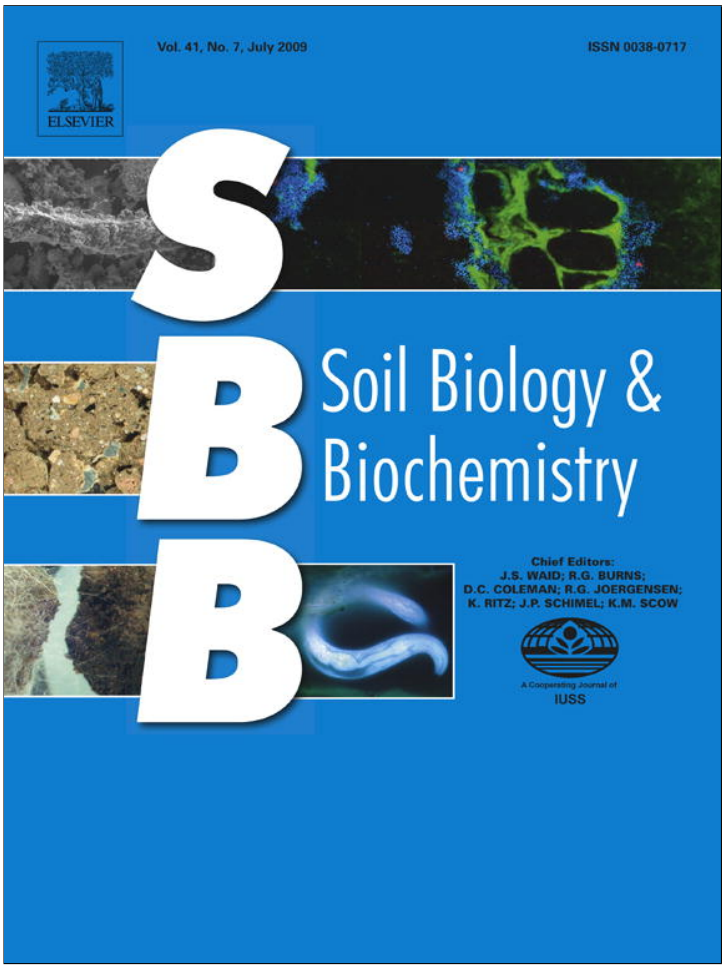

Soil Biology & Biochemistry 41 (2009) 1518–1522

Contents lists available at ScienceDirect

Soil Biology & Biochemistry

journal homepage: www.elsevier.com/locate/soilbio

Humic acids as electron acceptors in wetland decomposition

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ARTICLE INFO

Article history:
Received 15 August 2008
Received in revised form
25 February 2009
Accepted 17 April 2009
Available online 3 May 2009

Keywords:
Anaerobic decomposition
Carbon dioxide
Humic substances
Methane
Wetlands

ABSTRACT

Decomposition of organic matter in inundated wetland soils requires a number of interdependent microbial processes that ultimately generate CO_2 and CH_4. Largely as the result of anaerobic decomposition, wetland soils store globally significant amounts of organic carbon and are currently net sources of CH_4 to the atmosphere. Given the importance of wetlands in the global carbon cycle, it is important to understand controls on anaerobic decomposition in order to predict feedbacks between wetland soils and global climate change. One perplexing pattern observed in many wetland soils is the high proportion of CO_2 resulting from anaerobic decomposition that cannot be explained by any measured pathway of microbial respiration. Recent studies have hypothesized that humic substances, and in particular solid-phase humic substances in wetland soils, can support anaerobic microbial respiration by acting as organic electron acceptors. Humic substances may thus account for much of the currently unexplained CO_2 measured during decomposition in wetland soils. Here we demonstrate that humic acids extracted from a variety of wetland soils act as either electron donors or electron acceptors and alter the ratio of CO_2:CH_4 produced during anaerobic laboratory incubations. Our results suggest that soil-derived humic substances may play an important, and currently unexplored, role in anaerobic decomposition in wetland soils.

