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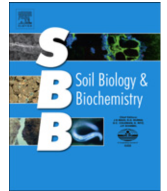

Review

Phenol oxidase, peroxidase and organic matter dynamics of soil

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ABSTRACT

Extracellular enzymes mediate the degradation, transformation and mineralization of soil organic matter. The activity of cellulases, phosphatases and other hydrolases has received extensive study and in many cases stoichiometric relationships and responses to disturbances are well established. In contrast, phenol oxidase and peroxidase activities, which are often uncorrelated with hydrolase activities, have been measured in only a small subset of soil enzyme studies. These enzymes are expressed for a variety of purposes including ontogeny, defense and the acquisition of carbon and nitrogen. Through excretion or lysis, these enzymes enter the environment where their aggregate activity mediates key ecosystem functions of lignin degradation, humification, carbon mineralization and dissolved organic carbon export. Phenol oxidases and peroxidases are less stable in the environment than extracellular hydrolases, especially when associated with organic particles. Activities are also affected, positively and negatively, by interaction with mineral surfaces. High spatiotemporal variation obscures their relationships with environmental variables and ecological process. Across ecosystems, phenol oxidase and peroxidase activities generally increase with soil pH, a finding not predicted from the pH optima of purified enzymes. Activities associated with plant litter and particulate organic matter often correlate with decomposition rates and potential activities generally increase with the lignin and secondary compound content of the material. At the ecosystem scale, nitrogen amendment alters the expression of phenol oxidase and peroxidase enzymes more broadly than culture studies imply and these responses correlate with positive and negative changes in litter decomposition rates and soil organic matter content. At the global scale, N amendment of basidiomycete-dominated soils of temperate and boreal forest ecoystems often leads to losses of oxidative enzyme activity, while activities in grassland soils dominated by glomeromycota and ascomycetes show little net response. Land use that leads to loss of soil organic matter tends to increase oxidative activities. Across ecosystems, soil organic matter content is not correlated with mean potential phenol oxidase and peroxidase activities. A multiple regression model that includes soil pH, mean annual temperature, mean annual precipitation and potential phenol oxidase activity accounts for 37% of the variation in soil organic matter (SOM) content across ecosystems ($n = 63$); a similar model for peroxidase activity describes 32% of SOM variance ($n = 43$). Analysis of residual variation suggest that suites of interacting factors create both positive and negative feedbacks on soil organic matter storage. Soils with high oxygen availability, pH and mineral activity tend to be substrate limited: high in situ oxidative activities limit soil organic matter accumulation. Soils with opposing characteristics are activity limited: low in situ oxidative activities promote soil organic matter storage.

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1. Introduction

Extracellular enzymes mediate the degradation, transformation and mineralization of soil organic matter. The activity of cellulases, phosphatases and other hydrolases has received extensive study and in many cases stoichiometric relationships and responses to disturbances are well established (Sinsabaugh et al., 2008). In contrast, phenol oxidase and peroxidase activities, which are often uncorrelated with hydrolase activities, have been measured in only a small subset of soil enzyme studies. These enzymes are expressed for a variety of purposes including ontogeny, defense and the acquisition of carbon and nitrogen. Through excretion or lysis, these enzymes enter the environment where their aggregate activity mediates key ecosystem functions of lignin degradation, humification, carbon mineralization and dissolved organic carbon export.

Within the soil biochemistry literature, enzymes that oxidize phenolic compounds using oxygen are often named in relation to a particular substrate (e.g. monophenol oxidase, tyrosinase, catechol

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oxidase, diphenol oxidase) even though the enzymes under consideration generally show activity to varying extents, against a broad range of molecules (Baldrian, 2006). The Enzyme Commission of IUPAC classifies these enzymes into several taxa. EC 1.10.3 includes enzymes that use oxygen as an electron acceptor. Within this group, EC 1.10.3.1 (o-diphenol: oxygen oxidoreductases) includes many enzymes described as tyrosinases or catechol oxidases and EC 1.10.3.2 (p-diphenol: oxygen oxidoreductases) includes laccases, which have multiple copper atoms at their reaction center. EC 1.13.11 includes enzymes that incorporate two oxygen atoms into their substrate (dioxygenases), e.g. EC 1.13.11.12 catechol dioxygenase. EC 1.14.18 includes enzymes that use an electron donor and incorporate a single oxygen into their substrate, e.g. EC 1.14.18.1 is defined as monophenol monooxygenase, a class that also encompasses enzymes variously described as tyrosinase, monophenol oxidase and laccase. Because assays of environmental samples may capture activity from some or all of these enzyme classes, I herein use the generic term “phenol oxidase” to describe the activity of enzymes that oxidize phenols and consume oxygen.

Peroxidases are enzymes that use H_2O_2 as an electron acceptor (EC 1.11.1). In soils, fungi produce manganese peroxidase (EC 1.11.1.13), lignin peroxidase (EC 1.11.1.14) and other broad spectrum peroxidases (EC 1.11.1.7) that are known for their role in depolymerizing lignin. As is the case for phenol oxidases, most assays of environmental samples do not discriminate individual enzymes, so herein I use the generic term “peroxidase” to describe the activity of enzymes that use H_2O_2 as an acceptor.

