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Short Communication

Does an ‘iron gate’ carbon preservation mechanism exist in organic–rich wetlands?

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ABSTRACT

Recent research suggested that iron oxidation may protect carbon from drought-accelerated decomposition in wetlands by promoting the sorption of lignin derivatives and decreasing phenolic oxidase activities. Here we examined whether this mechanism exists in organic-rich peatlands, which store over 30% of the world's soil carbon, by simulating drought and flooded conditions in peat soil with and without the addition of reduced iron. Our results suggest that iron does not protect carbon from decomposition in organic-rich peatlands, and in fact iron may exacerbate carbon decomposition via precipitation of phenolic compounds, which otherwise have been shown to inhibit microbial activity. In addition, scanning electron microscopy analyses of different types of peat soil from Minnesota to Peru showed evidence of iron-sulfide minerals (pyrite), indicating that some portion of the reduced iron in peatlands is effectively immobilized and therefore does not interact with the carbon cycle.

1. Introduction

Iron (Fe), as the fourth-most abundant element in the Earth's crust, plays an essential role in many fundamental biological and physical processes. In terms of climate change and carbon cycling, several studies have showed that Fe stabilizes organic carbon (C) in mineral-rich soils and sediments (Barber et al., 2017; Lalonde et al., 2012; Zhao et al., 2016). Recently Wang Y. et al. reported a new finding that Fe oxidation acts as an ‘iron gate’ in constraining carbon loss during drought by inhibiting phenol oxidase activity and promoting Fe-lignin association in an organic-rich peaty wetland (Wang et al., 2017). Coupled with some studies showing that low soil moisture limits phenolic oxidase activity and decomposition in unsaturated peatlands (Toberman et al., 2008; Wang et al., 2015), it appears that: 1) multiple mechanisms may protect soil carbon loss during short-term drought in peatlands, and 2) minerotrophic fens with substantial Fe inputs may present higher resilience to drought than oligotrophic bogs.

To test whether the ‘iron gate’ mechanism is applicable to preserving carbon in peatlands, we (1) set up an experiment by adding $FeSO_4$ or K_2SO_4 as control (0, 2.5, and 5 mmol L^{-1} $FeSO_4$ or K_2SO_4) to a high-lignin peatland soil to test how carbon decomposition responds to iron and iron oxidation, (2) ran scanning electron microscopy (SEM) to see whether, similar to mineral sediment (Lalonde et al., 2012), an iron coating forms outside of organic matter to protect carbon in peatlands, and (3) measured dissolved Fe in pore water from peatlands in North and South America to check Fe status in peatlands (detailed methods in Supplementary file). The soils for the experiment were collected from a pocosin shrub bog peatland in North Carolina, where phenol oxidase activity decreased under drought (Wang et al., 2015). Additionally, the organic-rich high-lignin soil in our experimental site matches Wang Y.‘s suggestion that ‘iron gate’ might be more important in high-lignin vascular plant-dominated wetlands (Wang et al., 2017). Flooding and drought conditions were simulated, with and without the addition of reduced Fe. For the drought treatment, the soils were drained and exposed to air for three days to oxidize ferrous Fe completely before measuring soil respiration. The concentration of ferrous iron in soil dropped from 0.5 –1.3 mg g^{-1} soil during flooding to below detection limit after drainage. The added Fe precipitated dissolved phenolics during flooding and significantly increased soil respiration under both saturated and unsaturated conditions (Fig. 1). Also, after drought, soluble phenolics in the water extractions from the soil were undetectable, which suggest that all free phenolics combined with the added iron. The added K_2SO_4 solution with the same pH as the $FeSO_4$ solution partially precipitated phenolics but did not affect soil respiration, which indicates that pH and SO_4^{2-} had negligible effects on decomposition in our experiment. Our results also suggest that Fe can actually stimulate carbon decomposition in peatlands through either decreasing dissolved phenolics upon Fe oxidation during drought,

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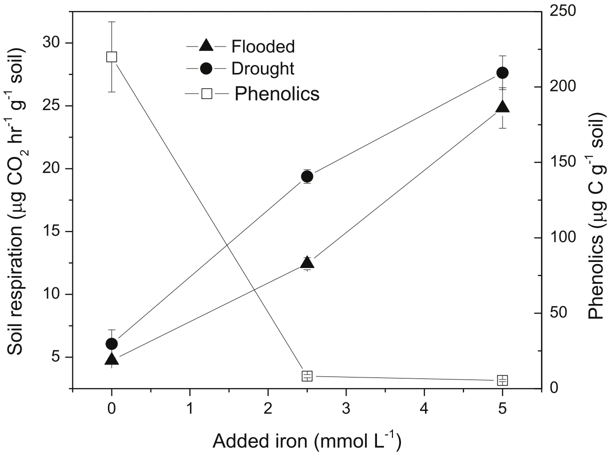