1. Introduction

Microbial decomposition in wetland ecosystems is fundamentally different than in upland systems. In most upland soils, organic carbon can be completely mineralized to carbon dioxide (CO_2) by a single microorganism using oxygen (O_2) as a terminal electron acceptor (TEA). In contrast, anaerobic decomposition in inundated wetland soils requires many interdependent microbial processes and can generate both CO_2 and methane (CH_4) as end products of mineralization (Megonigal et al., 2004). Anaerobic decomposition is less thermodynamically favorable than aerobic decomposition, and this limitation has resulted in the storage of ~500 Pg of carbon (19% of the terrestrial soil carbon pool) in wetland soils worldwide (Bridgham et al., 2006). Further, wetlands are currently responsible for between 15% and 40% of the global CH_4 flux (Denman et al., 2007). Wetlands could release additional CO_2 or CH_4 if carbon mineralization in wetland soils is stimulated by ongoing climate change, augmenting anthropogenic emissions of these important greenhouse gases (Gorham, 1995; Bridgham et al., 1995). Thus, understanding the factors that control anaerobic carbon decomposition in wetland soils has important implications for understanding the global carbon cycle.

In wetland soils, organic molecules are initially degraded by a series of hydrolysis and fermentation reactions that generate successively lower molecular weight products. Ultimately, the end products of these fermentation reactions are acetate, hydrogen (H_2) and CO_2, which are subsequently used as substrates for microbial respiration. In the absence of O_2, microbes preferentially reduce a variety of alternative TEAs for respiration. The primary inorganic TEAs are, in order of decreasing thermodynamic yield: NO_3^- (denitrification), Fe(III) (iron reduction), Mn(III, IV) (manganese reduction) and SO_4^{2-} (sulfate reduction). Reduction of these inorganic TEAs is coupled to oxidation of organic matter to CO_2 and competitively suppresses CH_4 production. Once more favorable TEAs have been depleted, methanogens produce CH_4 either by splitting acetate to CO_2 and CH_4 (acetoclastic methanogenesis) or reducing CO_2 in a reaction coupled to H_2 oxidation (hydrogenotrophic methanogenesis).

The ratio of the two terminal products of anaerobic decomposition – CO_2 and CH_4 – provides useful information on the dominant

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0038-0717/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.soilbio.2009.04.008

processes contributing to anaerobic decomposition. Under methanogenic conditions (i.e., once more favorable TEAs have been consumed), CO_2 and CH_4 are produced in equal amounts resulting in a 1:1 ratio of CO_2:CH_4 (Conrad, 1999). However, the ratio of CO_2:CH_4 produced during anaerobic incubations of wetland soils is often >1 (van Hulzen et al., 1999), suggesting reduction of non-methanogenic TEAs is important in these systems. Many freshwater peatland soils have high CO_2:CH_4 ratios (e.g., Bridgham et al., 1998; Blodau, 2002; Yavitt and Seidman-Zager, 2006) despite low availability of inorganic TEAs (i.e., NO_3^-, Fe(III), Mn(III, IV) and SO_4^{2-}). In a particularly striking example, Updegraff et al. (1995) observed a CO_2:CH_4 ratio of 883 after an 80-week anaerobic incubation of bog soil. A number of detailed process measurements in peatland soils demonstrate that most of the CO_2 produced during anaerobic incubations cannot be explained by microbial reduction of inorganic TEAs (summarized in Keller and Bridgham, 2007). Similarly, 80% of CO_2 produced in anaerobic incubations of an organic brackish marsh soil could not be accounted for by measured rates of sulfate reduction, iron reduction or methanogenesis (Neubauer et al., 2005).

