Chapter 12
Evolutionary-Economic Principles as Regulators of Soil Enzyme Production and Ecosystem Function

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12.1 Introduction

Extracellular enzymes are ubiquitous in soil environments. Produced by microorganisms and plant roots, these enzymes serve a dual function of degrading complex organic material into simpler forms and acquiring resources for the enzyme producer (Burns 1982; Sinsabaugh 1994). Without extracellular enzymes, microbes and plants would be unable to obtain resources from complex compounds, and cycles of carbon (C) and nutrients would grind to a halt.

Researchers have been measuring and interpreting soil enzyme activities for over 100 years (Eriksson et al. 1974; Skujins 1976). Although extracellular enzymes are clearly important for soil function, the factors regulating enzyme production remain unclear. For example, the mechanisms that determine the composition, timing, spatial location, and quantity of extracellular enzyme production in soil are still poorly known (Wallenstein and Weintraub 2008). Better knowledge of these mechanisms would improve our ability to predict how soil biogeochemical cycles will respond to changes in the environment. Increasing global temperatures, land use change, nutrient deposition, and invasive species are prominent examples of global changes that currently affect soil ecosystems (Trumbore 1997; Swift et al. 1998; Ehrenfeld 2003).

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Because extracellular enzyme producers are living organisms, they are subject to ecological constraints that may affect growth and enzyme production (Ekschmitt et al. 2005; Allison 2006). Although extracellular enzymes catalyze critical biogeochemical reactions, resource acquisition is the primary function of these enzymes from an organismal perspective. Therefore, enzyme production represents one of several possible foraging strategies, including direct uptake of simple resources, autotrophy, or nitrogen (N) fixation, depending on the resource in question. All these strategies involve costs and benefits that depend on environmental conditions.

The major organismal benefit of enzyme production is the release of organic monomers or mineral nutrients that microbes or plant roots can take up across the cell membrane and assimilate. Extracellular enzymes target nearly every macromolecule on earth, including proteins (proteases), carbohydrates (amylases, cellulases), amino sugar polymers (chitinases), organic phosphates (phosphatases), and lignins (oxidases, peroxidases) (Burns 1978; Allison et al. 2007a). The costs of enzyme production include the metabolic energy required for protein synthesis and excretion, as well as the C and nutrient content of the enzymes themselves. For example, between 50 and 70% of N acquired by microbes may be allocated to amino acids that are the building blocks of enzymes (Friedel and Scheller 2002), and extracellular enzyme production has been reported to consume 1–5% of C and N assimilation by bacteria (Frankena et al. 1988).

The main goal of this chapter is to explore the hypothesis that evolutionary and ecological forces minimize the cost:benefit ratio of extracellular enzyme production and thereby represent an important regulator of enzyme production and activity. We expect that soil physical properties, nutrient availability, and competitive interactions represent strong selective pressures that influence enzyme cost:benefit ratios. For both microbes and plants (the major groups of extracellular enzyme producers), natural selection should favor enzyme production strategies that minimize costs and maximize benefits (Table 12.1). The rationale is that increased costs of enzyme production reduce fitness because those resources cannot be allocated to reproduction. Conversely, the resource benefits of enzyme production can be invested in reproductive effort, thereby increasing fitness. These tradeoffs should apply generally to microbes (and plants) whose fitness often correlates with growth rate, since growth represents the difference between resource inputs and outputs to an organism. We argue that "evolutionary-economic" constraints apply to organisms foraging with extracellular enzymes and provide a mechanistic basis for predicting how they respond to changing environmental conditions.

