



# Peatland types influence the inhibitory effects of a humic substance analog on methane production



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## ABSTRACT

Methane (CH<sub>4</sub>) production is often impeded in many northern peatland soils, even though more thermodynamically favorable inorganic terminal electron acceptors (TEAs) used in anaerobic respiration are often present in low concentrations in these soils. Recent studies suggest that humic substances in wetland soils can be utilized as organic TEAs for anaerobic respiration and may directly inhibit CH<sub>4</sub> production. Here we utilize the humic analog anthraquinone-2, 6-disulfonate (AQDS) to explore the importance of humic substances, and their effects on the temperature sensitivity of anaerobic decomposition, in two peatland soils. In a bog peat, AQDS was not initially utilized as a TEA, but greatly inhibited the fermentative production of acetate by >98%, carbon dioxide by >49%, hydrogen by >90%, and CH<sub>4</sub> production by 86%. When added together with glucose, <47% of added AQDS was reduced after a lag period of 5 to 10 days. In contrast, no inhibitory effect of AQDS on fermentation was found in a fen peat, and AQDS was readily reduced. The addition of glucose and AQDS to both bog and fen peats caused complicated temporal dynamics in the temperature sensitivity of CH<sub>4</sub> production, reflecting temporal changes in the temperature responses of other decomposition processes with effects on methanogenesis. Our results show that the inhibitory effects of a humic analog on CH<sub>4</sub> production depend on peatland type, acting primarily as a toxic compound in bog soils and as a competitive TEA in fen soils. The results also suggest that the high concentrations of humic substances in northern peatlands may impact the temperature sensitivity of soil carbon cycling in these ecosystems.

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## 1. Introduction

Wetlands store globally significant amounts of soil organic carbon (SOC) (Maltby and Immirzi, 1993), which may decompose to either carbon dioxide (CO<sub>2</sub>) or methane (CH<sub>4</sub>) via anaerobic metabolism. Given that on a mass basis a sustained flux of CH<sub>4</sub> has a global warming potential 45 times greater than CO<sub>2</sub> over 100 years (Neubauer and Megonigal, 2015), the ratio of CO<sub>2</sub> to CH<sub>4</sub> produced during anaerobic C decomposition may have substantial impacts on the Earth's future climate. It is therefore essential to understand the fundamental controls over organic C mineralization to CO<sub>2</sub> and CH<sub>4</sub> in these systems.

Rates of anaerobic C mineralization and the ratio of its end products, CO<sub>2</sub> and CH<sub>4</sub>, are the result of a suite of complicated interactions among multiple microbial functional groups (Bridgham et al., 2013; Megonigal et al., 2004). In the absence of oxygen, organic polymers are initially hydrolyzed and degraded to alcohols, short-chain fatty acids, CO<sub>2</sub>, and dihydrogen (H<sub>2</sub>) during primary fermentation. Syntrophic bacteria

convert the alcohols and short-chain fatty acids to acetate, H<sub>2</sub>, and CO<sub>2</sub>. Subsequently, acetate and H<sub>2</sub> are utilized for microbial respiration and methanogenesis. In general, microbes will preferentially use a variety of thermodynamically favorable terminal electron acceptors (TEAs), such as nitrate (NO<sub>3</sub><sup>-</sup>), iron (Fe(III)), manganese (Mn(III, IV)), and sulfate (SO<sub>4</sub><sup>2-</sup>), for respiration before CH<sub>4</sub> production becomes important, which results in a higher ratio of CO<sub>2</sub>:CH<sub>4</sub> production. The relative importance of TEAs for anaerobic respiration will depend on the initial pool size of TEAs and the rate of electron supply from fermentation, which in turn depends on the availability of labile organic compounds and the temperature dependence of anaerobic respiration. After these more favorable TEAs have been depleted, methanogens use either acetate (acetoclastic methanogenesis) or CO<sub>2</sub>/H<sub>2</sub> (hydrogenotrophic methanogenesis) to produce CH<sub>4</sub>, resulting in an approximately equal molar production of CO<sub>2</sub> and CH<sub>4</sub> (Conrad, 1999). CO<sub>2</sub> acts as a TEA in hydrogenotrophic methanogenesis (a chemoautotrophic process), but here we more narrowly use the term TEAs to refer to those compounds that accept electrons in CO<sub>2</sub>-generating respiratory reactions.