What accounts for the 'unexplained' CO_2 produced during anaerobic decomposition in some wetland soils? It has been suggested that CO_2 produced directly during fermentation contributes to the high CO_2:CH_4 ratio in peatland soils (Vile et al., 2003). Many fermentation reactions do produce CO_2 in the processing of organic molecules (e.g., Schink, 1997); however, Yavitt and Seidman-Zager (2006) suggested that the amount of CO_2 produced during these reactions is typically smaller than the amount of H_2 produced. Thus, any CO_2 produced by fermentation reactions should be more than balanced by CH_4 produced by hydrogenotrophic methanogenesis, producing a CO_2:CH_4 ratio closer to the theoretical value of 1.

A number of researchers have hypothesized the utilization of humic substances as organic TEAs to explain the high CO_2:CH_4 ratio observed in many wetland soils (Segers, 1998; Neubauer et al., 2005; Heitmann et al., 2007; Keller and Bridgham, 2007). Lovley et al. (1996) first demonstrated that bacteria can use humic substances as organic electron acceptors, and bacteria capable of reducing the humic substance analog anthraquinone-2,6-disulfonate (AQDS) have been isolated from natural wetland environments (Coates et al., 1998). From a thermodynamic perspective, reduction of AQDS is more favorable than methanogenesis, which should lead to an increase in the CO_2:CH_4 ratio in soils where AQDS-like humics are being used for microbial respiration; however, direct inhibition of methanogenesis by AQDS-like humics is also possible (Cervantes et al., 2000). Recent research in a Canadian peatland demonstrated that dissolved organic matter is an important electron acceptor, contributing directly (through humic reduction) or indirectly (by regenerating oxidized sulfur species for sulfate reduction) to high CO_2:CH_4 ratios (Heitmann and Blodau, 2006; Heitmann et al., 2007). Although the total electron accepting capacity of dissolved humic substances was relatively small, it was hypothesized that the much larger pool of humic-like organic matter in the solid phase of wetland soils could be used in a similar manner (Heitmann and Blodau, 2006). Scott et al. (1998) also demonstrated that the electron accepting capacity of humic substances extracted from soils was much greater than dissolved humic substances across a number of aquatic systems.

Here we explore how humic substances extracted from wetland soils alter the ratio of CO_2:CH_4 produced during anaerobic incubations. In particular we hypothesize that if humic substances are used as terminal electron acceptors they will increase CO_2 production at the expense of CH_4 production, resulting in an increase in the ratio of CO_2:CH_4 produced.

2. Materials and methods

2.1. Soil collection

Soils were collected beneath plant species that represented a range of tissue chemistry in areas where each species was locally dominant. Soils from unvegetated patches were also collected. All soils were collected in wetlands of the upper Chesapeake Bay (Table 1). Pahokee peat reference soil from the International Humic Substances Society (IHSS) was also included in this experiment. Either one or two samples were collected from each sampling site (Table 1).

2.2. Humic acid extraction and yield

Humic acids were serially extracted from 2.5 g of field-moist soil using a modification of the IHSS protocol (Posner, 1966). An initial 1 M HCl pretreatment was used (pH = 1.5) to remove metals and fulvic acids. Samples were then serially extracted with 0.5 M Na_2CO_3:$NaHCO_3$ (2:1); 0.1 M $Na_4P_2O_7$; 0.5 M NaOH; and finally 1.0 M NaOH. After each extraction, samples were rinsed three times with deionized water The combined supernatant (extractant + 3 rinses) was pre-filtered through a 0.45 μm PES filter under vacuum then subsequently filtered through a 0.2 μm PES filter. Filtered supernatant was subjected to exhaustive dialysis (MWCO = 10,000Da) until it tested negative for chloride using the argentometric method (Clesceri et al., 1989). After dialysis, samples were freeze-dried. All extractions were performed in the ambient atmosphere (i.e., not under nitrogen). This modification was necessary for logistical reasons, but may have resulted in the oxidation of some humic substances. Thus, any reduction of humic acids in this experiment should be viewed as a potential rate, and not necessarily a reflection of rates in the field.