Table 12.1 Strategies to minimize extracellular enzyme cost: benefit ratio

Inducible enzyme production
End-product inhibition of enzyme production
Binding enzymes to the cell surface
Altering diffusive properties of secreted enzymes
Biofilm formation
Quorum sensing
Antibiotic production

12.2 The Evolutionary Economics of Extracellular Enzyme Production

Components of the evolutionary-economic mechanism of enzyme production have been suggested before across a range of systems, but this work has yet to be unified in a common framework. For example, Sinsabaugh and Moorhead (1994) were among the first to develop an explicit model of microbial allocation to extracellular enzyme production that assumed a tradeoff among enzymes that acquire C, N, and P. This model, called "Microbial Enzyme Allocation during Decomposition" (MEAD), treats microbial communities as economic units that maximize their productivity by allocating resources to extracellular pools of C-, N-, and P-releasing enzymes, depending upon substrate quality and environmental conditions. However, the main goal of this model as well as some more recent models (Schimel and Weintraub 2003; Moorhead and Sinsabaugh 2006) was to predict decomposition rates rather than to examine enzyme production as a foraging strategy.

There are other models that focus more directly on microbial foraging with extracellular enzymes. Based on an analytical model, Vetter et al. (1998) predicted that extracellular enzyme production would be a viable foraging strategy for marine bacteria attached to particulate organic material. The benefits of enzyme production exceeded the costs under the modeled diffusion and substrate conditions, thereby allowing bacterial growth to occur. This foraging concept was recently incorporated into a spatially explicit, individual-based model of enzyme production by bacteria (Allison 2005) that revealed the potential importance of diffusion, nutrient availability, and microbial competition as constraints on extracellular enzyme production. While valuable as a theoretical exercise, this model contains many untested assumptions and has yet to be confronted with experimental data. Therefore, a secondary goal of this chapter is to synthesize empirical and theoretical evidence to test the hypothesis that ecological-economic and evolutionary constraints regulate extracellular enzyme production in soils. In pursuit of this goal, we aim to build a more comprehensive conceptual framework for enzyme production that goes beyond the existing models.

12.3 Controls on Microbial Allocation to Enzyme Production

12.3.1 Microbial Demand

Microbes produce extracellular enzymes that target all essential macronutrients, including C, N, P, and S (enzymes from plant roots target only P and possibly N) (Burns 1978; Allison et al. 2007a). The availability of these nutrients fluctuates in space and time, and nutrient supply does not necessarily match microbial or plant nutrient requirements. The main function of most extracellular enzymes is therefore

to bring nutrient supply (from chemically complex resources) more closely in line with nutrient demand. If the supply of available resources is already aligned with microbial and plant requirements, there should be little ecological or evolutionary advantage to enzyme production due to the costs involved. Since nutrient demand effectively determines the relative quantities of resources that organisms need to acquire, understanding the factors that control nutrient demand could help explain patterns in soil enzyme production.

Ultimately, nutrient demand can be traced to constraints on organismal stoichiometry (Sterner and Elser 2002). Macromolecules, such as proteins, nucleic acids, carbohydrates, and cell wall components exhibit well-defined elemental ratios. Since macromolecular composition is a relatively inflexible trait in most organisms, it strongly determines organismal stoichiometry and nutrient demand. For example, because animal tissue is protein rich compared to plant tissue, animals have lower C:N ratios and greater N demand relative to plants (Reiners 1986). At a global scale, stoichiometric constraints on organismal biomass are apparent across a range of taxa. For example, molar ratios of C:N:P for marine phytoplankton are tightly constrained at 106:16:1 (Redfield 1958). Although the ratios differ and the variance is greater, similar patterns hold for plants and microbes in terrestrial systems. Tree foliage ratios average 1,212:28:1 (McGroddy et al. 2004), with a similar ratio of 1,158:24:1 observed in fine root biomass (Jackson et al. 1997). For soil microbial biomass as a whole, the average global ratio is 60:7:1 (Cleveland and Liptzen 2007), which reflects the much lower concentration of structural C and the lack of photosynthetic machinery in microbial cells relative to plant cells.