Despite northern peatlands generally having low concentrations of inorganic TEAs (Keller and Bridgham, 2007; Vile et al., 2003), their ratio of CO<sub>2</sub>:CH<sub>4</sub> production is often much greater than one (Duddleston et al., 2002; Hines et al., 2001; Keller and Bridgham,

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2007; Ye et al., 2012). Moreover, the production ratio of  $\text{CO}_2:\text{CH}_4$  can vary by several orders of magnitude among different types of peatlands, with higher ratios typical of bogs because of low  $\text{CH}_4$  production, suggesting distinctive pathways and controls of anaerobic decomposition (Bridgman et al., 1998; Hines et al., 2008; Ye et al., 2012). To date it is not clear what ultimately limits  $\text{CH}_4$  production and causes the large variations of  $\text{CO}_2:\text{CH}_4$  production in northern peatlands (Bridgman et al., 2013), but there is a growing consensus that these patterns cannot be explained solely by respiration of inorganic TEAs.

Humic substances have been hypothesized to play multiple roles in anaerobic C cycling beyond their effect as organic electron donors for decomposition. Humic substances are traditionally thought to be a unique, heterogeneous class of macromolecules, yet recent research suggests that they are collections of relatively small molecules derived from biological materials (Lehmann et al., 2008; Piccolo, 2002; Sutton and Sposito, 2005). Irrespective of the exact chemical nature of humic substances, aromatic substances have been shown to occur at high concentrations in peatlands (Collins and Kuehl, 2001; Tfaily et al., 2013). It is well recognized that humic substances can act as organic TEAs (Cervantes et al., 2000; Keller et al., 2009; Klupfel et al., 2014; Lovley et al., 1996). Galand et al. (2010) hypothesized that the unequal production of  $\text{CO}_2$  and  $\text{CH}_4$  in peat soils results from the reduction of humic substances as TEAs and that this process is more significant in bogs than in rich fens. Keller and Takagi (2013) verified in a bog soil that organic TEAs could explain a significant fraction of the  $\text{CO}_2$  produced during anaerobic respiration and that  $\text{CH}_4$  was not produced until the electron-accepting capacity of the organic TEAs was exhausted. In addition to serving as organic TEAs for microbial respiration, recent research has shown that humic substances are able to oxidize sulfur species, promoting sulfate reduction and contributing to high  $\text{CO}_2:\text{CH}_4$  production ratios (Heitmann and Blodau, 2006; Minderlein and Blodau, 2010). Humic substances can also promote iron reduction in wetland sediments by serving as electron shuttles (Roden et al., 2010). The use of humic substances as TEAs in the process of anaerobic  $\text{CH}_4$  oxidation in peatland soils has also been hypothesized (Gupta et al., 2013).

It is generally believed that quinone moieties contained in humic substances are important electron-accepting groups (Aeschbacher et al., 2009; Ratasuk and Nanny, 2007; Scott et al., 1998). Quinone moieties are aromatic molecules with an even number of carbonyl ( $\text{C}=\text{O}$ ) groups, which upon reduction are converted into hydroxyl groups ( $\text{C}-\text{OH}$ ) in the resulting hydroquinone (Cory and McKnight, 2005). Humic respiration has been investigated with a functional analog, anthraquinone-2,6-disulfonate (AQDS), in many systems (Cervantes et al., 2000; Keller et al., 2009; Lovley et al., 1996). AQDS reduction (i.e., quinone respiration) to anthrahydroquinone-2,6-disulfonate (AHQDS) is thermodynamically more favorable than methanogenesis, which should lead to an increase in  $\text{CO}_2:\text{CH}_4$  production ratio in soils where AQDS-like humics are being utilized for microbial respiration (Cervantes et al., 2000). Keller et al. (2009) demonstrated that additions of AQDS to wetland soils resulted in decreased  $\text{CH}_4$  production and increased ratios of  $\text{CO}_2:\text{CH}_4$ , although this pattern was confounded by changes in pH. Amendment of AQDS to Arctic peat soils also stimulated iron reduction and resulted in higher production ratios of  $\text{CO}_2:\text{CH}_4$  (Lipson et al., 2010).

In addition to serving as electron acceptors, organic matter in peatlands is well known to inhibit microbial processes. For example, extracts from peat (Minderlein and Blodau, 2010) and *Sphagnum* mosses (Medvedeff et al., 2015), a dominant component of the plant community of many peatlands, have been shown to selectively inhibit various anaerobic microbial processes. This inhibition is often attributed to the phenolic moieties of organic matter (Freeman et al., 2012; Wang et al., 2015). However, quinone compounds also have strong antibiotic effects (Monks et al., 1992) and Cervantes et al. (2000) suggested that AQDS may have a direct toxic effect on methanogens.