2.3. Soil incubations

Soil used for incubations was collected on 3 January 2008 from the Jug Bay Wetlands Sanctuary in Lothian, Maryland, USA (38° 47′ N, 76° 43′ W). The soil at this site is highly organic (59.3% ± 1.6% organic content; mean ± 1 SE; $n = 7$) and CH_4 production dominates anaerobic decomposition (Keller et al., unpublished data). Soil was collected using four steel cores with an inner diameter of 5 cm to a depth of 20 cm, and immediately capped to limit oxygen exposure. Cores were returned to the Smithsonian Environmental

Table 1
Location of soil sampling sites in the upper Chesapeake Bay.

Collection site	Plant species	n[a]	Sample code
Battle Creek Cypress Swamp (Prince Frederick, MD)	*Taxodium distichum*	1	BCC-TD
Blackwater National Wildlife Refuge (Cambridge, MD)	*Morella* sp.	1	BWR-MC
	Schoenoplectus americana	2	BWR-SC
	Unvegetated	2	BWR-UV
Hoopers Island Fire Station (Fishing Creek, MD)	*Phragmites australis*	2	HIF-PA 1
	P. australis	2	HIF-PA 2
Jug Bay Wetland Sanctuary (Lothian, MD)	*Nuphar advena*	2	JUG-NL
	P. australis	2	JUG-PA
	Quercus phellos	1	JUG-QL
	Salix nigra	1	JUG-SN
	Typha latifolia	2	JUG-TA
	Unvegetated	2	JUG-UV
Muddy Creek (Edgewater, MD)	Filamentous, benthic algae	1	MUC-BA
	Najas sp.	1	MUC-SA
International Humic Substance Society	Pahokee peat reference soil	1	PEAT 1
	Pahokee peat reference soil	1	PEAT 2

[a] Number of replicate extracts from each soil.

Research Center where live roots were removed by hand in an anaerobic chamber with a headspace of ~98% nitrogen and <2% hydrogen (Coy Laboratory Products, Grass Lake, Michigan). Root-free soil from all cores was mixed in a Mason jar which was tightly capped in the anaerobic chamber. The Mason jar was covered with aluminum foil and the headspace was flushed with nitrogen for 30 min. The soil was pre-incubated at room temperature to allow methanogenic conditions to develop prior to treatments, and lasted until headspace concentrations of CO_2 and CH_4 were equal (i.e., CO_2:CH_4 ratio = 1).

On 15 January 2008, the Mason jar was returned to the anaerobic chamber (headspace of ~99% nitrogen and <1% hydrogen) and opened. The soil was once again mixed by hand. Subsequently, 5 g of field-moist soil was added to 100 mL serum bottles and slurried with 10 mL of one of the following treatments ($n = 4$): control (deionized water); 10 mM organic carbon (as 35,000–50,000 Da dextran); 10 mM $FeCl_3$; 10 mM $Fe_2(SO_4)_3$; 1 mM AQDS; or 10 mM AQDS. Dextran is a polyglucose and was used as a fermentable organic carbon source (i.e., a known electron donor, but not an electron acceptor). $FeCl_3$ and $Fe_2(SO_4)_3$ were added as known inorganic TEAs. AQDS has been used as a homologue for quinone moieties in natural humic substances (e.g., Cervantes et al., 2000), and was added as a known organic TEA. Freeze-dried humic acids from each of the four serial extracts were quantitatively transferred from scintillation vials with two successive rinses with deionized water (10 mL total volume), and used to create a soil slurry with 5 g of field-moist soil.

The different soil types resulted in different yields of humic acids and the distribution among the four serial extracts also differed dramatically. For these incubations, we combined the humic acids from all serial extract fractions and did not correct the mass of the incubated soils for mass of extracted humic acids added, which varied among the different wetland soil types. Thus, we amended 5 g (wet weight) of a single soil type with the total extractable humic acid pool from 2.5 g (wet weight) of a variety of soil types. The yield of humic acids from the Pahokee peat reference soil was considerably greater than other soil samples. For the first replicate ('PEAT 1'), four successive washes with distilled water (20 mL total volume) were used to transfer the humic acids from the 0.5 M Na_2CO_3:$NaHCO_3$ (2:1) extract to the incubation bottles. For the second replicate ('PEAT 2'), 6 successive washes with distilled water (30 mL total volume) were used to transfer the humic acids from each of the four serial extracts to the incubation bottles. Even with these additional washes, visual inspection suggested that there was not a quantitative transfer of Pahokee peat humic acids and that the quantities added to the incubations were lower than the total yield.