Fig. 1. Soil respiration (mean ± SE) from a wooded peatland soil in response to added ferrous iron under flooding, following drought, and the concentration of soluble phenolics (mean ± SE) in soil during flooding.

which is in line with findings in humid tropical forest soil (Hall and Silver, 2013), or by increasing activity of phenol oxidase (Van Bodegom et al., 2005; Wang et al., 2017) during flooding. These findings run contrary to Wang Y. et al.'s 'iron gate' mechanism (Wang et al., 2017).

Similar to Freeman's 'enzyme latch' theory that oxygen constraints on a single enzyme, phenol oxidase, can minimize the activity of hydrolytic enzymes responsible for peat decomposition (Freeman et al., 2001), the 'iron gate' theory needs to be verified by simultaneously measuring decreases in both phenol oxidase activity and carbon decomposition during water-table decline (WTD). Hence, WTD should increase dissolved phenolics and decrease heterotrophic respiration in Wang Y et al.'s experiment if an 'iron gate' exists. However, Wang Y. et al., did not measure dissolved phenolics and heterotrophic respiration (Wang et al., 2017). Although they observed decreased phenol oxidase activity with increased sorption of lignin derivatives under WTD, this does not necessarily mean more dissolved phenolics were kept in the system to inhibit microbial activity. On the contrary, our experiment indicates that less dissolved phenolics are available, likely resulting from the precipitation of phenolics upon Fe oxidization, which removes the phenolic inhibitory effect on microbial activity. In contrast to the interpretation of Wang Y. et al., their results likely complement the understanding of Freeman's 'enzyme latch' theory. The difference between these studies is that iron in fens and mineral-rich peaty wetlands vs. oxygen in bogs plays the major role in controlling phenol oxidase activity.

Instead of an 'iron gate,' our experiments show Fe in peatlands is likely a key to unlocking stored carbon. Therefore, the presence and availability of Fe in peatlands may substantially impact peat decay. To investigate the potential for Fe to interact with carbon in peatlands, we measured dissolved Fe in porewater from several peatlands in North and South America. Iron concentrations in porewater spanned nearly two orders of magnitude; in bogs in the Everglades in Florida and the pocosins in North Carolina Fe concentrations ranged from 0.03 to 0.6 mg L^{-1}, while in a fen in Peru, Fe concentrations ranged from 0.8 to 1.8 mg L^{-1}. Although solid-phase total Fe in soils from bogs is generally low, the wide range of Fe in porewater indicates that Fe transformations during reduced conditions may substantially affect Fe availability in peatlands. Collectively, the porewater Fe concentrations (0–12 mg L^{-1}) that we measured in the Peru fen and other fens (Moore, 1988) along with our manipulation experiment suggest that dissolved Fe in some mineral rich fens may substantially affect carbon decay.

The ability of sulfides to immobilize reduced Fe is well-known in studies of anoxic lake sediments, which have generally focused on the resulting release of phosphate (Caraco et al., 1989). Hence, under highly reduced conditions in peatlands, sulfides may also bind with Fe (II) in porewater, forming stable authigenic Fe-sulfide minerals such as FeS_2, and resulting in lower Fe(II) concentrations in porewater. Our SEM analyses of peat did not detect any appreciable Fe-coating of organic matter (more information in Supplemental Methods). However, we did find numerous pyrite clusters in the peat samples collected from several different types of peatlands: shrub peatlands in North Carolina, *Sphagnum* peatlands in Minnesota, and sawgrass peatlands in Florida (Fig. 2). Collectively, we argue that 'iron gate' carbon-preservation mechanism may not exist in these peatlands; in fact, our data suggest for peatlands with low mineral content and anoxic conditions, much of the reduced Fe pool may be immobilized via stable pyrite formation, decreasing porewater Fe(II) concentrations and thus the magnitude of Fe oxidation in drought conditions.

