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# Anaerobic oxidation of methane: an underappreciated aspect of methane cycling in peatland ecosystems?

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Received: 30 August 2010 – Accepted: 19 October 2010 – Published: 29 October 2010

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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## Abstract

Despite a large body of literature on microbial anaerobic oxidation of methane (AOM) in marine sediments and saline waters and its importance to the global methane ( $\text{CH}_4$ ) cycle, until recently little work has addressed the potential occurrence and importance of AOM in non-marine systems. This is particularly true for peatlands, which represent both a massive sink for atmospheric  $\text{CO}_2$  and a significant source of atmospheric  $\text{CH}_4$ . Our knowledge of this process in peatlands is inherently limited by the methods used to study  $\text{CH}_4$  dynamics in soil and sediment and the assumption that there are no anaerobic sinks for  $\text{CH}_4$  in these systems. Studies suggest that AOM is  $\text{CH}_4$ -limited and difficult to detect in potential  $\text{CH}_4$  production assays against a background of  $\text{CH}_4$  production. In situ rates also might be elusive due to background rates of aerobic  $\text{CH}_4$  oxidation and the difficulty in separating net and gross process rates. Conclusive evidence for the electron acceptor in this process has not been presented. Nitrate and sulfate are both plausible and favorable electron acceptors, as seen in other systems, but there exist theoretical issues related to the availability of these ions in peatlands and only circumstantial evidence suggests that these pathways are important. Iron cycling is important in many wetland systems, but recent evidence does not support the notion of  $\text{CH}_4$  oxidation via dissimilatory Fe(III) reduction or a  $\text{CH}_4$  oxidizing archaea in consortium with an Fe(III) reducer. Calculations based on published rates demonstrate that AOM might be a significant and underappreciated constraint on the global  $\text{CH}_4$  cycle, although much about the process is unknown, in vitro rates may not relate well to in situ rates, and projections based on those rates are fraught with uncertainty. We suggest electron transfer mechanisms, C flow and pathways, and quantifying in situ peatland AOM rates as the highest priority topics for future research.

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## 1 Introduction

Anaerobic oxidation of methane (AOM; (per Valentine, 2002)) linked to microbial sulfate reduction (SR) is thought to consume most of the methane ( $\text{CH}_4$ ) produced in and diffusing through marine sediments (Reeburgh and Heggie, 1977; Valentine, 2002).

5 The process consumes an estimated 20–100 (Reeburgh, 1989) to 300 (Hinrichs and Boetius, 2002)  $\text{Tg CH}_4 \text{ yr}^{-1}$ , which is equivalent to 5 to 60% of the global annual  $\text{CH}_4$  flux into the atmosphere. AOM is therefore important to the present-day global  $\text{CH}_4$  cycle, and it has been suggested that AOM played a role in the rise of atmospheric  $\text{O}_2 \sim 2.4$  Gyr ago (Catling et al., 2007). Considering that atmospheric  $\text{CH}_4$  has a mass-based warming potential up to 72 times that of carbon dioxide ( $\text{CO}_2$ ) and has increased considerably due to human activity (IPCC, 2007), AOM represents a potential mechanistic constraint on global warming. Despite the global significance of AOM and considerable effort to identify the exact mechanisms and organism(s) involved in marine sediment AOM (e.g. Boetius et al., 2000; Hinrichs et al., 1999; Thomsen et al., 2001), much about the process and organisms responsible remains unclear and little is known about the occurrence and importance of the process in non-marine systems.

Evidence for AOM in non-marine systems has been reported in a few lakes (e.g. Pan-ganiban et al., 1979; Smith et al., 1993), two landfills (Bjerg et al., 1995; Grossman et al., 2002), anoxic waste slurries (Malek and Weismann, 1988), a contaminated aquifer (Smith et al., 1991), and flooded-rice paddies (Miura et al., 1992; Murase and Kimura, 1994a), but much of that evidence is anecdotal in nature and strong evidence for AOM in freshwater systems has been limited. Work by Islas-Lima et al. (2004) and Raghoe-barsing et al. (2006) has demonstrated that AOM in some freshwater systems is linked to denitrification and denitrifying bacteria, which provides an energetically favorable alternative to marine AOM linked to SR. Further work has suggested that AOM can be carried out by denitrifying bacteria in the absence of an archeal consortium (Ettwig et al., 2008) and that this process might be linked to nitrite ( $\text{NO}_2^-$ ) reduction and the production of oxygen ( $\text{O}_2$ ) as an electron acceptor (Ettwig et al., 2010); hence, implying

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aerobic metabolism under anoxic conditions.

Many freshwater wetlands and peatlands provide habitat for methane-producing microorganisms, and these ecosystems collectively are the most significant source of atmospheric CH<sub>4</sub> (Fletcher et al., 2004). Wetlands in northern latitudes (>45° N; northern peatlands), in particular, cover just 3% of the continents, yet they represent a significant fraction of this CH<sub>4</sub> flux and are a massive and continued sink for atmospheric CO<sub>2</sub> (Limpens et al., 2008; Nilsson et al., 2008), storing between 270 and 370 Tg C (Turunen et al., 2002), which is comparable to nearly half of the C in the atmosphere (IPCC, 2007). A net annual carbon balance near zero and high latitude location also suggest that these systems are sensitive to environmental changes (Gorham, 1991). For example, decomposition, C storage, and CH<sub>4</sub> emission in peatlands are sensitive to both warming and precipitation patterns (Updegraff et al., 2001), and climate warming is expected to be more pronounced at higher latitudes. Nevertheless, studies addressing potential alternative consumptive fates of CH<sub>4</sub> in anoxic wetland soils and in peatlands have been lacking, and previous research has argued – but without experimental data – that AOM is unimportant in such systems (Segers, 1998; Topp and Pattey, 1997).

Recent evidence presented by Smemo and Yavitt (2006, 2007) challenges this assumption and suggests a potentially important role for AOM in a variety of peatland ecosystems. They found that AOM occurs simultaneously with methanogenesis, can consume a significant amount of gross CH<sub>4</sub> production, appears to depend upon CH<sub>4</sub> accumulation to large concentrations in peat porewater, and can constrain atmospheric CH<sub>4</sub> flux under certain conditions. AOM might be more common than previously thought, but the relationship between AOM in peatlands and the two known mechanisms (SR and denitrification) is unclear. The focus of this paper is to analyze evidence for AOM in relation to peatland CH<sub>4</sub> cycling and the global CH<sub>4</sub> cycle, address uncertainties pertaining to the known mechanisms and pathways, and propose future directions. In addition, we briefly review past evidence from marine and other freshwater systems to provide mechanistic insights into AOM in peatland ecosystems.