The first report of phenol oxidase activity in soil, using guaiacol as a substrate, was made by Cameron and Bell (1905, as cited in Skujins (1978)). Few studies followed. The text “Soil Enzymes” (Burns, 1978) included reviews of polysaccharidase, urease, phosphatase and sulfatase activities, but scant coverage and few references to phenol oxidase and peroxidase activities (Ladd, 1978). Studies by Mayaudon et al. (1973) and Ross and McNeilly (1973) increased interest in these activities, but 35 years later, I estimate that only about 150 papers have been published that include quantitative measurements from environmental samples.

2. Biochemistry

2.1. Phenol oxidases

Much of the research on fungal and bacterial degradation of aromatic compounds has been driven by biotechnical interests in the degradation of lignocellulose for pulp products and transportation fuels and the bioremediation of soils contaminated with pesticides, dioxins and other halogenated “xenobiotic” products. These topics are frequently reviewed (Duran et al., 2002; Claus, 2003; Rabinovich et al., 2004; Baldrian, 2006; Masai et al., 2007). Here, I include only a brief overview of this research to provide context for the synthesis of soil ecology studies that is the subject of this review.

Microorganisms and plants produce intracellular and extracellular phenol oxidases for a variety of purposes. Plants use phenol oxidases to synthesize lignin and other secondary compounds. Many fungi, but particularly ascomycetes and basidiomycetes use intracellular phenol oxidases to synthesize protective compounds like melanin, often in conjunction with spore formation or other morphogenic processes. Some organisms use extracellular phenol oxidases to degrade lignin and humus to gain carbon and other nutrients. More generally, extracellular phenol oxidases are deployed by both fungi and bacteria to mitigate the toxicity of phenolic molecules and metal ions, and aid in antimicrobial defense. But whatever their origin and initial function, phenol oxidases released into the environment whether by secretion or cell lysis are independent agents that catalyze non-specific reactions, including the oxidation of Mn^{+2} and Fe^{+2}, that can polymerize, depolymerize or transform a broad spectrum of phenolic molecules. These reactions, in turn, affect the activity and composition of soil microbial communities because phenolic molecules are inherently toxic.

The biochemistry of laccases, probably the largest class of phenol oxidases in soil, has been extensively reviewed (Duran et al., 2002; Claus, 2003; Rabinovich et al., 2004; Baldrian, 2006; Hoegger et al., 2006; Masai et al., 2007). Laccases are part of the multicopper oxidase protein family (Hoegger et al., 2006). Most enzymes have four copper atoms at their reaction center, and four single electron oxidations are needed to reduce oxygen to water. This stepwise process creates reactive semiquinones, quinones and phenoxy radicals. Laccases can also oxidize chelated Mn^{+2}. When used for lignin degradation, depolymerization is probably the result of diffusion of these reactive species rather than direct enzyme contact with the polymer.

Most basidiomycetes and many ascomycetes produce extracellular laccases. Based on analyses of more than 100 purified enzymes, fungal laccases have a median molecular size of 66 kD and median optimum temperature of 55 °C, but the range is wide for both values (Baldrian, 2006). Optimal pH values also vary widely because they depend on the substrate as well as the structure of the enzyme, but optima generally fall in the acidic range for extracellular enzymes, with more circumneutral values for intracellular enzymes. Extracellular laccases are glycoproteins with a typical saccharide content of 10–25%. Extracellular production can be constitutive or inducible with 1–8 isozymes produced per organism. Redox potentials range from 450 to 800 mV, less than that of lignin peroxidases (>1000 mV) but greater than that of catechol oxidases (200–300 mV).

Laccases can oxidize a broad range of small molecules including humics to form stable radicals, termed redox mediators, whose redox potentials are substantially greater than those of the laccases themselves (Leonowicz et al., 2001; Camarero et al., 2005). Many white rot fungi (Basidomycetes) lack peroxidases and depolymerize lignin using a system of laccase and redox mediators Laccases can also interact with Mn peroxidases by oxidizing chelated Mn^{+2}. In addition to lignin degradation, laccase production can be induced by presence of various phenols and as a component of a general antimicrobial defense. Production is also modulated by the availability of Cu.

Laccases are widely produced by white rot basidiomycetes and soft rot ascomycetes, but not by chytridiomycetes or zygomycetes (Bending and Read, 1997; Gunther et al., 1998; Lyons et al., 2003; Luis et al., 2005; Pointing et al., 2005; Kilaru et al., 2006; Zavarzina and Zavarzin, 2006; Kellner et al., 2008). Brown rot basidiomycetes produce intracellular laccases, which contribute to the degradation of lignocellulose upon cell lysis. The laccases of white rot fungi, generally have lower pH optima (4.0–5.0) than the laccases of brown rot and coprophilic fungi (6.0–7.5). The enzymes of the former group are primarily involved in lignin breakdown, often acting in concert with redox mediators, while the latter act primarily as detoxification agents, polymerizing soluble phenols and thereby contributing to humification. The laccases of ectomycorrhizal basidiomycetes do not cluster with the lignin-degrading laccases of white rot basidiomycetes (Courty et al., 2009). Some of these enzymes have ontogenetic roles, but others appear to function in concert with proteolytic and chitinolytic enzymes to extract nitrogen from humic complexes (Hobbie and Horton, 2007; Talbot et al., 2008; Courty et al., 2009).

Laccases are traditionally considered to be fungal enzymes. However, laccase genes, or more generally laccase-like multicopper oxidases (LMCO), are broadly distributed among bacteria and

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