Within microbes, there are clear stoichiometric differences across taxa that could affect intrinsic demand for different resources. For instance, bacteria have C:N ratios of ~5:1, while fungi show C:N ratios closer to 15:1 (Sterner and Elser 2002). These differences arise because fungi produce cell walls made of C-rich polysaccharide polymers and chitin (Bartnicki-Garcia 1968), while bacterial cell walls are primarily composed of more N-rich peptidoglycans (Schleifer and Kandler 1972). Similarly, C:P and N:P ratios differ across taxa, with P content hypothesized to relate to growth rate because more ribosomes with high P content are required to sustain rapid growth rates (Sterner and Elser 2002; Makino et al. 2003). Although broad groups of microbes (i.e., fungi and bacteria) clearly differ in stoichiometry, more studies of the C:N:P ratios of specific microbial taxa would aid in predicting resource investment in different extracellular enzymes. Based on taxon-specific differences in cell wall chemistry, the stoichiometric variation within bacteria and fungi is likely to be substantial (Bartnicki-Garcia 1968; Schleifer and Kandler 1972).

12.3.2 Enzyme Regulation

Due to the resource costs of enzyme synthesis, microbes (and plant roots) should be under selection to regulate enzyme production. Induction and de-repression are

regulatory mechanisms that can potentially mitigate enzyme costs by up-regulating enzyme production only when this strategy will be beneficial to the producer. These mechanisms require additional regulatory machinery at the genetic level, such as promoters that interact with inducer and repressor molecules to signal environmental conditions, such as resource availability. Although not an extracellular enzyme system, the *lac* operon in *E. coli* is a textbook example of how the availability of external resources (lactose and glucose) can interact with a regulatory pathway to control enzyme synthesis (Jacob and Monod 1961).

Regulation of most extracellular enzyme systems has been poorly studied in soil, but there is evidence for regulatory control of extracellular enzyme production in aquatic and laboratory systems. Enzymes that are produced continually with little regulatory control are constitutive, while inducible enzyme activity is produced only under particular environmental conditions. Enzyme production by bacteria can be induced in the laboratory by intermediate degradation products that signal availability of the substrate (Priest 1977). Similarly, extensive work in lake systems has demonstrated that the presence of enzyme substrates can induce the production of alkaline phosphatase and leucine aminopeptidase activity (Chróst 1991). In contrast, high concentrations of low-molecular weight catabolites (e.g., glucose, amino acids) inhibit community enzyme activity either through repression of enzyme gene transcription or through competitive inhibition of the enzyme itself (Hanif et al. 2004).

Although enzyme production is clearly inducible in these systems, some level of constitutive production may be advantageous as a mechanism to detect the presence of substrate. With no baseline level of extracellular enzyme production, it would be difficult to generate intermediates that could act as inducers for additional enzyme synthesis (Chróst 1991; Koroljova-Skorobogatko et al. 1998). Consistent with this idea, Raab et al. (1999) found that protease activities were positively related to soil amino acid concentrations at the low levels typically found in soil. These regulatory mechanisms ensure that enzymes are produced only when substrate is available and the end-products of the enzymatic reaction are scarce.

12.4 Resource Availability in Soil

Although mechanisms of extracellular enzyme regulation were first identified in aquatic ecosystems, there is evidence that the same conceptual models apply in soils. In fact, the model proposed by Sinsabaugh and Moorhead (1994) is effectively a model of end-product inhibition, whereby available forms of N and P suppress the production of N- and P-acquiring enzymes and stimulate microbial allocation to C-degrading enzymes. Empirical evidence provides strong support for the MEAD model. Across a range of sites, the model was able to explain $>62\%$ of the variation in decomposition rate of birch wood (Sinsabaugh and Moorhead 1994). In laboratory cultures, proteomic studies have shown that *Bacillus* bacteria produce specific enzymes in response to limitation by C, N, or P (Voigt et al. 2006).