Serum bottles were removed from the anaerobic chamber, capped with gray butyl septa and flushed with N_2 for 30 min. Bottles were covered with aluminum foil and incubated in the dark at 20 °C. Headspace concentrations of CO_2 and CH_4 were measured on days 1, 2, 3, 4 and 7. Headspace pressure was maintained by replacing sampled volume with N_2. CO_2 was measured on a LiCor LI-7000 and CH_4 was measured on Shimadzu GC-14A equipped with a flame ionization detector. Dissolved CH_4 and CO_2 were calculated using Henry's Law, adjusting for solubility, temperature and pH (Clesceri et al., 1989; Drever, 1997). Headspace concentrations of CO_2 and CH_4 were corrected for headspace pressure measured at the end of the incubation using an Omega HHP 520 pressure meter (Omega Engineering, Stanford, Connecticut). Following the incubation, pH was measured on the soil slurries and all samples were dried at 60 °C for 1 week. Values from the first sampling point were set to zero and the subsequent production of CO_2 and CH_4 was expressed as μmol C gdw^{-1}. Rates of CO_2 and CH_4 production were generally linear over the course of the incubation; however, we focus on the total CO_2 and CH_4 at the end of the incubation to allow for comparisons among all treatments regardless of the temporal patterns of gas production.

3. Results and discussion

The addition of humic acids extracted from a variety of wetland soils altered the relative production of CO_2 and CH_4, resulting in a change in the CO_2:CH_4 ratio at the end of a 7 d anaerobic incubation (Fig. 1). This suggests that solid-phase humic acids in wetland soils can play a significant role in anaerobic decomposition, with important implications for wetland carbon cycling.

Untreated control soil was methanogenic with a CO_2:CH_4 ratio of 0.7 ± 0.04 (mean ± 1 SE) at the end of the 7 d incubation (Fig. 1). This ratio is below the predicted theoretical CO_2:CH_4 ratio of 1. One explanation for this lower than expected ratio is a stimulation of hydrogenotrophic methanogenesis, which consumes CO_2, due to the presence of excess H_2 in the headspace of the incubations. H_2 is a reactant for removing O_2 in the anaerobic chamber. Despite flushing with N_2 prior to starting the incubation, excess H_2 was possibly present at the start of the incubation. However, we cannot rule out the possibility that this ratio was a result of uptake of CO_2 through other processes (e.g., homoacetogenesis) or simply a reflection of non-equilibrium conditions (Conrad, 1999). Regardless, the CO_2:CH_4 ratio of <1 demonstrates that anaerobic

