



Iron-organic matter complexes accelerate microbial iron cycling in an iron-rich fen

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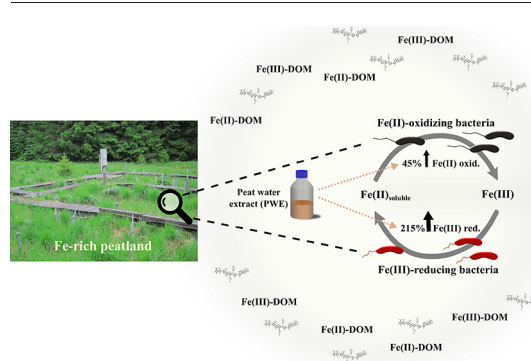
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HIGHLIGHTS

- This field study of an Fe-rich peatland underlies the importance of Fe species determination.
- The majority of Fe is complexed by DOM and keeps Fe(II) and Fe(III) in solution.
- DOM stabilizes Fe(II) in oxic soil layers and contributes to the redox equilibria.
- Fe-DOM-complexes enhance microbially-mediated Fe cycling.
- Fe(II) and Fe(III) across all depths allows co-existence of Fe-cycling microorganisms.

GRAPHICAL ABSTRACT



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ABSTRACT

The accessibility of iron (Fe) species for microbial processes is dependent on solubility and redox state, which are influenced by complexation with dissolved organic matter (DOM) and water-extractable organic matter (WEOM). We evaluated the complexation of these pools of organic matter to soluble Fe(II) and Fe(III) in the slightly acidic Schlöppnerbrunnen fen and subsequent effects on Fe(II) oxidation and Fe(III) reduction. We found the majority of soluble Fe(II) and Fe(III) is complexed to DOM. High-resolution mass spectrometry identified potential complexing partners in peat-derived water extracts (PWE), including compound classes known to function as ligands or electron shuttles, like tannins and sulfur-containing compounds. Furthermore, we observed clear differences in the stability of Fe(II)- and Fe(III)-DOM, with more labile complexes dominating the upper, oxic layers (0–10 cm) and more stable complexes in lower, anoxic layers (15–30 cm). Metal isotope-coded profiling identified a single potential chemical formula ($C_{42}H_{57}O_{13}N_9Fe_2$) associated with a stable Fe-DOM complex. Fe(III) reduction and Fe(II) oxidation incubations with *Geobacter sulfurreducens* PCA and *Shewanella oneidensis* MR-1 or *Sideroxydans* CL-21, respectively, were used to determine the influence of Fe-DOM complexes on Fe cycling rates. The addition of PWE led to a 2.3-fold increase in Fe(III) reduction rates and 0.5-fold increase in Fe(II) oxidation rates, indicating Fe-DOM complexes greatly influence microbial Fe cycling by potentially serving as electron shuttles. Molecular analyses revealed Fe(III)-reducing and Fe(II)-oxidizing bacteria co-exist across all depths, in approximately equal proportions (representing 0.1–1.0% of the total microbial community), despite observed changes in redox potential. The activity of Fe(III)-reducing bacteria might explain the presence of the

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detected Fe(II) stabilized via complexation with DOM even under oxic conditions in upper peat layers. Therefore, these Fe(II)-DOM complexes can be recycled by microaerophilic Fe(II)-oxidizers. Taken together, these results suggest Fe-DOM complexation in the fen accelerates microbial-mediated redox processes across the entire redox continuum.

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1. Introduction

Iron (Fe) is the fourth most abundant element in the Earth's crust, thus implicating the role of Fe cycling in nature is both ubiquitous and widespread. The majority of Fe found in natural environments, such as soils and sediments, is in the form of Fe minerals. The two redox states in which these Fe minerals are found include ferrous Fe, Fe(II), and ferric Fe, Fe(III), and can act as electron donors or acceptors for a variety of microbial metabolic processes (Davison, 1993; Stumm and Sulzberger, 1992; Weber et al., 2006). Abiotic and microbially mediated redox cycling of Fe plays an essential role in biogeochemistry, for example, in the preservation and degradation of organic matter as well as the fate of nutrients and contaminants for living organisms (Borch et al., 2010; Melton et al., 2014). Fe bioavailability can act as a limiting factor for primary production in marine systems, and also influences the biogeochemical functioning of soil and sediment environments (Daugherty et al., 2017). In aquatic environments, the bioavailability of Fe is significantly influenced by complexation with organic ligands as well as by redox reactions. Above pH 3, free Fe(III) is hardly available, because it rapidly forms oxyhydroxide minerals. However, complexation with organic ligands can increase the solubility of Fe(III). In marine environments, for example, >99% of the pool of dissolved Fe(III) is bound to organic compounds (Rue and Bruland, 1995). In contrast, dissolved Fe(II) is typically more stable over a broad pH range except under oxic conditions. Thus, the amount of free Fe(II) found in reducing environments can be high, and it can also be complexed by organic matter, such as fulvic acids (Bligh and Waite, 2010; Ephraim, 1992; Rose and Waite, 2003).