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## 2 Evidence for AOM

### 2.1 Marine systems

Reviews of the geochemical and microbiological evidence can be found in Alperin and Reeburgh (1984), Valentine and Reeburgh (2000), Valentine (2002), Reeburgh (2007), and Caldwell et al. (2008). Sulfate ( $\text{SO}_4^{2-}$ ) is the most common oxidant used in organic matter decomposition in marine sediments. As  $\text{SO}_4^{2-}$  is reduced and concentrations are depleted with depth,  $\text{CH}_4$  production (methanogenesis) becomes the most common organic matter decomposition process after that. Sulfate reduction outcompetes methanogenesis, based upon thermodynamic and kinetic reasons, and depth distribution profiles of  $\text{SO}_4^{2-}$  and  $\text{CH}_4$  clearly show the transition zone where decomposition processes shift from SR to methanogenesis. However, geochemical gradients in sediments indicated that  $\text{CH}_4$  concentrations decrease rapidly in the zone of SR and provided the first evidence for AOM linked to SR (Barnes and Goldberg, 1976; Reeburgh, 1976). For instance, these and other studies (see Valentine (2002) for a more complete list of references) indicated that the remaining  $\text{CH}_4$  pool is highly enriched with respect to  $^{13}\text{C}$ , which is consistent with high C fractionation during AOM (Alperin and Reeburgh, 1985). Tracer measurements using  $^{14}\text{CH}_4$ ,  $\text{C}^3\text{H}_4$ , and  $^{35}\text{SO}_4^{2-}$  provided further confirmation that AOM is linked to sulfate-reducing bacteria (SRB) that utilize  $\text{CH}_4$  as a carbon or energy source Reaction (1).



Other studies suggested that SRB did not carry out AOM directly, but rather a consortium with unknown organisms and SRB was involved (Alperin and Reeburgh, 1985; Hoehler et al., 1994; Sørensen, 1988).

More recent studies shifted to dynamic methane seeps in marine environments, where archaeal specific lipid biomarkers (Hinrichs et al., 1999; Michaelis et al., 2002; Pancost et al., 2000) and molecular techniques (Boetius et al., 2000; Orphan et al.,

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2001; Thomsen et al., 2001) suggest that AOM is carried out by a consortium between an organism(s) phylogenetically related to methanogens (Hallam et al., 2004) in a syntrophic relationship with SRB. A similar consortium from sediments near CH<sub>4</sub> hydrate was cultured in vitro with continuous supplies of CH<sub>4</sub> and SO<sub>4</sub><sup>2-</sup> (Nauhaus et al., 5 2007). AOM rates increased from 20 to 230 μmol day<sup>-1</sup> and the number of microbial aggregates increased 10-fold. However, at experimental conditions (1.4 Mpa CH<sub>4</sub> and sea water SO<sub>4</sub><sup>2-</sup> concentrations) consortia growth was slow, with a doubling time of ~7 months. This evidence led researchers to revisit studies by Zehnder and Brock (1980; 1979) and Hoehler et al. (1994) suggesting that AOM could proceed via methanogenesis “operating in reverse”. This mechanism was further substantiated by recent work 10 showing that the AOM “back reaction” is actually catalyzed by methyl-coenzyme M reductase (MCR), the key enzyme in methanogenesis (Scheller et al., 2010).

Despite such compelling evidence to explain the occurrence and importance of AOM in marine systems and anoxic SO<sub>4</sub><sup>2-</sup>-rich waters, many uncertainties regarding the distribution and mechanism of the process remain (Alperin and Hoehler, 2010; Caldwell et al., 2008). For instance, the organisms responsible have not been isolated in pure culture, and there is evidence suggesting that some anaerobic bacteria can oxidize CH<sub>4</sub> in the absence of a syntrophic relationship (Ettwig et al., 2009). Moreover, H<sub>2</sub>, formate, and acetate are the most likely molecules involved in interspecies electron transfer 20 from methanogenic archaea to SRB (Thauer and Shima, 2008). Although evidence suggests that the some of these electron donors can stimulate SRB in freshwater systems (Westermann and Ahring, 1987), none of these compounds have been found to stimulate SRB or inhibit AOM in marine systems, which they should if they were intermediates in the reaction (Thauer and Shima, 2006). Sørensen et al. (2001) argue that interspecies H<sub>2</sub> transfer is thermodynamically constrained and therefore unlikely to be 25 important in marine sediments. For a more detailed discussion of H<sub>2</sub>-syntrophy and alternative mechanisms refer to Valentine and Reeburgh (2000), Valentine (2002), and Caldwell et al. (2008).

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## 2.2 Freshwater systems

As mentioned above, AOM has been observed in a few freshwater or non-marine saline systems. Panganiban et al. (1979) demonstrated that AOM consumed a portion of  $\text{CH}_4$  production in the anoxic zone of Lake Mendota (Wisconsin, USA). They found that organisms could be grown in enrichment studies using acetate and  $\text{CH}_4$  as the sole energy and carbon source, along with  $\text{SO}_4^{2-}$  as the electron acceptor. Radiocarbon tracer methods also showed that acetate was assimilated into biomass while  $\text{CH}_4$  was evolved as  $\text{CO}_2$ . In a similar study, Iversen et al. (1987) quantified pelagic methanogenesis and AOM in a meromictic lake in Nevada, USA. In contrast, they found that AOM actually exceeded rates of net  $\text{CH}_4$  production in all depths studied and that little or no coupling with SR existed. The anoxic column of an Antarctic lake, covered by permanent ice, was found to oxidize almost all of  $\text{CH}_4$  production with very little escaping the water column (Smith et al., 1993). This study did not address potential electron acceptors, but oxidation did occur in the  $\text{SO}_4^{2-}$ -rich zone of the water column. A more recent study of  $\text{CH}_4$  dynamics in a ferruginous lake (Lake Matano, Indonesia) demonstrated AOM in the water column when  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were not available but Fe oxides were abundant (Crowe et al., 2010).

Smith et al. (1991) used  $^{13}\text{C}\text{-CH}_4$  as a conservative tracer in small-scale natural-gradient test in a contaminated anoxic sand and gravel aquifer on Cape Cod, Massachusetts, USA. The aquifer was naturally  $\text{CH}_4$ -deficient and no response to the addition was expected. Surprisingly,  $\text{CH}_4$  was readily oxidized to  $\text{CO}_2$  in the anoxic portion of the aquifer. Moreover, the aquifer had high nitrate ( $\text{NO}_3^-$ ) concentrations but low  $\text{SO}_4^{2-}$ . Nitrate seemed the most likely electron acceptor due to the high  $\text{NO}_3^-$  concentration and thermodynamic favorability of the reaction (Table 1).

AOM was demonstrated in tank reactors (Islas-Lima et al., 2004) and a sediment receiving agricultural runoff high in  $\text{NO}_3^-$  (Raghoebarsing et al., 2006). Islas-Lima et al. (2004) used 2 L tank reactors with anoxic sewage sludge inoculums and  $\text{CH}_4$  as the sole electron donor. Results showed clear  $\text{NO}_3^-$  depletion in the presence of  $\text{CH}_4$ ,

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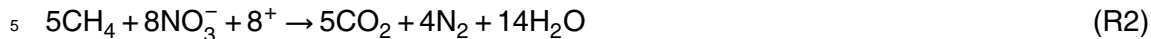
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and depletion rates increased as CH<sub>4</sub> concentration increased. Raghoebarsing et al. (2006) enriched a microbial consortium from anoxic canal sediment that oxidized CH<sub>4</sub> to CO<sub>2</sub> coupled to denitrification (see Table 1) according to Reaction (2) (from Raghoebarsing et al., 2006).