When soil microorganisms are P limited, they produce acid or alkaline phosphatases (depending upon pH and microbial community composition) that release inorganic phosphate from organic matter (Haynes and Swift 1988; Antibus et al. 1992). Moreover, phosphatase activity has been shown to be inversely related to inorganic P availability in both aquatic and soil systems (Chróst 1991; Olander and Vitousek 2000; Treseder and Vitousek 2001; Allison et al. 2007b). This relationship also holds at the global scale, where the ratio of P- to C-acquiring extracellular enzymes increases in tropical ecosystems where P is more likely to limit productivity due to increased P weathering rates (Sinsabaugh et al. 2008). Similarly, the activities of N-acquiring enzymes such as peptidases and chitinases are stimulated by low N availability but inhibited by high concentrations of inorganic N in many systems (Chróst 1991; Olander and Vitousek 2000; Weintraub and Schimel 2005).

As with aquatic systems, there is evidence that soil extracellular enzymes are also inducible in the presence of substrate and that adequate substrate availability may be a requirement for enzyme production. In an infertile Hawaiian soil, addition of available N and P failed to stimulate β-glucosidase activity, but this enzyme activity increased when cellulose substrate was also added in combination with N and P (Fig. 12.1a; Allison and Vitousek 2005). Similarly, glycine aminopeptidase production was unchanged when available C and P were added, but induced when collagen protein was also added (Fig. 12.1b). Thus, extracellular enzyme induction in soil appears to depend on at least two conditions: (1) producers are limited by the resource targeted by the enzyme and (2) a suitable substrate for the enzyme is present in the soil.

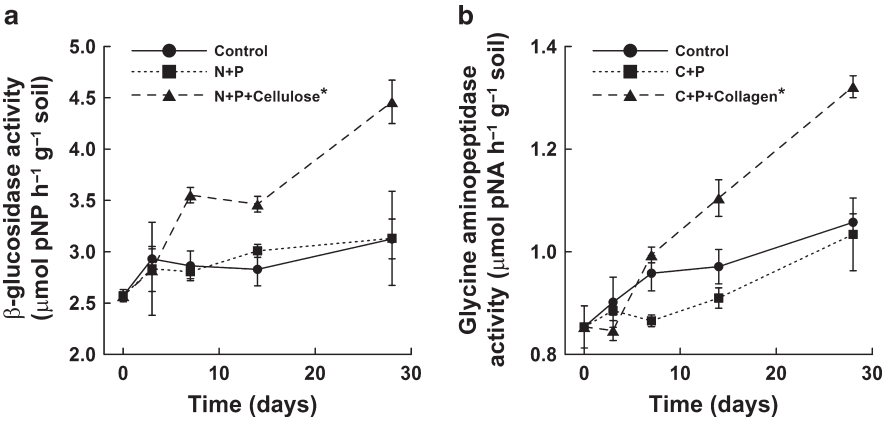

Fig. 12.1 β-glucosidase (**a**) and glycine aminopeptidase activities (**b**) in Hawaiian rainforest soils with carbon and nutrient amendments. *Symbols* and *bars* represent means and standard errors of 2–6 replicates. *Asterisks* denote significant differences from controls at $P < 0.05$. C = sodium acetate; N = ammonium chloride; P = sodium phosphate

12.5 Implications of Enzyme Allocation

12.5.1 Protection of Investment

Because extracellular enzymes act outside the producer cell, other organisms may also derive benefits from the producer investment in enzyme production. If these organisms intercept enough of the resource benefit (or damage the enzyme itself), then the cost:benefit ratio of enzyme production would increase. However, we expect that enzyme producers would evolve strategies to protect their enzyme investment and reduce competition and interference from other organisms. One way of protecting enzymes is to bind them to the cell surface. This helps ensure that neither the direct investment in the enzyme itself nor the products of the enzymatic reaction will be lost. However, the cost of having an enzyme bound to the surface is that distant substrates will not be accessible (Vetter et al. 1998). Alternatively, enzyme-producing microbes may use chemical defenses, such as antibiotics, to eliminate competitors or aggregate with other enzyme producers in a quorum or biofilm (Ekschmitt et al. 2005). This strategy allows microbes to exploit the diffusion losses of their neighbors and increases the chance of taking up reaction products before they diffuse away from the aggregation of cells. Some mycorrhizal fungi employ this strategy by forming dense, hydrophobic mats of hyphae that exude enzymes in water droplets that are later reabsorbed by the fungus, along with the products of decomposition (Sun et al. 1999).