Natural organic matter (NOM) is a highly varied mixture of compounds, differing in size and structure (Stevenson, 1994). The major proportion of NOM is comprised of soil organic matter (SOM), the largest and most significant carbon pool in terrestrial ecosystems (Cotrufo et al., 2015; Lal, 2004). SOM plays an essential role in many ecosystem processes, such as co-transport of metals (Jirsa et al., 2013), soil carbon stabilization (Strahm et al., 2009), nutrient availability (Marschner and Kalbitz, 2003), pH buffering (Oliver et al., 1983), and shuttling ions between the solid and the surrounding aqueous phase (Jenne, 1975). The other proportion of NOM is comprised of dissolved organic matter (DOM) and water extractable dissolved organic matter (WEOM), typically defined as the fraction of NOM capable of passing through a <0.45 µm filter (Zsolnay, 2003) and is a complex heterogeneous mixture containing individual compounds as well as supramolecular assemblies (Avneri-Katz et al., 2017; Nebbioso and Piccolo, 2013). Particulate organic matter (POM) is separated through this procedure (Kleber et al., 2015). In spite of the fact that DOM and WEOM represent only a small part of NOM, they appear to play an essential role in biological activities in soils and aquatic environments. These compounds might affect various physiochemical processes, such as chelating of metal ions and binding of organic pollutants to soil particles and co-precipitation with metal oxides (Avneri-Katz et al., 2017; Barriuso et al., 2011; Gustafsson et al., 2007; Muller et al., 2007; Shimizu et al., 2013). Notably, a high percentage of DOM (50–80%) is comprised of dissolved compounds which are known to function as ligands and electron shuttles in soils (Farjalla et al., 2009; Jiang and Kappler, 2008). Thus, DOM-metal-complexes have the potential to influence metal transport, solubility, bioavailability, and toxicity (Stenson, 2009). It is important to note that the major process governing the fate of DOM and the accompanying stability of carbon in soils and sediments is the

adsorption of DOM to mineral surfaces, for example Fe(II) and Fe(III) oxyhydroxides. The reactivity of DOM is mediated by the type and number of functional groups comprising the DOM composition which ultimately determine the specific interactions with soil minerals, including ligand exchange with OH groups occupying metal oxide surfaces (Avneri-Katz et al., 2017; Gu et al., 1995; Wang et al., 1997). Chelation of carboxyl and phenolic groups found in the vicinity of each other is considered to be the primary mode of metal complexation by humates (Morel and Hering, 1993). The capacity of metal oxides to form complexes with NOM is likely due to the high content of functional groups, such as carboxyl-, hydroxyl- or carbonyl-groups as well as nitrogen- and sulfur-containing groups (Evangelou and Marsi, 2001; Vairavamurthy et al., 1997). Additionally, the increasing aromatic carbon content leads to an increase in Fe(III) binding capacity at circumneutral pH (Fujii et al., 2014).

Previous studies have identified mixed Fe(II)/Fe(III)-NOM complexes in both stream water and soil solutions in a boreal catchment (Sundman et al., 2014). The presence of Fe(II) can be attributed to a variety of potential mechanisms, including photochemical reduction, microbially mediated Fe(III) reduction, and increased stability resulting from binding of Fe(II) with organic ligands (Barbeau et al., 2001; Daugherty et al., 2017; Melton et al., 2014; Millero et al., 1987; Voelker et al., 1997). Interestingly, previous studies investigating Fe-NOM oxidation-reduction chemistry have shown that Fe(II)-NOM complexation enhances, inhibits, or has no impact on the rate of Fe(II) oxidation suggesting that specific complexes have to be considered. For example, complexation of tannic acid has been shown to inhibit, salicylate and citrate have been shown to enhance oxidation, while the complexation of some amino acids, including alanine and glutamine, have no impact on Fe(II) oxidation (Daugherty et al., 2017). Furthermore, investigations using environmental samples indicate NOM to have varying effects on Fe(II) oxidation kinetics. Additionally, most studies do not account for NOM redox activity or comprehensive characterization of binding interactions between organic molecules and Fe species.

Peatlands provide essential ecological, biogeochemical, and hydrological functions by serving as unique transitional environments between aquatic and terrestrial ecosystems (Joosten and Clarke, 2002; Kruger et al., 2015; Mitra et al., 2005). In spite of covering only 3% of all continents (Joosten et al., 2012), peatlands store approximately 10% of all freshwater and 30% of land-based organic carbon (Bragazza et al., 2013; Mitra et al., 2005). Acidic peatlands (pH < 5.0) represent a significant proportion of northern wetlands in North America and Eurasia (Harriss et al., 1993). In these environments, accumulation of organic carbon is favored due to waterlogging, low temperatures, and low nutrient quality of plant litter, and subsequent low rates of plant litter decomposition (Küsel et al., 2008). Thus, NOM is an important component in peatland soils due to the significant role of NOM in the global carbon cycle. Peatlands are replete in carbon-, nitrogen- and/or sulfur-sources readily available for microbial metabolic and redox processes. In minerotrophic fens connected to groundwater flow, Fe(III) functions as an additional electron acceptor and Fe(II) concentration profiles imply a microbial reduction of Fe(III) in pH neutral fens (Todorova and Costello, 2006). The ability of most Fe reducing microorganisms to utilize a variety of terminal electron acceptors (Lovley et al., 2004) is perceived to be advantageous in the upper peat layers characterized by recurrent fluctuations in redox potential due to changes in the water-table level and release of oxygen in plant root exudates

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