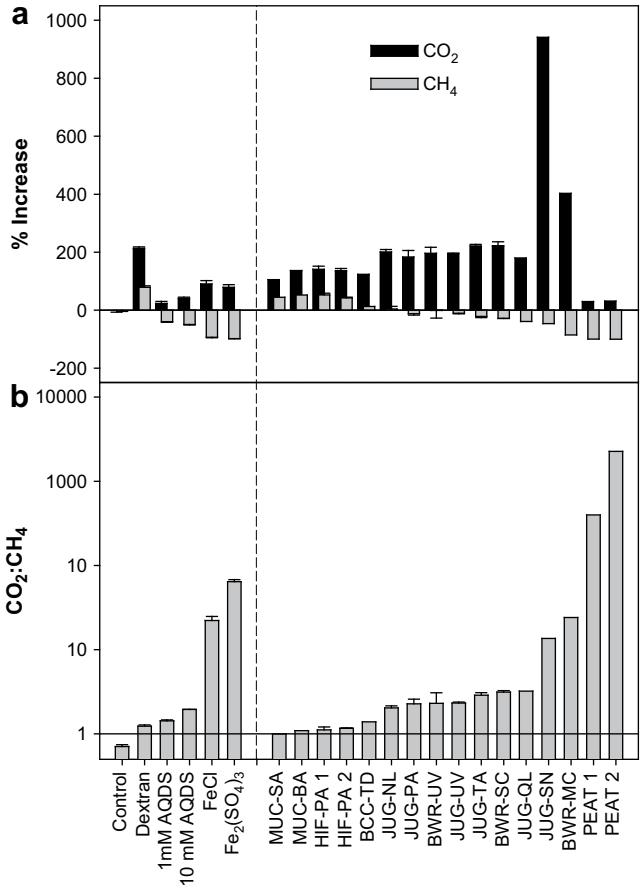

Fig. 1. (a) Percent increase in CO_2 and CH_4 production relative to the control treatment at the end of a 7 d anaerobic incubation. Negative values represent a decrease in CH_4 concentrations. (b) Ratio of CO_2 and CH_4 concentration in the same samples. Data are means ± 1 SE in cases where multiple replicates were available. Codes for extracted soil humic acids are described in Table 1.

decomposition in the control treatment was dominated by methanogenesis.

The addition of dextran, a fermentable carbon source (i.e., an electron donor), stimulated both CO_2 and CH_4 production as predicted for a methanogenic system. The final CO_2:CH_4 ratio of 1.2 ± 0.04 (mean ± 1 SE), was close to the theoretical ratio of 1 predicted for methanogenic conditions (Fig. 1). The slightly elevated ratio could be the result of excess CO_2 released during fermentation of dextran; although this would not be expected if excess H_2 was present in the incubation headspace leading to a stimulation of hydrogenotrophic methanogenesis (Yavitt and Seidman-Zager, 2006). A second possibility is that slow growth of methanogens able to respire fermentation end products delayed CH_4 production compared to CO_2 production (i.e. the system was not at steady state). Our experimental design does not allow us to explore the dynamics of fermentation intermediate and end products. In contrast, the addition of known organic (AQDS) or inorganic (FeCl or $Fe_2(SO_4)_3$) TEAs stimulated CO_2 production while inhibiting CH_4 production, resulting in final CO_2:CH_4 ratios ranging from 1.4 ± 0.04 for the 1 mM AQDS treatment to 64.2 ± 3.67 for the $Fe_2(SO_4)_3$ treatment (Fig. 1). These patterns are presumably the result of a shift in the dominant pathway of anaerobic decomposition from methanogenesis to the utilization of more thermodynamically favorable TEAs.

The comparison of CO_2 and CH_4 dynamics in incubations amended with humic acids to the patterns produced by known electron donors and acceptors provides valuable insights into the role humic substances may play in anaerobic decomposition. In some cases, the net effect of humic acid addition was an electron donor-like response in which both CO_2 and CH_4 production were stimulated (Fig. 1A), resulting in a final CO_2:CH_4 ratio near 1 (Fig. 1B). In other cases, there was an electron acceptor-like response in which CO_2 production increased while CH_4 production decreased, resulting in increased CO_2:CH_4 ratios. A number of humic acids had a final CO_2:CH_4 ratio >2, suggesting that humic acids from some wetland soils may strongly limit the production of CH_4 by serving as thermodynamically favorable organic electron acceptors. We hypothesize that the observed range in CO_2:CH_4 ratios is a result of differences in the chemical makeup of humic substances extracted from different wetland soils; however, we also discuss the potential importance of humic yield and humic-induced changes in pH in this experiment.

