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# Biogeochemical Controls on Wood Degradation as a Source of Bioavailable Carbon in Denitrifying Bioreactors

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Denitrifying woodchip bioreactors (WBRs) are important tools for the passive removal of nitrate from a variety of nonpoint sources, including agricultural drainage. WBRs depend on the degradation of lignocellulosic wood residues into bioavailable forms of carbon to fuel denitrifying microorganisms. However, denitrification in WBRs is often carbon-limited due to the slow degradation of wood in saturated anoxic conditions. Here, we examine the biogeochemical factors regulating wood degradation and wood-derived carbon bioavailability in saturated woodchip beds, with a focus on the effects of dissolved oxygen (DO), iron (Fe), and manganese (Mn). We specifically evaluate the potential roles of Fe and Mn in generating oxidative activity that can depolymerize wood biopolymers and thereby enhance decomposition into bioavailable carbon vs. mineral protection processes in which Fe and Mn shield wood-derived carbon from microbial activity.

We first characterized spatial variability in wood decomposition and denitrification rates with woodchips collected from a 10-yr old WBR. Woodchips collected near the bioreactor inlet, and exposed to higher DO in influent waters, were more degraded, had higher surface concentrations of Fe and Mn, and supported faster denitrification rates. Using a novel combination of µX-ray scattering and µXRF, we showed that the depletion of crystalline cellulose at woodchip surfaces was associated with higher concentrations of Fe and Mn. µXANES analysis of Fe and Mn redox gradients at wood surfaces revealed a microenvironment where oxygenation reactions of Fe(II) and Mn(II) are capable of generating reactive oxidants involved in the degradation of lignocellulose, providing a mechanistic link between metals, wood degradation, and denitrification rates. These links were further tested by coating fresh woodchips with synthetic ferrihydrite or birnessite and incubating under anoxic or cycling oxic-anoxic conditions for 8 months. Mineral-coated woodchips exhibited more advanced degradation than non-coated woodchips under oxic-anoxic cycling, while under static anoxia the presence of minerals slowed wood decomposition. The presentation will conclude with a discussion of the implications of these findings for the design and operation of sustainable wood-based denitrifying systems for managing nitrogen in agricultural drainage waters.