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Oxic transformation and translocation of ferrihydrite by fungal secondary metabolites

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It has been established that brown-rot (BR) [1] and some ectomycorrhizal (ECM) [2] fungi use a non-enzymatic Fenton reaction ($\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot\text{OH}$) to decompose carbon. This Fenton reaction is driven by secondary metabolites, namely hydroquinones (H_2Q), and to date studies of H_2Q with redox reactive minerals have primarily been conducted under anoxic conditions and in batch setups. This approach introduces two shortcomings: Firstly, oxic iron(III) (oxyhydr)oxide (FeOOH) transformation and vertical translocation in the soil is ignored. Secondly, as the redox potential (E_{H}) of FeOOH decrease as a function of increasing Fe^{2+} concentration in solution, the reductive dissolution stops when the E_{H} of $\text{Q}/\text{H}_2\text{Q}$ is higher than E_{H} of $\text{FeOOH}/\text{Fe}^{2+}$ [3]. It follows that in order to investigate the full potential of H_2Q driven Fe mobilization an experimental setup, in which the solution is removed from the interface of the reaction, is needed. Consequently, this study will investigate the Fe mobilization potential of 2,6-dimethoxyhydroquinone (DMHQ, a stable analogue to a common secondary metabolites produced by BR fungi) in a flow setup with continuous application of H_2Q and removal of Fe^{2+} under oxic and natural relevant concentrations. A low-tech column set-up with synthesized ferrihydrite coated sand (1-0.5 mm) were supplied with 100 mL 20 μM DMHQ bi-daily over a three months period (50 times in all) and pH and Fe^{2+} concentration was monitored in the outlet. Before and after DMHQ application the coated ferrihydrite's crystallinity was investigated with dithionite-citrate-bicarbonate and ammonium oxalate extractions. Results will be presented showing that DMHQ can reduce ferrihydrite and mobilize Fe^{2+} under oxic conditions and further that the ferrihydrite becomes increasingly crystalline, thus less reactive, after exposure to 100 μmol of 2,6-DMHQ. In light of the wide distribution of the Fenton reaction, with BR fungi dominating C sequestration in the boreal forest and ECM fungi being abundant in the boreal forest, eucalyptus forest and heathlands, these findings have interesting implications. Moreover, the results support that podsolization, i.e. the translocation of sesquioxides and soil organic matter associated with the above mentioned ecosystems, is linked to reductive dissolution of FeOOH by fungal secondary metabolites as previously suggested [4].

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