin CC, Li H, Sun G (2002) An integrated model of soil, hydrology, and vegetation for carbon dynamics in wetland ecosystems. *Global Biogeochemical Cycles*, **16**, 1061. doi: 10.1029/2001GB001838

Zhu XD, Zhuang QL, Chen M *et al.* (2011) Rising methane emissions in response to climate change in Northern Eurasia during the 21st century. *Environmental Research Letters*, **6**, 045211. doi: 10.1088/1748-9326/6/4/045211

Zhuang Q, Melillo JM, Kicklighter DW *et al.* (2004) Methane fluxes between terrestrial ecosystems and the atmosphere at northern high latitudes during the past century: a retrospective analysis with a process-based biogeochemistry model. *Global Biogeochemical Cycles*, **18**, GB 3010.

Zhuang Q, Melillo JM, Sarofim MC *et al.* (2006) CO_2 and CH_4 exchanges between land ecosystems and the atmosphere in northern high latitudes over the 21st century. *Geophysical Research Letters*, **33**, L17403. doi: 10.1029/2006gl026972

Zhuang Q, Melack JM, Zimov S, Walter KM, Butenhoff CL, Khalil MAK (2009) Global methane emissions from wetlands, rice paddies, and lakes. *Eos*, **90**, 37–44.

Zinder SH (1993) Physiological ecology of methanogens. In: *Methanogenesis: Ecology, Physiology, Biochemistry & Genetics* (ed. Ferry JG), pp. 128–206. Chapman and Hall, New York.

Supporting Information

Additional Supporting Information may be found in the online version of this article:

Table S1. Methane emissions from anthropogenic and natural sources.
Table S2. Global distribution of methane emissions in freshwater aquatic ecosystems, wetlands, and rice fields.
Data S1. Supplemental references.