The consortia consisted of an archaeon that is closely related to an archaeal anaerobic methane oxidizer (ANME), and a bacterium, presumably a denitrifier, that has not been cultured. Additions of <sup>13</sup>C-labelled CH<sub>4</sub> and analysis of lipid biomarkers indicated that CH<sub>4</sub>-derived C was incorporated into the biomass of both the bacterium and the archaeon, but to a lesser degree in the archaeon. It is not clear what is driving this pattern, but it is important to point out that the enrichment culture in this study utilized nitrite (NO<sub>2</sub><sup>-</sup>) in preference to NO<sub>3</sub><sup>-</sup>, and the process would stop in the presence of CH<sub>4</sub> and NO<sub>3</sub><sup>-</sup> if NO<sub>2</sub><sup>-</sup> became exhausted. Recent work by Ettwig et al. (2010; 2008) showed that NO<sub>2</sub><sup>-</sup>-driven AOM can occur in the absence of an archaeal partner and is carried out by an anaerobic denitrifying bacterium that oxidizes CH<sub>4</sub> aerobically by reducing nitric oxide to N<sub>2</sub> and O<sub>2</sub>. This could explain why less of the labeled CH<sub>4</sub>-C was recovered from the archaeon.

Results from landfill-leachate plumes, on the other hand, have demonstrated less consistent results. A leachate plume study in Grinsted, Denmark showed that CH<sub>4</sub> disappeared completely in the zone of NO<sub>3</sub><sup>-</sup> reduction, thus agreeing with the conclusions of Smith et al. (1991), Islas-Lima et al. (2004), and Raghoebarsing et al. (2006), suggesting that CH<sub>4</sub> is an electron donor in the reduction of NO<sub>3</sub><sup>-</sup> (Bjerg et al., 1995). In contrast, Grossman et al. (2002) found that AOM consumed some of the CH<sub>4</sub> in an Oklahoma, USA leachate plume. Hydrochemical data suggested indirectly that AOM was most likely associated with a methanogen/SRB consortium.

In a more direct study of contaminant effects on CH<sub>4</sub> production, Malek and Weismann (1988) reported cyclic shifts from net CH<sub>4</sub> production to net anoxic CH<sub>4</sub> consumption when they incubated fresh and saltwater biomass, petroleum, oil shale

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bitumen, kerogen and sewage sludge digest with inert gas headspaces. Regardless of substrate, they recorded several cyclic episodes. No mechanisms were examined in this study, but results suggest a substrate limitation on AOM.

Although they are functionally man-made wetlands, rice-paddy soils are relatively high in organic matter and represent a significant atmospheric CH<sub>4</sub> source (Roy and Conrad, 1999). AOM has been hypothesized as an important mechanism in flooded rice paddies (Daniel et al., 1999), but published reports are few and evidence is circumstantial. Miura et al. (1992) determined that AOM linked to the reduction of Fe(III) consumed CH<sub>4</sub> that had percolated into the subsoil. Murase and Kimura (1994c; 1994b; 1994a) reported similar results from incubations of rice straw amended paddy soil, but identified SO<sub>4</sub><sup>2-</sup> leached from the plow layer as the electron acceptor in the process. Overall, AOM accounted for a small percentage of the total CH<sub>4</sub> budget in these systems and mechanistic discussion was purely speculative.

### 2.3 Peatland ecosystems

Despite the importance of peatlands to global C and atmospheric CH<sub>4</sub> cycles and the need for a process-based understanding of controls on wetland CH<sub>4</sub> fluxes. (Segers, 1998), our understanding of AOM as a potential CH<sub>4</sub> sink in peatlands is rudimentary. AOM as a sink for CH<sub>4</sub> has been alluded to in peat soils (Nedwell and Watson, 1995; Yavitt et al., 1988), but until recently no data had been presented. Rather, conceptual models of CH<sub>4</sub> cycling in peat-forming wetlands (Fig. 1) describe CH<sub>4</sub> fluxes as the balance between anaerobic methanogenesis and aerobic CH<sub>4</sub> consumption (Whalen and Reeburgh, 2000). Indeed, many peatlands are seasonally dry at the surface, resulting in an oxic zone that CH<sub>4</sub> must pass through; detecting AOM against such a large aerobic sink might be one reason the process is unappreciated.

Geochemical evidence for AOM, such as depth distribution profiles of electron acceptors and donors, is difficult in peat soils. The biogeochemical heterogeneity of these soils means that anaerobic processes overlap each other spatially, and zones of rhizospheric influence create spatial and temporal redox variability that further complicate

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studies of gross CH<sub>4</sub> cycling rates and controls on atmospheric flux (Fig. 1). However, many studies have looked at the distribution and importance of electron acceptors in peat (e.g. Bauer et al., 2007; Deppe et al., 2010; Keller and Bridgham, 2007) and experimentally manipulated electron acceptor variability (e.g. Dettling et al., 2006; Dise and Verry, 2001; Vile et al., 2003) to understand controls on CH<sub>4</sub> flux. The accepted model (as depicted in Fig. 1) suggests that methanogenesis is a primary C mineralization process in permanently anoxic peat, but more thermodynamically favorable reactions involving alternative electron acceptors, such as SO<sub>4</sub><sup>2-</sup> and Fe, suppress CH<sub>4</sub> production and drive organic carbon oxidation in surface peat that is seasonally oxygenated and around plant roots (Roden and Wetzel, 1996; Watson et al., 1997).

Although variations in CH<sub>4</sub> flux have been explained using correlations with environmental variables (e.g. Bubier, 1995; Bubier et al., 1995a; Bubier et al., 1995b; Dise, 1993; Frolking and Crill, 1994; Mikkela et al., 1995; Moore and Knowles, 1989; Whiting and Chanton, 1993), this approach describes only a portion of the observed variation in fluxes (Segers, 1998). Process-based studies using potential CH<sub>4</sub> production and oxidation assays (Coles and Yavitt, 1996; Sundh et al., 1995; Yavitt and Lang, 1990; Yavitt et al., 1997) also are limited in terms of explaining and predicting CH<sub>4</sub> fluxes (Bellisario et al., 1999). A study by Smemo and Yavitt (2006) suggests a more complicated CH<sub>4</sub> dynamic in some peatlands; despite the expectation of high CH<sub>4</sub> fluxes during warm wet periods, low potential CH<sub>4</sub> production rates due to AOM (Fig. 1) might have served as an additional process controlling net fluxes and might help explain why anaerobic CO<sub>2</sub> production often is greater than consumption of known electron acceptors (Blodau et al., 2007; Knorr and Blodau, 2009; Watson and Nedwell, 1998).

Based on the anecdotal evidence from that study, Smemo and Yavitt (2007) used CH<sub>4</sub>-amended laboratory incubations of anoxic peat to demonstrate and quantify AOM occurrence in a peat-forming wetland in central New York State. They used specific (2-bromoethanesulfonate (BES)) and non-specific (NO<sub>3</sub><sup>-</sup>) methanogenic inhibitors, as well as both stable isotope tracer and <sup>13</sup>C fractionation techniques, which allowed them to separate production and consumption processes occurring simultaneously and

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estimate gross rates of CH<sub>4</sub> production and consumption. Data showed not only net AOM rates nearly as high as reported net aerobic CH<sub>4</sub> oxidation rates, but also that AOM can consume a significant portion of gross CH<sub>4</sub> production when net CH<sub>4</sub> production is measured; suggesting that commonly used potential CH<sub>4</sub> production assays truly measure net CH<sub>4</sub> dynamics and not gross production. Their results further imply that AOM is CH<sub>4</sub>-limited (Fig. 2). Hence, AOM would not be observed in most laboratory assays in which incubations generally have no CH<sub>4</sub> at the outset and CH<sub>4</sub> is not allowed to accumulate for extended periods. These findings suggest, therefore, that in situ AOM occurs only where CH<sub>4</sub> accumulates to sufficient concentrations, or that the process may be important at different times of the year. Hoehler et al. (1994), while studying AOM dynamics and mechanisms in a marine sediment, also found that AOM is a net sink for CH<sub>4</sub> in the SO<sub>4</sub><sup>2-</sup>-depleted zone at 26 °C, but AOM proceeded in the lower portion of the SR zone at 10 °C in the absence of CH<sub>4</sub> production. Similar dynamics related to the seasonal relative importance of methanogenesis versus AOM, and therefore the apparent CH<sub>4</sub> sink strength due to AOM, might exist in peatlands.