Even if enzymes are not bound to the cell surface, microbes may have strategies to mitigate enzyme loss. The size and structure of an enzyme help determine its diffusivity, and these properties could be altered (as a result of cellular regulation and/or natural selection) to produce different isozymes that optimize enzyme foraging. We used a spatially explicit and individual-based model (Allison 2005) to examine the costs and benefits of changes in enzyme diffusion under different conditions. If substrate availability is high, then the optimal enzyme diffusivity is low because enzymes remain concentrated near the producer and substrate does not become limiting (Fig. 12.2). As substrate availability declines, the model predicts that the optimal enzyme diffusivity increases, allowing the producer to access more distant substrates, once closer substrates become exhausted (Figs. 12.2 and 12.3). However, interception of reaction products by microbial “cheaters” that do not produce enzymes may counter this effect and select for low enzyme diffusivity even under low substrate conditions (Allison 2005).

Secreting extracellular polysaccharides to form a biofilm is another strategy that microbes could employ to restrict the diffusion of extracellular enzymes to an optimal level (Davey and O’Toole 2000). Additionally, microbes may produce autoinducer molecules that allow them to sense the diffusion properties of the environment. Although typically thought to be involved in quorum sensing, Redfield (2002) has proposed that autoinducers are also used by microbes to determine the rate at which secreted molecules move away from the cell. Thus, it is possible that microbes use these autoinducers to sense when diffusion rates are favorable for

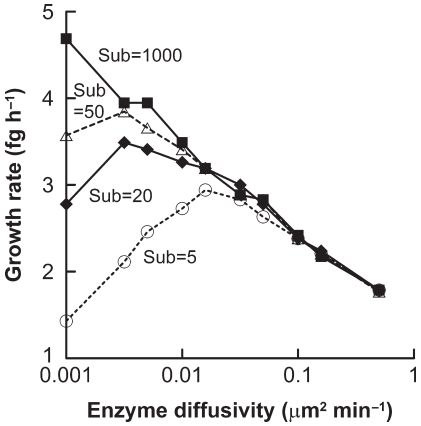

Fig. 12.2 Model output of bacterial growth rates as a function of enzyme diffusivity at different substrate (Sub) concentrations (fg μm^{-3})

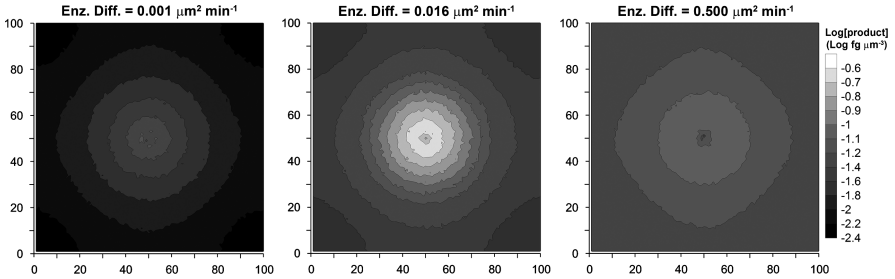

Fig. 12.3 Modeled product concentrations after 50 h on a spatial grid with an enzyme-producing microbe in the center and enzyme diffusivities (EDiff) of 0.001, 0.016, and 0.500 μm^2 min^{-1}. Substrate concentration = 5.0 fg μm^{-3}. Note that product concentrations around the microbe are greatest at intermediate enzyme diffusivity (0.016 μm^2 min^{-1})

enzyme production and extracellular foraging. Autoinducers would be ideal for this regulatory role because they are relatively cheap for cells to produce and are not naturally present in the extracellular environment.