When all four serial extracts were combined, the total yield of humic substances was generally less than 0.10 g. Although there was a positive relationship between the final CO_2:CH_4 ratio and the mass of humic acids added to the incubations, the relationship was weak and explained only 8% of the variation (Fig. 2). This suggests that humic chemistry – and not simply humic quantity – determines the extent to which humic substances may act as terminal electron acceptors. The humics extracted from Pahokee peat soil were not included in this regression as they yielded dramatically more humic substances than other soils (Fig. 2). Interestingly, the incubations with Pahokee peat soils had the highest final CO_2:CH_4 ratios (~400 and ~2300), driven by a near complete inhibition of CH_4 production along with a relatively minor (~30%) stimulation of CO_2 production (Fig. 1). This pattern is intriguing given the comparably high CO_2:CH_4 ratios observed in some peatland soils that are characterized by very low rates of CH_4 production (e.g., Updegraff et al., 1995). Given the importance of peatland soils in the global carbon cycle, additional research is necessary to further explore the importance of peat-derived humic substances in anaerobic decomposition.

A potentially confounding artifact in our experimental design was soil pH. Soils with higher CO_2:CH_4 ratios consistently had a lower pH at the end of the 7 d incubation (Fig. 3A). This pattern

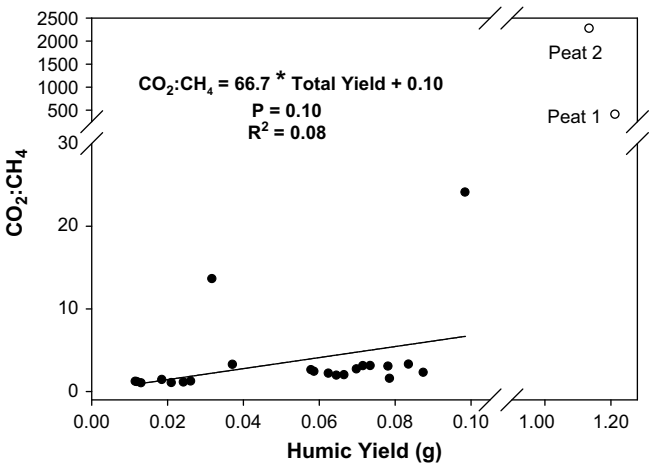

Fig. 2. Relationship between final CO_2:CH_4 ratio and mass of humic acids added to incubations ("Humic Yield"). Samples incubated with humic acids extracted from Pahokee peat soils (open symbols) were not included in the regression.

generally reflected a negative relationship between the final pH and the final concentration of CO_2, as well as a positive relationship between the final pH and the final concentration of CH_4 (Fig. 3B). It is unlikely that CO_2 production by non-methanogenic respiration was stimulated by more acidic conditions, and we interpret the relationship between pH and CO_2:CH_4 to be a consequence of well-known changes in carbonate chemistry that occur as CO_2