For instance, methanogens in non-marine environments have shown growth optima at 35 °C and methanogenesis is greatly limited at temperatures below 15 °C (Zinder, 1993). In contrast, laboratory assays using peat from a wetland in central New York State, amended with BES as a methanogenic inhibitor and headspace CH<sub>4</sub> additions (*p*CH<sub>4</sub> = ~500 Pa), demonstrated that net AOM rates were essentially zero when incubated at 70 and at 37 °C, whereas maximum rates occurred at 25 °C and still significant rates occurred at 6 °C (Fig. 3; data from Smemo, 2003). Thus, methanogenesis and AOM might have different temperature optima in peatlands and opens the possibility that AOM is out of phase with CH<sub>4</sub> production and might occur during periods when peat temperatures are below the ideal for methanogenesis, such as periods that are infrequently studied. This suggests a seasonal pattern for CH<sub>4</sub> cycling where AOM functions as a significant CH<sub>4</sub> sink by consuming CH<sub>4</sub> when methanogenesis rates are small. Alternatively, AOM could proceed during cold periods when the wetland surface is frozen, diffusion transport and ebullition are limited, and CH<sub>4</sub> accumulates.

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Furthermore, AOM assays conducted using peat from a suite of sites (Smemo and Yavitt, 2007) demonstrated that AOM occurs in a variety of peatlands ranging from nutrient-poor (ombrotrophic) bogs to nutrient-rich (minerotrophic) fens. Because they found AOM was quantitatively more important in minerotrophic systems with ground-water and surface water inputs, it seemed possible that potential electron acceptors for the process were supplied by hydrologic inputs. Temporal patterns in a nutrient-rich fen showed seasonal and annual water table height and redox status patterns, and the authors suggested that such patterns could drive re-oxidation of reduced compounds and therefore represent an electron acceptor replenishment mechanism necessary to maintain AOM.

### 3 Biogeochemistry

#### 3.1 Electron acceptor

AOM in peatlands has remained somewhat of an enigma. Not only has evidence for the process been lacking, but the terminal electron acceptor has remained elusive. Recent evidence provides strong support for the occurrence of AOM in peat soils (Smemo and Yavitt, 2007), yet conclusive evidence describing the mechanism and electron acceptor has not been reported. Peatlands are organic matter rich, metal poor, and often acidic (Damman, 1978). Metal concentrations are lower in peat than in mineral soils, and peat microbial communities have unique adaptations for scavenging metals. This may even be the case in less acidic peatlands like some fens, where organic matter binds metals tightly (e.g. Fe and Mn oxides rapidly reduced). Because known mechanisms of AOM involve high concentrations of metals, which likely do not exist in most peatlands, these pathways might be quantitatively unimportant in peat soils.

Sulfate-dependent AOM is barely favorable thermodynamically (Caldwell et al., 2008; Thauer and Shima, 2006; Wake et al., 1977), and the available evidence suggests that it proceeds at very slow rates even when  $\text{SO}_4^{2-}$  concentrations are large. This presents

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a dilemma for  $\text{SO}_4^{2-}$ -dependent AOM in peatlands because  $\text{SO}_4^{2-}$  concentrations, with a few exceptions, are presumably too small for the process to be beneficial (Wieder and Lang, 1988). Some evidence has suggested that AOM linked to SR occurs in flooded paddy soils (e.g. Murase and Kimura, 1994a), and Grossman et al. (2002) reported possible AOM in a landfill leachate plume that was likely associated with SR. Smemo and Yavitt (2007) found significant reductions in net  $\text{CH}_4$  flux with additions of  $\text{SO}_4^{2-}$ , but the effect was associated with suppression of gross  $\text{CH}_4$  production and not AOM stimulation.

Many peatland ecosystems do receive significant  $\text{SO}_4^{2-}$  inputs via acid deposition (Gauci et al., 2005; Wieder et al., 1992) and significant rates of SR do occur in peatlands (Dise and Verry, 2001; Keller and Bridgham, 2007), even though  $\text{SO}_4^{2-}$  concentrations remain very small compared to marine systems even under such conditions. Sulfate concentrations were found to increase at depth in Russian peatlands, which corresponded with zones of low  $\text{CH}_4$  production (Kravchenko and Sirin, 2007), but no mechanism was discussed. However, they suggested that competitive interactions between methanogens and SRB can occur in both  $\text{SO}_4^{2-}$ -rich and mineral-poor oligotrophic peatlands.

It is possible that a complex sulfur cycle in peat soil maintains AOM linked to SR; a process that depends on a relatively constant pool of internally cycled sulfur instead of external inputs (Blodau et al., 2007). Several potential mechanisms might drive this cycle. First, reduced sulfur compounds could be oxidized to  $\text{SO}_4^{2-}$  by aerobic sulfur-oxidizing organisms when seasonal water table fluctuations lead to oxic conditions in the surface peat, which can influence sulfur speciation and oxidation/reduction (Prietzel et al., 2009). Alternatively,  $\text{SO}_4^{2-}$  could be cycled in the oxic/anoxic interface surrounding plant roots. The highest rates of SR in flooded rice-paddy soils have been found to occur in the rhizosphere (Liesack et al., 2000), and high rates of sulfur cycling have consistently been measured in systems with low sulfur concentrations (Stubner et al., 1998). Finally, oxidation and reduction of sulfur compounds could occur under anaerobic conditions (Blodau et al., 2007) and the process could be related to an

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organic C electron acceptor (Heitmann and Blodau, 2006). Hence, a relatively small amount of S could be recycled and fuel significant organic C mineralization. Smemo and Yavitt (2007) measured significantly greater rates of AOM in surface peat associated with the plant rooting-zone than in deep peat that is permanently anoxic. Sulfur cycling in this zone could provide a mechanism for electron acceptor replenishment, but direct evidence was not reported.