Untangling the multiple ways that humic substances can potentially influence anaerobic C mineralization remains a challenge. We have recently observed different rates of  $\text{CO}_2$  and  $\text{CH}_4$  production in soils from six peatland types across a hydrogeomorphic landscape gradient, ranging from ombrotrophic bogs (i.e., atmospheric inputs only) to minerotrophic rich fens (i.e., with surface- or groundwater inputs) even when incubated at common pHs (Ye et al., 2012). All of the peats contained minimal concentrations of inorganic TEAs, yet none of them exhibited the equal molar production of  $\text{CO}_2$  and  $\text{CH}_4$  expected under methanogenic conditions during a 43-day incubation. Bog peats exhibited particularly high  $\text{CO}_2:\text{CH}_4$  production ratios (Ye et al., 2012), and we hypothesized that humic substances may explain low  $\text{CH}_4$  production in these bog peats.

Temperature is another important control over anaerobic respiration,  $\text{CO}_2:\text{CH}_4$  production ratios, and  $\text{CH}_4$  emissions; however, it is unclear to what extent the multiple roles of humic substances are related to these temperature relationships. Reported apparent  $Q_{10}$  values for  $\text{CH}_4$  production vary greatly in wetland soils, ranging from 1.3 to 28 (Segers, 1998). Better defining the temperature response of overall anaerobic C cycling and  $\text{CH}_4$  production was recently identified as a major impediment to modeling  $\text{CH}_4$  emissions from wetlands in response to climate change (Bridgman et al., 2013). van Hulzen et al. (1999) suggested that while the processes controlling  $\text{CH}_4$  production, e.g., TEA reduction, fermentation reactions, and methanogenesis, all have intrinsic  $Q_{10}$  values of ~2, typical for microbial processes, their complex temporal dynamics could give very high apparent  $Q_{10}$  values for  $\text{CH}_4$  production. In direct opposition to this hypothesis, a meta-analysis recently showed that  $\text{CH}_4$  production from pure cultures of methanogens had similar  $Q_{10}$  values to  $\text{CH}_4$  production and  $\text{CH}_4$  emissions in natural ecosystems (Yvon-Durocher et al., 2014). Additionally based upon net emission data, this study suggested that the temperature response for  $\text{CH}_4$  production was substantially greater than that for  $\text{CO}_2$  production at an ecosystem level. Thus, the mechanisms controlling the temperature dependence of anaerobic respiration is an important topic, and the role of humic substances in this regard remains largely unstudied.

In the present study, we used the humic analog AQDS to 1) compare the effects of humic substances on  $\text{CH}_4$  production in bog and rich fen peats, and 2) investigate how humic substances influence the temperature responses of methanogenesis in these peat soils. We hypothesized that 1) thermodynamic competition between AQDS reduction and methanogenesis for common substrates, i.e., acetate and  $\text{H}_2$ , is more significant in bog than fen peat, explaining the higher  $\text{CO}_2:\text{CH}_4$  ratio observed in bog peat, and 2) by acting as a TEA, AQDS enhances the temperature sensitivity of  $\text{CH}_4$  production, especially in the bog soil.

## 2. Methods and materials

### 2.1. Site description

We collected soil samples from a bog and a rich fen in the Upper Peninsula of Michigan, USA in June 2011. The bog (N46°6'6", W88°16'25") had a soil pH of 3.7 and a peat depth of ~3.8 m with an average water table in hollows of ~27 cm during the growing season. It is dominated by >90% of cover of *Sphagnum* spp. mosses with stunted (<1-m height) ericaceous shrubs such as leatherleaf (*Chamaedaphne calyculata* (L) Moench), small cranberry (*Vaccinium oxycoccos* L.), and bog Labrador tea (*Rhododendron groenlandicum* Oeder), and scattered low-stature black spruce (*Picea mariana* (Mill.) Britton, Sterns & Poggen). The rich fen (N46°13'27", W89°29'53") had a soil pH of 5.9 and a peat depth of ~6.4 m with consistent standing water. It is dominated by upright sedge (*Carex stricta* Lam.) tussocks with leatherleaf also present on the tussocks. These sites were previously described as "Bog 1" and "Rich Fen" in Ye et al. (2012).

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