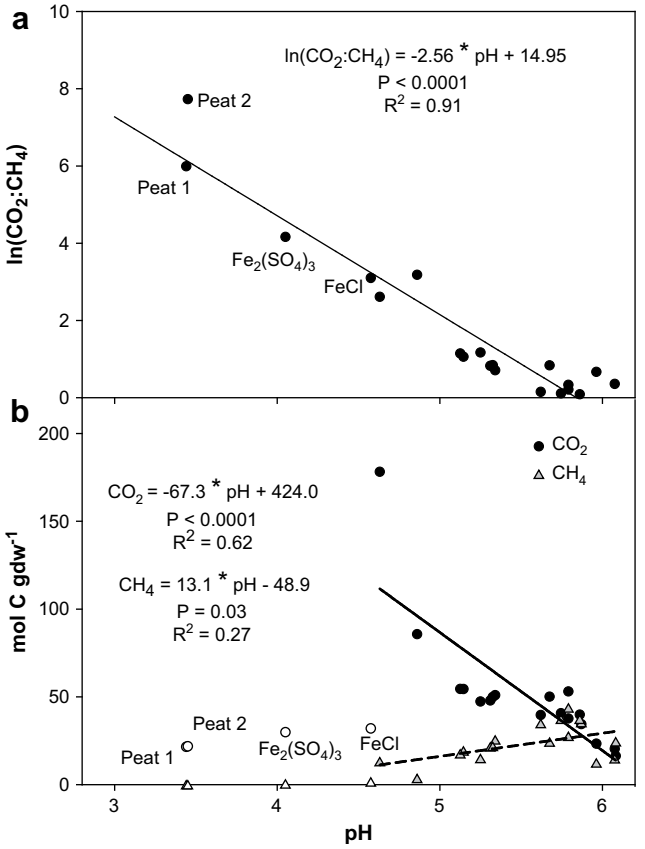

Fig. 3. (a) Relationship between final CO_2:CH_4 ratio and pH measured at the end of a 7 d anaerobic incubation. The natural logs of CO_2:CH_4 ratios are presented. (b) Relationship between final pH and final CO_2 and CH_4 concentrations. Treatments indicated with open symbols were not included in the regressions. Data are means where multiple replicates were available.

accumulates over the course of the incubations (Stumm and Morgan, 1995). There were a few exceptions to this pattern in which samples with low pH had relatively low rates of CO_2 production. In these cases, the amendments were the two known inorganic TEA treatments and the treatments that were amended with comparatively high quantities of Pahokee Peat humic acids (Fig. 3B). We interpret the high CO_2:CH_4 ratios in these four treatments to be primarily the result of direct pH effects from adding humic acids or inorganic TEAs. As we did not measure the initial pH of the incubations, we cannot fully evaluate to what extent differences in final pH were caused by the initial addition of humic acids or by changes in carbonate chemistry.

Our results demonstrate that soil-derived humic acids can serve as either electron donors or electron acceptors during anaerobic decomposition in a wetland soil. Although largely descriptive, this raises the intriguing possibility that solid-phase humic substances may inhibit CH_4 production by serving as thermodynamically favorable organic TEAs. The extent to which this process contributes to decomposition in natural wetlands needs to be further explored, particularly in highly organic peatland soils where humic substances are found in high concentrations.

We suggest four future directions that will likely prove fruitful in understanding how humic substances influence microbial decomposition in wetland soils. (1) The confounding effect of pH must be removed to demonstrate conclusively that humic substances are acting as TEAs rather than influencing microbial decomposition solely through changes in pH. (2) Comparisons between the CO_2:CH_4 ratios observed in incubations with highly modified extracted soil humic substances and *in situ* CO_2:CH_4 production potentials from the source soils would put the laboratory incubations into a stronger ecological context. (3) There is evidence that the abiotic reduction of soil-derived humics (i.e., chemical reducing capacity) is related to the microbial reduction of these compounds (Peretyazhko and Sposito, 2006). As we did not measure abiotic electron accepting capacity of humics extracted in this experiment, it remains to be seen if this property is related to the reduction of humic substances by the diverse, natural wetland microbial community in our experiment. The measurement of the abiotic electron accepting capacity of soil-derived humic substances over longer-term incubations may also demonstrate that this pool is being reduced in the course of anaerobic decomposition. (4) It appears that humic chemistry and not simply humic quantity is important when considering the role of humic reduction in wetland soils. However, it remains to be seen which functional groups are responsible for the range of electron accepting capacities observed in humic substances from wetland soils. Quinone moieties are generally considered important in humic redox chemistry (Scott et al., 1998), but other functional groups have also been identified (Struyk and Sposito, 2001; Ratasuk and Nanny, 2007). Relationships between the functional composition of humic substances and the electron accepting capacity of those substances would allow for mechanistic hypotheses about where and when humic reduction is likely to be important in natural wetlands, and how this process may respond to ongoing global change.

Acknowledgements

Sara McQueeney provided valuable assistance in the field and the laboratory. JKK was supported by a Smithsonian Institution Post-Doctoral Fellowship. PBW conducted her work at the Smithsonian Environmental Research Center as a Smithsonian Institution research intern. This work was funded by grants from the National Science Foundation to JKK and JPM. Comments from an anonymous reviewer greatly improved this manuscript.

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