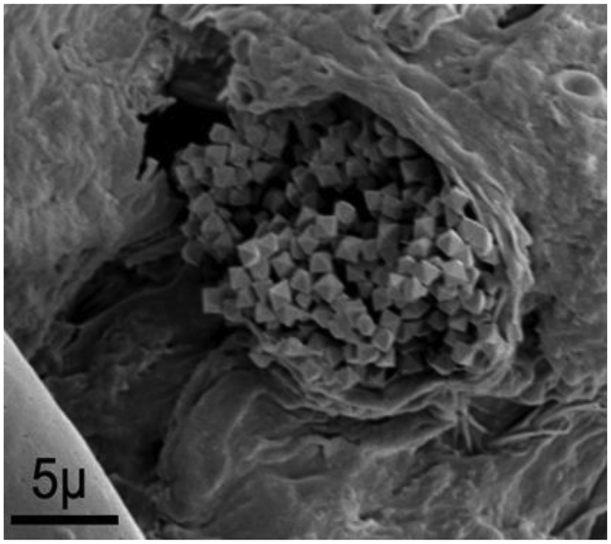

Fig. 2. Scanning Electron Microscope (SEM) image of framboidal pyrite (FeS_2) in a sawgrass-dominated peatland (bog) in the Florida Everglades.

To investigate whether most peatlands contain enough sulfur to potentially form stable pyrite (FeS_2), we analyzed the sulfur-iron data ($n = 696$) in peatlands in the USA from the Provisional Peat Database provided by USGS (https://energy.usgs.gov/Coal/Peat.aspx#378847-data). We found that approximately 56% of peatlands across the USA contain enough sulfur to potentially immobilize Fe via pyrite formation; as mineral content of a wetland increases, the S:Fe ratio generally declines, suggesting that pyrite likely plays less of a role in Fe immobilization in mineral-rich wetlands due to excess Fe (Fig. 3).

In summary, wetlands with high mineral content, may have enough Fe to co-precipitate and/or directly chelate carbon, thus protecting carbon (Lalonde et al., 2012). However, Fe content is generally low in most organic-rich peatlands, and thus Fe oxidation primarily precipitates dissolved organic carbon, phenolics in particular (Riedel et al., 2013) and can only partially coat soil organic matter, which means most soil organic matter is still exposed to air and microbes under drought. The loss of phenolics, a major controller of organic carbon decay (Freeman et al., 2004; Wang et al., 2015), may accelerate carbon loss in peatlands. Therefore, the 'iron gate' mechanism (Wang et al., 2017) may not be applicable to organic-rich peatlands.

Declarations of interest

None.

Author contribution

H.W., M.R. and C.J. R. designed the research; H.W. and M.R. conducted the analysis and all contributed to the writing of the paper.

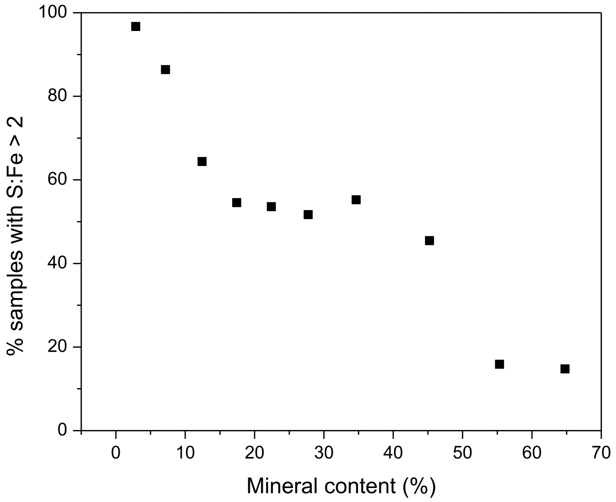

Fig. 3. Percentage of USGS peat samples in the USA, grouped by percentage of mineral content, containing enough elemental sulfur to form pyrite (S/Fe > 2). Samples (*n* = 699) are grouped by ash contents of 0–5% (*n* = 91), 5–10% (*n* = 66), 10–15% (n = 73), 15–20% (*n* = 55), 20–25% (*n* = 56), 25–30% (*n* = 60), 30–40% (*n* = 105), 40–50% (*n* = 67), 50–60% (*n* = 63), 60–70% (*n* = 61). X-value represents the average mineral content of each group. Y-value represents percentage of samples in each group containing enough elemental sulfur to form pyrite. Original data are from the Provisional Peat Database provided by USGS (https://energy.usgs.gov/Coal/Peat.aspx#378847-data).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.soilbio.2019.04.011.

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