Although AOM using  $\text{NO}_3^-$  as an electron acceptor provides nearly as much free energy as aerobic  $\text{CH}_4$  oxidation (Table 1), it proceeds by a very different mechanism than AOM linked to SR, as redox couples with  $\text{NO}_3^-$  are more positive than that required for reverse methanogenesis with MCR (Thauer and Shima, 2008). The mechanism remains elusive but appears to involve  $\text{NO}_2^-$  and other nitrogen oxides as electron acceptors for the oxidation of  $\text{CH}_4$  (Oremland, 2010). Although seasonal oxygenation of the peat surface can increase porewater  $\text{NO}_3^-$  concentrations (e.g. Schmalenberger et al., 2007), this mechanism seems less probable in peatlands because, in general, low nitrification (Westbrook et al., 2006) or rapid denitrification rates (Gorham et al., 1985), fueled by organic C sources other than  $\text{CH}_4$ , limit the availability of  $\text{NO}_3^-$  and other nitrogen oxides in the system. Moreover, plants are a rapid sink for outside N inputs (Moore et al., 2005). Kravchenko and Sirin (2007) did see increased  $\text{NO}_3^-$  concentrations deeper in the peat profile of three Russian peatlands (>1 m), in correspondence with decreased rates of  $\text{CH}_4$  production, but no explanation for presence of  $\text{NO}_3^-$  or nitrification at depth was provided. Nevertheless, the  $\text{NO}_3^-$  concentrations reported in Raghoebarsing et al. (2006) are uncommon in most peat-forming systems (Eriksson et al., 2010; Gorham et al., 1985). Nitrite turnover is very rapid in peat soil, and nitrogen oxides furthermore are consumed quickly via chemodenitrification under acidic conditions (Vancleemput and Baert, 1984). Thus, chemical processes compete with biological denitrification. Recent evidence (Ettwig et al., 2010), however, does suggest that the role of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  in peatland AOM needs further consideration.

It is important to also point out that  $\text{NO}_3^-$  can function as a non-specific methanogenic inhibitor, thereby decreasing the amount of  $\text{CH}_4$  available to  $\text{CH}_4$  oxidizers. This can

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happen because methanogens are simply out-competed energetically, but also because denitrification intermediates such as  $\text{NO}_2^-$  are known to suppress methanogenesis (Kluber and Conrad, 1998; Roy and Conrad, 1999). Raghoebarsing et al. (2006) observed that AOM rates were greater when  $\text{NO}_2^-$  was abundant with rates declining as  $\text{NO}_2^-$  became exhausted. It is possible the effect was due to suppression of  $\text{CH}_4$  production and then an apparent decrease in AOM as  $\text{NO}_2^-$  was used up and  $\text{CH}_4$  production increased. See Smemo and Yavitt (2007) for a discussion of  $\text{NO}_3^-$  effects on  $\text{CH}_4$  dynamics.

For these reasons we wonder whether Fe(III) could fuel AOM because the reaction is energetically favorable (Table 1). Fe(III) is an important electron acceptor in many wetland soils (Frenzel et al., 1999; Jäckel and Schnell, 2000; Roden and Wetzell, 1996) and it functions in organic C re-mineralization (Lovley and Phillips, 1986, 1988). Moreover, a recent study of  $\text{CH}_4$  cycling in ferruginous Lake Matano, Indonesia provides anecdotal evidence for AOM linked to Fe-oxides in the water column (Crowe et al., 2010). AOM was measured in the absence of both  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  suggesting Fe as the most likely terminal electron acceptor, but direct measurements were not provided.

Iron (III) could be mechanistically linked to AOM in peatlands in a few ways. The first, based on the work of Lovley et al. (1996) and Scott et al. (1998), involves humic substances serving as intermediate electron acceptors in the transfer of electrons between Fe-reducing organisms and an acetate-consuming microorganism (e.g. *Geobacter* sp.). Given the inherently high humic content of many wetland soils and the availability of  $\text{CH}_4$  as a C source, a similar mechanism could function to oxidize  $\text{CH}_4$  (Fig. 4) and Heitmann et al. (2007) demonstrated that electron transfer from dissolved organic matter to ferric iron is viable. The role of dissolved organic matter in electron transfer and the consequences for anaerobic metabolism is a contemporary area of inquiry and an important aspect of wetland C cycling (Heitmann et al., 2007).

It is possible that a consortium of organisms mediates AOM, much like the  $\text{SO}_4^{2-}$ -dependent process, but with a Fe-reducing bacterium such as *Geobacter* sp. or

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*Shewanella* sp. according to:



Zehnder and Brock (1980) were the first to propose that an unknown metal oxide could serve as the electron acceptor for AOM, though no evidence was presented. Other authors have since proposed this mechanism as well (e.g. Daniel et al., 1999; Murase and Kimura, 1994a), but the only supporting data is from rice paddies and is circumstantial (Miura et al., 1992). Smemo and Yavitt (2007) hypothesized the role of Fe(III) based on field observations of flocculated Fe(III) in surface waters of minerotrophic peatlands, Fe<sup>total</sup> concentrations in peat samples, and the potential for seasonal and annual re-oxidation of Fe(II). Laboratory experiments failed to exhibit any stimulation of AOM with a addition of 50 mmoles of amorphous Fe(III)-oxide, yet all of the Fe(III) additions were readily reduced in the peat (96 h incubation period). Experiments were unable to determine if the form of the Fe(III) was not available to AOM organism(s), or if the addition was rapidly chemically reduced and therefore not available to an AOM organism(s). Futhermore, Keller and Bridgham (2007) studied anaerobic C cycling pathways across a peatland trophic gradient in Michigan, USA, and found that Fe reduction was an insignificant component of anaerobic C mineralization. This finding was contradicted in a study of Fe reduction in an acidic fen (Küsel et al., 2008) where Fe reduction accounted for 27–72% of anaerobic C mineralization in fens receiving exogenous Fe and 7% with only internally cycled Fe. In a further study in the same peatlands (Reiche et al., 2008), Fe reduction was a significant process that inhibited methanogenesis. The authors also found that the addition of a methanogenic inhibitor (BES) resulted in a 45% decrease in Fe reduction, a result that could be explained by the hypothesized link between Fe reduction and reverse methanogenesis (Crowe et al., 2010). Given the importance of iron cycling processes in many ecosystems and the potential for this process, further work is needed to better understand forms of microbially available Fe in humic-rich environments and how it might be linked to AOM.

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## 3.2 Organism(s) responsible

Zehnder and Brock (1979) first proposed the idea of reverse methanogenesis, and they found that nine strains of methanogens were able to produce  $\text{CH}_4$  and carry out  $\text{CH}_4$  oxidation. However, the measured oxidation accounted for <1% of  $\text{CH}_4$  production, and there was some question whether carbon monoxide contamination of the  $^{14}\text{C}\text{-CH}_4$  used in the oxidation assays biased the results (Miller et al., 1999). Notwithstanding, recent work by Scheller et al. (2010) demonstrated that MCR (key enzyme in methanogenesis) does indeed catalyze AOM by converting  $\text{CH}_4$  into methyl-coenzyme M. Although all methanogens have MCR, not all are capable of AOM. Furthermore, the reverse methanogenesis mechanism with MCR works when  $\text{SO}_4^{2-}$  is the ultimate electron acceptor, but  $\text{NO}_3^-$ , Fe(III), or Mn(IV) availability is low in most peatlands (Damman, 1978) and it is therefore doubtful that reverse methanogenesis linked to these alternate electron acceptors is quantitatively important.

In marine systems, the archaeal methanogens and ANMEs fall into three phylogenetic groups; ANME-1 (with subgroups a and b) and ANME-2 (with subgroups a, b, and c) related to the *Methanosarcinales* (Boetius et al., 2000; Orphan et al., 2002), whereas ANME-3 is related to *Methanococoides* spp. (Knittel and Boetius, 2009). Whether these are the only members that mediate AOM is unclear. For instance, Scholten et al. (2005) reported AOM in an alkaline,  $\text{SO}_4^{2-}$ -rich lake mediated by a SRB, whereas known ANMEs were not involved; they suggested the SRB acts alone, meaning that yet undiscovered mechanisms might exist. For peatlands, most contain a high diversity of methanogens (Cadillo-Quiroz et al., 2008); however, ANME relatives appear to be restricted to nutrient-rich, grass dominated fen peatlands, at very low numbers, and they do not appear to occur in the extensive acidic peatlands dominated by mosses and shrubs (Dettling et al., 2007).