12.5.2 Enzyme Responses to Global Environmental Change

At the ecosystem level, one important consequence of efficient allocation to extracellular enzyme production is a stronger correspondence between resource supply and demand. Microbes (and plant roots) have ecological and evolutionary incentives to use enzymes to extract nutrients from otherwise unavailable organic sources when nutrients are limiting. This allocation pattern suggests that the release of nutrients from complex organic sources will decrease when simple resources are

more available. Thus, adding available nutrients should suppress the turnover of complex organic nutrients.

Because extracellular enzymes often control organic matter solubilization – the rate-limiting step in organic matter turnover – shifts in enzyme allocation could have major consequences for rates of C and nutrient cycling under global change. Environmental changes can alter allocation to different enzymes through regulatory pathways as well as shifts in community composition. Altered composition may result from changes in the competitive interactions within microbial communities (Koide et al. 2005). Depending on their competitive abilities, the relative abundances of enzyme producers may increase or decline as the soil environment changes. Although an exhaustive review of enzyme responses to global environmental change is beyond the scope of this chapter, we describe several examples of how enzyme allocation theory can be used to understand ecosystem responses to environmental change.

12.5.2.1 Increase in Atmospheric CO_2

Increasing concentrations of atmospheric CO_2 can alter the microbial production of soil extracellular enzymes through changes in belowground C availability and quality. Elevated CO_2 often stimulates the production of C-rich exudates from plant roots, which increases microbial demand for other elements (Hungate et al. 1997; Hamilton and Frank 2001). In tussock tundra, CO_2 fumigation increased soil phosphatase activity, presumably because plants and microbes were mitigating P deficiency (Moorhead and Linkins 1997). A similar trend has also been observed for N-degrading enzymes at a FACE site in Rhinelander, Wisconsin (Larson et al. 2002). Although the evidence is still somewhat equivocal, there may be changes in plant litter quality under elevated CO_2 that influence substrate availability for C-degrading enzymes (Franck et al. 1997). For example, increasing cellulose concentrations could stimulate cellulase production during litter decomposition if sufficient nutrients are available for enzyme production (Allison and Vitousek 2005).

One important consequence of microbial allocation to nutrient-releasing enzymes under elevated CO_2 is increased mining of nutrients from soil organic sources. Such a response could contribute to enhanced C sequestration if plants gain access to the released nutrients in order to support biomass growth. This mechanism would help alleviate progressive N limitation, which has been hypothesized to constrain plant C sequestration under elevated CO_2 (Johnson 2006). Alternatively, enhanced microbial growth as a result of nutrient-releasing enzyme activity could increase decomposition rates and offset additional C storage. Increased microbial allocation to C-degrading enzymes would have a similar effect; even as greater quantities of litter C enter the soil under elevated CO_2, enzyme-catalyzed decomposition could increase proportionately (Chung et al. 2007; Drissner et al. 2007).

12.5.2.2 Increases in N Deposition

Because extracellular enzymes are N rich and many ecosystems are N limited (at least in terms of plant communities) (Vitousek and Howarth 1991; LeBauer and Treseder 2008), N deposition often has strong impacts on enzyme activity. Based on allocation theory, greater N availability should increase microbial and plant demand for other elements such as C and P. The activities of cellulose-degrading enzymes increase with N addition in deciduous forests (Waldrop et al. 2004a; Sinsabaugh et al. 2005), tallgrass prairies (Ajwa et al. 1999), and California annual grasslands (Henry et al. 2005). N fertilization also increases soil phosphatase activity in grasslands (Ajwa et al. 1999; Phoenix et al. 2004; Henry et al. 2005; Chung et al. 2007), heathlands (Johnson et al. 1998), tropical forests (Olander and Vitousek 2000), and deciduous forests (Saiya-Cork et al. 2002). Furthermore, N fixation by plants has been shown to increase soil phosphatase activity (Zou et al. 1995; Allison et al. 2006). N addition to soil may also inhibit the production of phenol oxidase and peroxidase activities by soil fungi (Fog 1988; Carreiro et al. 2000; Saiya-Cork et al. 2002; Waldrop et al. 2004a). This response is consistent with culture studies, suggesting that oxidative enzymes are typically produced under N limitation and may aid in the acquisition of N from complex polymers such as lignin and humic substances (Fog 1988).

