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No evidence for trace metal limitation on anaerobic carbon mineralization in three peatland soils

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ABSTRACT

Peatlands store roughly one-third of the terrestrial soil carbon and release the potent greenhouse gas methane (CH_4) to the atmosphere, making these wetlands among the most important ecosystems in the global carbon cycle. Despite their importance, the controls of anaerobic decomposition of organic matter to carbon dioxide (CO_2) and CH_4 within peatlands are not well understood. It is known, however, that the enzymes responsible for CH_4 production require cobalt, iron and nickel, and there is a growing appreciation for the potential role of trace metal limitation in anaerobic decomposition. To explore the possibility of trace metal limitation in peatlands, we washed 3 peat soils with either $PbCl_2$, to remove available trace metals, or distilled water. Following these washes, we added trace metals (as $CoCl_2$, $CuCl_2$, $FeCl_2$, $PbCl_2$ and $NiCl_2$) to each soil. We measured anaerobic CH_4 and CO_2 production in laboratory incubations over 4 weeks before adding glucose as a labile carbon source and measuring CH_4 and CO_2 production for an additional 4 weeks. In all 3 soils, neither CH_4 nor CO_2 production were limited by individual trace metals, even following the wash with $PbCl_2$ to remove available metals. Further, in response to the addition of a labile carbon substrate, all soils supported increased rates of CH_4 and CO_2 production without progressive trace metal limitation. Taken together, our findings suggest that individual trace metals may not be limiting to anaerobic decomposition in many peatland soils.

1. Introduction

Peatlands are a diverse group of wetlands that store nearly 500 Pg of carbon in their soils, an estimated one-third of the terrestrial soil carbon (Bridgham et al., 2006; Kolka et al., 2016). Further, peatlands contribute a significant fraction of the flux of methane (CH_4) attributed to global wetland ecosystems (Bridgham et al., 2013; Keller and Medvedeff, 2016). Given that CH_4 has 45-times the sustained-flux global warming potential of CO_2 (on a per mass basis over the 100 year time period; Neubauer and Megonigal, 2015), CH_4 cycling within peatlands can have important implications for the climate. Understanding the role of peatlands in the global climate hinges on our mechanistic understanding of CH_4 and CO_2 dynamics within peatland ecosystems.

At the landscape scale, peatlands are generally classified along a hydrogeomorphic gradient, ranging from precipitation-fed (ombrotrophic) bogs to predominately groundwater-fed (minerotrophic) rich fens. While this gradient is defined by the degree of groundwater influence, a number of other factors, including: pH, dominant vegetation, nutrient availability, cation exchange capacity and trace metal availability also co-vary along this gradient (Bridgham et al., 1996; Kolka et al., 2016). In addition, microbial carbon cycling varies along this gradient with more minerotrophic sites generally exhibiting higher rates of overall carbon mineralization and soils from minerotrophic rich fens producing more CH_4 than soils from ombrotrophic bogs (e.g., Keller and Bridgham, 2007; Updegraff et al., 1995; Ye et al., 2012). Understanding the mechanistic reasons for these differences in CH_4 production among peatland types is crucial for understanding the potential feedbacks between peatland carbon cycling and global climate change.

There is a growing appreciation for the role that trace metals may play in regulating the production of CH_4 in natural ecosystems. In particular, it is known that the enzymes responsible for the production of CH_4 require large amounts of iron, nickel and cobalt (Glass and Orphan, 2012; Jarrell and Kalmokoff, 1988). These trace metals are often found in low concentrations in peatlands (Basiliko and Yavitt, 2001; Gogo et al., 2010; Gorham and Janssens, 2005), which may limit the potential for CH_4 production in these ecosystems. This trace metal limitation may be particularly pronounced in ombrotrophic bogs (often characterized by low CH_4 production) because of small inputs of trace metals from precipitation. Further, *Sphagnum* mosses, which dominate ombrotrophic peatlands, have a high cation exchange capacity and may

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effectively bind trace metals (Gogo and Pearce, 2009a; Thomas and Pearce, 2004). In support of this enhanced trace metal limitation in ombrotrophic peatland soils, Basiliko and Yavitt (2001) reported that a mix of trace metals (iron, nickel, cobalt and sodium) increased rates of CH_4 production in an ombrotrophic bog peatland soil, but not in a minerotrophic fen soil. Similarly, the release of trace metals (e.g., iron, nickel and cobalt) from cation exchange sites (by saturation with lead (Pb^{2+}) or aluminum (Al^{3+})) stimulated CH_4 production in a *Sphagnum*-dominated bog soil, but not in a more minerotrophic fen soil (Gogo and Pearce, 2009b).

These past projects have utilized various 'cocktails' of trace metals (in different combinations and concentrations) to explore for potential limitation of anaerobic carbon cycling. This approach is justified given that carbon mineralization could be co-limited by multiple trace metals; however, as suggested by Basiliko and Yavitt (2001), there is also a need to explore if individual trace metals can limit CH_4 production in peatland soils. In the current project, we tested for limitation of anaerobic carbon mineralization, as CH_4 and CO_2 production, by adding cobalt (Co), copper (Cu), iron (Fe), nickel (Ni), and lead (Pb) individually to 3 peatland soils, ranging from an ombrotrophic bog to a minerotrophic rich fen. We tested for trace metal limitation under multiple experimental conditions in each soil. First, we attempted to induce trace metal limitation by saturating cation exchange sites with $PbCl_2$ and thoroughly washing soils to remove released trace metals. Second, we stimulated rates of anaerobic carbon mineralization by adding a labile carbon substrate (glucose) to test the possibility that progressive trace metal limitation would occur due to increased microbial activity. We hypothesized that (i) the addition of trace metals would stimulate decomposition in ombrotrophic soils more than minerotrophic soils and (ii) trace metal limitation would be exacerbated by both the removal of trace metals following the saturation of cation exchange sites as well as by the increased carbon mineralization following the addition of a labile carbon substrate.