The SRB linked to AOM in marine sediments belong to Deltaproteobacteria, in particular the genera *Desulfosarcina*, *Desulfococcus*, and *Desulfobulbus* (Knittel and Boetius, 2009). However, these SRB are found mostly in  $\text{SO}_4^{2-}$ -rich and/or saline

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sediments, and are rare to absent in freshwater sediments (Miletto et al., 2008). The SRB in peat soils are poorly known and they are not members known to associate with ANME. Loy et al. (2004) found that acidic fens with low in situ  $\text{SO}_4^{2-}$  concentrations have a significant SR capacity and despite the presence of known SRB groups, they detected the presence of several novel SRB types that were unrelated to all known SRB. They suggested that these types belonged to a specialized group of SRB associated with low  $\text{SO}_4^{2-}$  environments. More recent work (Schmalenberger et al., 2007) has suggested that these previously undescribed groups are present in permanently anoxic peat and may act as fermentors in a syntrophic relationship with methanogens. This potential mechanism leaves the door open for the AOM linked to SR mechanism discussed previously.

A facultative dissimilatory Fe(III)-reducing organism that uses  $\text{CH}_4$  as a C or energy source also is a possible explanation for AOM in wetland soils (Fig. 4; Reaction 3), but the process was not observed in past studies of known Fe(III)-reducers or in AOM studies in peat soils (Smemo and Yavitt, 2007). A study by Daniel et al. (1999) found that Fe(III) reduction can be coupled to methanol oxidation by a syntrophic relationship between *Shewanella putrefaciens* and *Clostridium sphenoides*. They proposed a potentially beneficial reaction ( $\Delta G^{\circ} = -782 \text{ kJ reaction}^{-1}$ ) and claimed that this reaction would be slow due to the nature of the syntrophic relationship, but they did not account for the fact that Fe(III) is not available at pH 7.0 in natural waters. Thus, this energy yield is unrealistic. Table 1 provides a more realistic number. Despite proposed mechanisms, it is also unclear why an Fe(III)-reducing organism would utilize  $\text{CH}_4$  in peat soil where the pool of other organic compounds is often so vast.

Another possible pathway relates to anaerobic ammonium ( $\text{NH}_4^+$ ) oxidation (ANAMMOX), which is an important process in anoxic wastewaters (Jetten et al., 1999) and marine systems (Dalsgaard et al., 2003; Dalsgaard and Thamdrup, 2002; Kuypers et al., 2003). Although ANAMMOX likely plays a significant role in controlling N fluxes in marine systems (Capone and Knapp, 2007; Devol, 2003), it is possible that organisms responsible for ANAMMOX may be able to utilize  $\text{CH}_4$  in addition to  $\text{NH}_4^+$ . The

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two molecules are very similar, and oxygenase enzymes tend to be non-specific. In the case of aerobic environments, *ammonium monooxygenase* can readily utilize either  $\text{NH}_4^+$  or  $\text{CH}_4$  depending on which is more available. The same is true for *methane monooxygenase*, which has been shown to utilize  $\text{NH}_4^+$  (Bosse et al., 1993). There is no evidence to suggest that enzymatic pathways in anoxic environments are analogous to those in oxic environments, and ANAMMOX bacteria are not known to be ubiquitous in wetland ecosystems (Zhu et al., 2010), but the possibility does exist. Smith et al. (1991) found that a  $\text{CH}_4$  tracer was readily oxidized in an anoxic aquifer with high  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentrations and no ambient  $\text{CH}_4$ . The  $\text{CH}_4$ , therefore, could have been oxidized by an anaerobic  $\text{NH}_4^+$  oxidizing organism if that organism was biochemically able to utilize  $\text{CH}_4$  when introduced in sufficient concentrations (Richard L. Smith, USGS, Boulder, Colorado, USA, personal communication, 2000). Recently, Zhu et al. (2010) discussed the role of ANAMMOX and AOM coupled to denitrification in wetland ecosystems as a control on N cycling; suggesting that N transformations could be a sink for  $\text{CH}_4$  in wetlands. The authors further suggest that environmental conditions for the coupling of these processes exist, but evidence is lacking and many wetlands do not have high  $\text{NO}_2^-$  availability needed to support it. Aerobic  $\text{NO}_2^-$  production in peat could provide a mechanism for coupling of aerobic and anaerobic processes and reveal such an AOM pathway.

Finally, the role of bacterial methanotrophs, usually thought to be strictly aerobes, needs to be considered in future studies of AOM. Recent genomic insights into the methanotrophic bacteria *Methylococcus capsulatus* (Bath) revealed unexpected metabolic flexibility, including chemolithotrophic abilities and the ability to function at low redox potentials (Ward et al., 2004). *M. capsulatus* (Bath) produces enzymes usually associated with fermentative activity, and is thought to possess high molecular-weight cytochromes that are often associated with metal-ion reducing genera such as *Shewanella* and *Geobacter*. Ward et al. (2004) point out that *M. capsulatus* (Bath) could benefit from oxidizing  $\text{CH}_4$  under low oxygen conditions by physically living near or in zones where  $\text{CH}_4$  production occurs. The discovery that AOM coupled to denitrification

is carried out by an oxygenic bacterium in freshwater sediments (Ettwig et al., 2010) only underscores the need to consider metabolic flexibility when studying AOM in peatlands.

#### 4 Global CH<sub>4</sub> cycle

AOM appears to be a potential sink for CH<sub>4</sub> production in some peatland ecosystems and therefore a constraint on CH<sub>4</sub> fluxes to the atmosphere. Nevertheless, it is unclear whether the process is quantitatively important at the ecosystem or global scale, or simply a novel process that occurs but consumes less than the annual variation in global CH<sub>4</sub> fluxes. Smemo and Yavitt (2006) reported circumstantial evidence that suggested AOM might be a significant constraint on CH<sub>4</sub> fluxes during very wet years in a peatland in Central New York State. Fluxes were much less than expected given redox conditions and porewater CH<sub>4</sub> concentrations. Smemo and Yavitt (2007) also reported net AOM rates in the same peatland up to 176 nmol kg peat<sup>-1</sup> s<sup>-1</sup>, with mean a mean rate of 17 nmol kg<sup>-1</sup> s<sup>-1</sup>. Using an AOM rate of 10 nmol kg<sup>-1</sup> s<sup>-1</sup> with ~3 months of activity per year, each kg of dry peat could oxidize 1–2 grams of CH<sub>4</sub> annually. This represents about 50% of CH<sub>4</sub> efflux into the atmosphere. With the exception of experiments using methanogenic inhibitors, Smemo and Yavitt (2007) presented net oxidation rates that potentially underestimate gross CH<sub>4</sub> oxidation rates, and the rates from this study were similar to many published rates of CH<sub>4</sub> production and aerobic CH<sub>4</sub> oxidation (e.g. Moore and Dalva, 1997). AOM might then function to stabilize peatland CH<sub>4</sub> fluxes. In contrast, AOM could be sensitive to initial conditions and thermodynamically constrained in natural environments, thus not quantifiably important in terms of annual CH<sub>4</sub> budgets.