Reallocation of microbial and plant resources under N deposition has strong implications for C and nutrient cycling in ecosystems. Stimulation of cellulase activity can lead to faster decomposition of cellulose-rich litter, whereas inhibition of oxidative enzyme activity may slow the decomposition rate of more recalcitrant litter and soil organic material (Carreiro et al. 2000). Thus, the enzyme-mediated effect of N deposition on soil C cycling depends on the chemical quality of the litter and soil organic matter in a given ecosystem (Carreiro et al. 2000; Neff et al. 2002; Waldrop et al. 2004b). Given that added N may cause secondary P limitation and often increases soil phosphatase activity, enzymes may also contribute to faster rates of P cycling under increased N availability. This pattern may have occurred following invasion of native, nutrient poor Hawaiian ecosystems by the N-fixing tree *Falcataria moluccana* (Allison et al. 2006). The invasion disproportionately stimulated soil phosphatase activities, and P cycling through the ecosystem increased almost as dramatically as N cycling (Hughes and Denslow 2005). In contrast, the degradation of complex organic N probably declines in soil following N addition, as the activities of N-releasing extracellular enzymes decline. N fertilizer suppression of protein- and chitin-degrading enzymes has been observed across a range of ecosystems (Olander and Vitousek 2000; Allison et al. 2008), suggesting that depolymerization of organic N may decline despite increases in N mineralization and the cycling of available N forms.

12.5.2.3 Changes in Temperature and Moisture

There are several mechanisms by which changes in climate could directly or indirectly affect enzyme allocation. One indirect effect could occur through increasing soil temperature, which could result in higher rates of nutrient mineralization (Rustad et al. 2001). Under these conditions, microbes and plant roots may decrease their allocation to nutrient-acquiring enzymes as nutrients become more available. However, this effect could be offset by higher metabolic and growth rates under warmer conditions that could increase rates of constitutive enzyme production.

Changes in soil moisture may impact extracellular enzyme allocation more directly due to alteration of diffusion rates. As soils become drier, the volume of water available to dissolve enzymes and substrates declines and the effective concentrations of these constituents increase. Depending on the initial concentration of substrate and the original diffusion rate of the enzyme, such changes could increase or decrease the return on enzyme investment. Where substrate is not limiting near the enzyme producer, a reduced effective diffusion rate could localize more of the reaction products near the producer for uptake, thereby increasing growth rates. However, if substrate concentrations are low near the producer, then restricting diffusion would reduce enzyme access to more distant substrates (Fig. 12.3). Whether changes in diffusion rates would alter allocation among different enzymes would depend on the relative availabilities of different substrates. It is possible that changes in soil moisture would have similar effects on all enzymes, leaving relative allocation among them unchanged and simply favoring or disfavoring enzyme production relative to other strategies.

12.6 Conclusions

Empirical evidence and existing models support the idea that microbes and plant roots produce soil enzymes according to principles of resource supply and demand. Like the related field of ecological stoichiometry (Elser 2006), these principles are valuable because they link evolutionary theory and ecosystem ecology – the mechanisms that determine resource allocation at the organismal level also scale up to regulate fluxes of elements and energy at the ecosystem level. The stoichiometry of cellular biomass is the major determinant of resource demand, and extracellular enzyme production represents a strategy for acquiring resources to match that demand. There is also good evidence that enzyme producers maximize the benefits of enzyme production while minimizing the costs. Cost reductions can be achieved through regulatory mechanisms, while the benefits can be increased by manipulating enzyme diffusion and suppressing competition for enzyme reaction products. Allocation strategies for soil enzyme production may also help predict ecosystem responses to environmental change. Perturbations to soil resource availability (e.g., N addition, elevated CO_2) cause enzyme producers to shift their allocation patterns and thereby alter rates of C and nutrient cycling. Thus, resource

allocation theory based on evolutionary and economic principles can improve our ability to predict ecosystem feedbacks to environmental change.

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