2. Materials and methods

2.1. Site description and sampling

Soil samples for this project were collected from 3 peatlands located on the property of the University of Notre Dame Environmental Research Center in the Upper Peninsula of Michigan, USA. These sites represent a subset of peatlands selected as part of a larger project to represent the ombrotrophic-minerotrophic peatland gradient in this region based on differences in dominate vegetation, soil pH and anaerobic carbon cycling. These sites have been described previously (Ye et al., 2012), and a brief description is provided below. For consistency, we use the same site names utilized by Ye et al. (2012).

"Bog 2" (N46°13′57″, W89°34′7″) is dominated by > 90% cover by *Sphagnum* spp. mosses with scattered short-statured black spruce (*Picea mariana* (Mill.) Britton, Sterns & Poggen) and ericaceous shrubs, including: leatherleaf (*Chamaedaphne calyculata* (L.) Moench), small cranberry (*Vaccinium oxycoccos* L.) and bog Labrador tea (*Rhododendron groenlandicum* Oeder). Average water-table depth (reported below hollow surfaces) during the growing season (~May–October) was −16 cm and the pH was 4.1. Soil from Bog 2 had a von Post index of H3 and a rubbed fiber volume content of 38 ± 10% (values from Ye et al., 2012; mean ± 1 standard error) suggesting that the peat at this site was less decomposed than at the other sites. "Acidic Fen" (N46°12′48″, W89°30′2″) has a *Sphagnum* spp. lawn with minimal cover from other species in the area of sampling. The average water-table depth was −10 cm and the pH was 4.1. Soil from Acidic Fen had a von Post index of H3/H4 and a rubbed fiber volume content of 35 ± 9% (values from Ye et al., 2012). "Rich Fen" (N46°13′27″, W89°29′53″) is dominated by the upright sedge (*Carex stricta* Lam.) although leatherleaf shrubs are also present on tussocks. This site was consistently flooded with ~30 cm of standing water during the 2009 growing season. The average pH was 5.9 and soil from Rich Fen had a von Post index of H5 and a rubbed fiber volume content of 15 ± 5% (values from Ye et al., 2012), suggesting that this peat was the most decomposed of the sites studied.

Soil were collected from 30 cm below the water table measured in the field in each peatland in August of 2009 using 10-cm diameter PVC cores. Cores were 30 cm in length and were inserted into the soil with the aid of a serrated knife to minimize compaction. Cores were extruded into large Ziploc bags, frozen and shipped to Chapman University in Orange, CA. Prior to the initiation of this experiment, individual cores were allowed to thaw and large roots and living vegetation were removed by hand in the ambient atmosphere. The remaining root-free peat was refrozen. The length of time a core was thawed varied, but was generally < 1 week.

2.2. Determination of water-extractable cations and cation exchange capacity

Concentrations of water-extractable cations were measured by adding 20 g of field-moist, root-free peat to 20 mL of deionized water and shaking at 200 rpm for 1 h. Following the extraction, the slurry was centrifuged at 4100 rpm for 5 min and the supernatant was filtered through a P8 qualitative filter and frozen until analysis for cations at the Soil and Plant Tissue Testing Laboratory at the University of Massachusetts.

Soil cation exchange capacity (CEC_{Ca}) was determined by compulsive exchange with Ca^{2+} (Gogo and Pearce, 2009a). Briefly, 0.15 g of air-dried peat was washed twice with 20 mL of 0.01 M HCl for 5 min to remove background levels of Ca^{2+}. Following each wash, the samples were centrifuged at 4100 rpm for 5 min and the supernatant was discarded. After both HCl washes, the remaining soil was washed twice with deionized water. Subsequently, the soil was saturated with 20 mL of 0.01 M $CaCl_2$. This slurry was centrifuged for 5 min at 4100 rpm and the supernatant was discarded. After the $CaCl_2$ saturation, the remaining soil was washed twice with deionized water. Finally, 20 mL of 0.01 M HCl was added to the soil three times. After each addition, the soil was centrifuged at 4100 rpm for 5 min and the supernatant was collected. After all three washes, the combined supernatant was brought to 100 mL with 0.01 M HCl and this solution was analyzed for Ca^{2+} at the Soil and Plant Tissue Testing Laboratory at the University of Massachusetts.

2.3. Experimental design

For logistical reasons, peat from each site was treated separately in this experiment (i.e., the treatments described below were applied to each peat at a separate time). This approach was appropriate as our intention was to focus on the importance of trace metals on carbon mineralization within a peatland while focusing on the more qualitative patterns (i.e., stimulation or inhibition by a given trace metal) between sites.

2.3.1. Wash treatments

To explore the role of trace metals bound to cation exchange sites, soils were initially washed with either deionized water or $PbCl_2$. The water wash treatment was intended to remove dissolved cations. In contrast, the $PbCl_2$ wash treatment was intended to release soil-bound cations by saturating cation exchange sites with Pb^{2+} (Gogo and Pearce, 2009b), and thus to induce trace metal limitation. Both wash treatments also removed dissolved organic matter, with important implications for the interpretation of our results (see Discussion section for additional details). For each replicate soil core, 100 g of field-moist peat was added to a Mason jar, amended with 100 mL of 2 mM $PbCl_2$ or 100 mL of deionized water, and shaken at 200 rpm for 1 h. The peat was then transferred into 50-mL centrifuge tubes and centrifuged at 3000 rpm for 5 min. The resulting supernatant was discarded and the