Scaling process rates to annual global fluxes is tricky business because published peatland AOM rates are few and in situ measurements are lacking. Laboratory assays often fail to reflect the actual conditions of the study environment and tend to select for organisms that may not be ecologically significant (Liesack et al., 2000).

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Nevertheless, we can make rough estimates using the AOM rates reported by Smemo and Yavitt (2007). Although the rates reported in this study are low with respect microbial metabolic rates, they are 4–5 orders of magnitude higher than in marine sediments and anoxic waters. This disparity is realistic because Bacteria and Archaea in many marine sediments have slow metabolic rates due to low temperatures and small inputs of organic C to drive metabolism. Reported rates of AOM tied to denitrification in agricultural canals (Raghoebarsing et al., 2006) were also lower than this estimate, but these estimates were from inoculated sequencing batch reactors where CH<sub>4</sub> was the primary C source. This is not the case in most wetland soils where organic C sources are plentiful. If we assume a modest AOM rate of 5 nmol kg<sup>-1</sup> s<sup>-1</sup> as an average for peatlands between 50 and 70° N (area = 2.65 × 10<sup>12</sup> m<sup>2</sup> (Matthews and Fung, 1987)), a peat bulk density of 0.1 g cm<sup>-3</sup>, and 3 months of AOM activity each year in 50% of the top 50 cm of peat, northern peatlands could anaerobically consume 41 Tg of CH<sub>4</sub> on average each year. This is roughly equal to CH<sub>4</sub> flux estimates for northern peatlands of ~38 Tg (Bartlett and Harriss, 1993). In other words, enhanced aerobic CH<sub>4</sub> oxidation rates notwithstanding, northern peatland CH<sub>4</sub> emission rates could be 2x the current rate in the absence of AOM. Better studies to confirm this hypothesis are certainly needed given the inherent temporal and spatial variability of microbial processes in peatlands, but such estimates imply that the process can be globally significant and deserves further attention.

## 5 Challenges and future directions

Considering the massive CO<sub>2</sub> sink and significant CH<sub>4</sub> source that peatlands represent and their sensitivity to environmental changes (Gorham, 1991), it behooves us to better understand the patterns and processes that control C cycling in these systems. New evidence suggests that AOM may be one of these processes, yet despite current findings (Smemo and Yavitt, 2007) we still know little about the process and the organisms involved and many challenges remain (Caldwell et al., 2008). Compared

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to deep marine sediments that are more or less constant in regards to temperature, chemistry, pH, and organic C inputs, peat soils represent a complex matrix in which to study the processes and mechanisms controlling C cycling. Wetlands in general are highly heterogeneous environments that experience temperature, pH, hydrologic, chemistry and redox fluctuations at a variety of scales. Moreover, the presence of plant roots further increases redox, nutrient and C substrate gradients. This heterogeneity directly and indirectly influences factors controlling AOM. Studying specific processes in peat is consequently a daunting task, and new techniques and methods are needed to address questions pertaining to electron acceptors, pathways, and ecosystem importance.

A first logical step towards achieving these goals is to focus effort on obtaining in situ AOM measurements in peatlands, and then generating and testing new hypotheses relating to mechanisms. Laboratory methods are useful as they provide a controlled environment for constraining variability, selecting for particular processes, identifying novel processes, and asking basic mechanistic questions. Laboratory studies are, however, inherently limited when one attempts to quantify the importance of the process in nature (Liesack et al., 2000). In short, potential activity does not necessarily equate with function, particularly with respect to systems such as peatlands that are biogeochemically complex across space and time. New field-based techniques, such as those involving isotopic tracers or specific inhibitors, are clearly needed. We also should further facilitate the use of modern molecular techniques that have expanded our knowledge of AOM in marine (e.g. Boetius et al., 2000; Orphan et al., 2001; Pancost et al., 2000; Thomsen et al., 2001) and freshwater systems (e.g. Raghoebarsing et al., 2006; Ettwig et al., 2008, 2010).

We have focused on AOM in peatland ecosystems, but AOM may be broadly important across wetland type and location. In fact, if AOM in freshwater systems is related to Fe or S cycling, then AOM may be quantitatively more important in non peat-forming wetlands where organic matter turnover is fast and CH<sub>4</sub> fluxes are high, such as those in the tropics (Bartlett and Harriss, 1993). Hence, there is a need for studies

addressing the occurrence and importance of AOM in tropical swamps and marshes, including saline systems such as coastal mangroves.

*Acknowledgements.* We would like to thank all of those who provided comments on earlier drafts of this manuscript, including Stephen H. Zinder, Timothy J. Fahey, Peter M. Groffman, and Wendy M. Mahaney. Their insight and comments led to considerable improvements. We would also like to thank Andria Blackwood for help with graphics in the conceptual figure. Funding for this work was provided by the US National Science Foundation and US Department of Agriculture.

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**Table 1.** Gibbs Free Energy ( $\Delta G'$ ) for  $\text{CH}_4$  oxidation using various inorganic electron acceptors at 28 °C and pH 7.0. Calculations assume these peat porewater conditions;  $[\text{CH}_4]= 10 \text{ kPa}$ ;  $[\text{HCO}_3^-]= 20 \text{ mM}$ ;  $[\text{H}_2]= 10^{-3} \text{ kPa}$ ;  $[\text{O}_2]= 20 \text{ kPa}$ ;  $[\text{NO}_3^-]= 1.6 \text{ }\mu\text{M}$ ; [soluble Fe(III)]= 0.5 mM; [soluble Fe(II)]= 10 mM;  $[\text{SO}_4^{2-}]= 0.2 \text{ mM}$ ;  $[\text{HS}^-]= 30 \text{ }\mu\text{M}$ . Values for  $\text{CH}_4$ ,  $\text{HCO}_3^-$ ,  $\text{NO}_3^-$ , Fe(III) and Fe (II) are from measurements taken by Smemo and Yavitt (2007) for a wetland in central New York State.

Electron Acceptor	$\Delta G'$ (kJ rxn <sup>-1</sup> )
$\text{O}_2$	-488.5
$\text{NO}_3^-$	-372.8
$\text{Fe}(\text{OH})_3$	-115
$\text{SO}_4^{2-}$	-19.3

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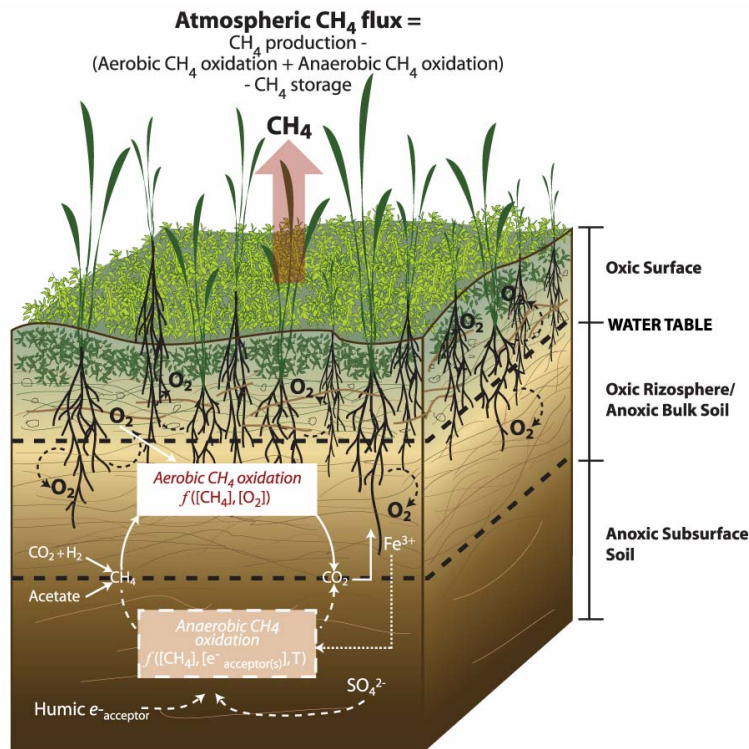
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**Fig. 1.** Conceptual model of CH<sub>4</sub> cycling in the profile of *Sphagnum* sp. and *Carex* sp. covered peat-forming wetland that depicts the relationship between water table depth, plant rooting zone, and redox status. Solid boxes and arrows represent known processes and controls on CH<sub>4</sub> flux, dashed black arrows represent O<sub>2</sub> flux from plant roots, and dashed white boxes and arrows represent recently quantified or hypothesized processes and controls. The proposed equation at the top illustrates the sum of the processes and factors controlling net atmospheric CH<sub>4</sub> flux rates from wetland ecosystems.

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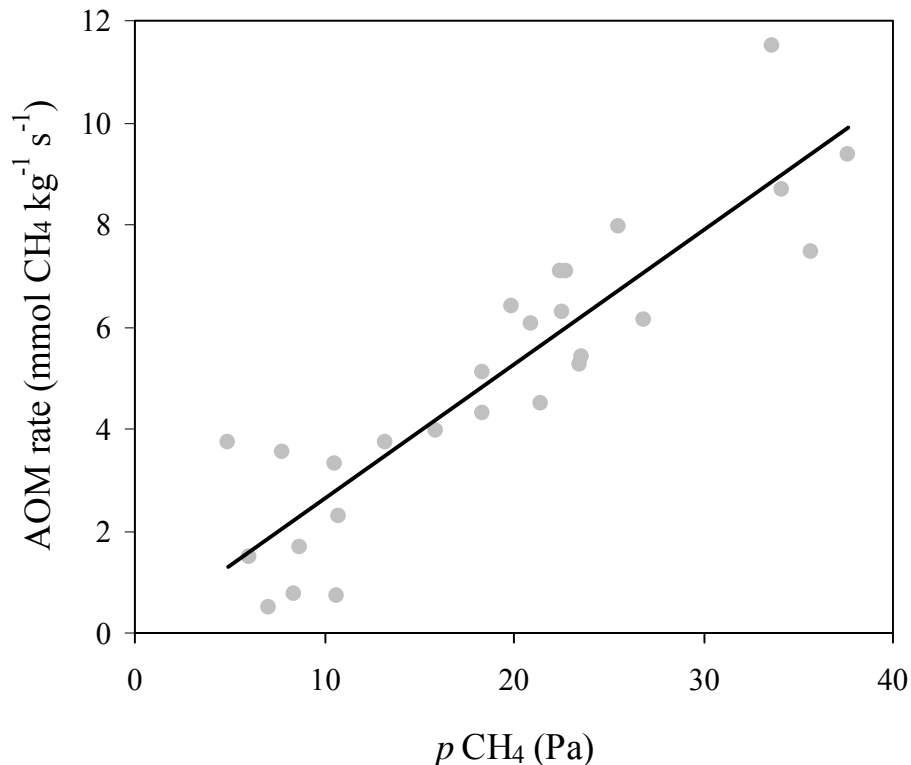
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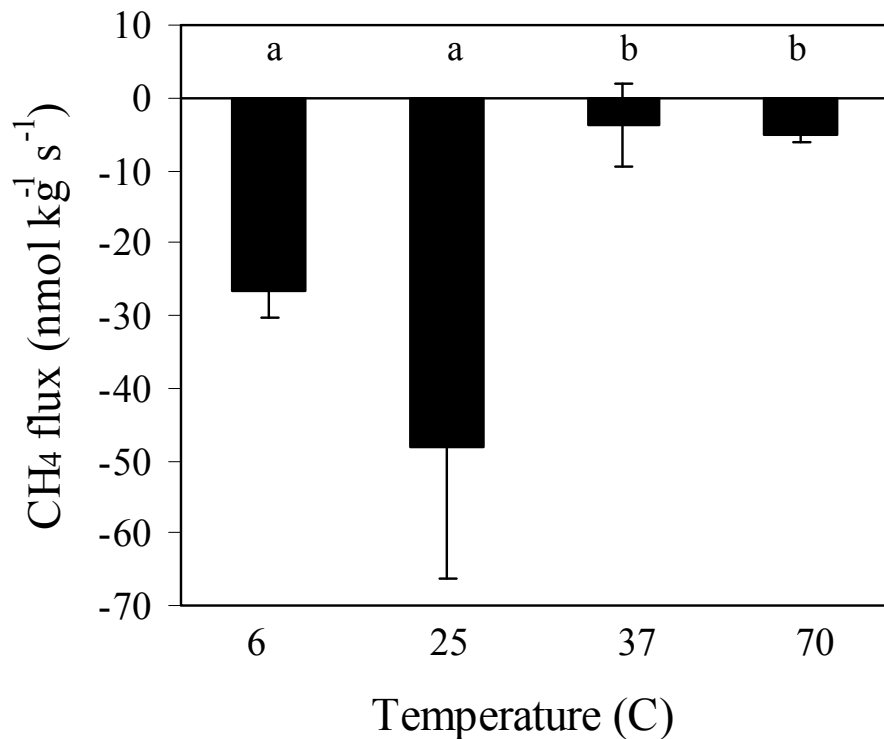
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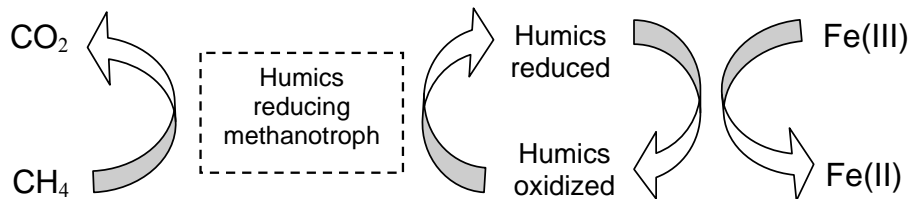




**Fig. 2.** Porewater  $\text{CH}_4$  concentration dependent rates of AOM. Line derived from a regression model ( $r^2 = 0.89$ ) of rates calculated from  $\text{CH}_4$  production data presented in Smemo and Yavitt (2007). Experiment involved homogenized peat incubated with varying headspace  $\text{CH}_4$  concentrations ranging across 3 orders of magnitude.  $\text{CH}_4$  concentration is presented as  $p\text{CH}_4$  of peat porewater in equilibrium with the headspace.



**Fig. 3.** Mean rates ( $N=4$ )  $\pm$  SE of  $\text{CH}_4$  flux in anoxic peat incubations at four different temperatures using a methanogenic inhibitor (BES). Negative values denote oxidation/consumption. Different letters are significantly different at  $p < 0.05$ .



**Fig. 4.** Conceptual mechanism for  $\text{CH}_4$  oxidation linked to humic substance mediated  $\text{Fe(III)}$  reduction. Adapted from Scott et al. (1998).

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