

CHAPTER **8**

The Rhizosphere and Soil Formation

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There are not many differences in mental habit more significant than that between thinking in discrete, well defined class concepts and that of thinking in terms of continuity, of infinitely delicate shading of everything into something else, of the overlapping of essences, so that the whole notion of species comes to seem an artifact of thought, not truly applicable to fluency, the so to say universal overlapping of the real world.

A.O. Lovejoy (1936)

8.1 INTRODUCTION

By most accounts, the rhizosphere is narrowly conceived in space and time. Since first described by Hiltner (1904), the rhizosphere is taken as the soil volume that interacts directly and immediately with living plant roots, the near-root environment nanometers to centimeters in radial distance from the root surface. As intimate interface between roots and the mineral world, rhizospheres are remarkable environments, and have ecological feedbacks, chemical interactions, and inter-organism communication as complex as any in the above-ground world. There are excellent reasons that the rhizosphere concept has been narrowly focused in its first 100 years of use, and that it is distinguished from the bulk soil, that is the soil not in direct and immediate interaction with active roots.

Yet, over pedogenic time, all of the soil's A and B horizons are greatly influenced by plant roots. In fact, this chapter is written to advance the idea that rhizospheres typically affect, even transform, a large soil environment, that

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is all of the so-called “bulk soil.” Although not often appreciated, rhizosphere processes stimulate mineral weathering and direct the ultimate formation of soils. While the narrow definition of the rhizosphere has helped emphasize that actively growing roots create unique and special environments with great consequence for plants and microbes, the rhizosphere also has a wide range of significant effects on soil formation and biogeochemistry. The rhizosphere is the critical interface between biota and geologic environment, the locale where roots exert intense physical pressures on surrounding soils, the chemical environment where biogeochemical reactions interact with minerals, and the special habitat for a wide assemblage of well-adapted microbes (see Chapters 1, 3, and 4). Rhizospheres are thus fundamentally important to soil formation, including the formation of the earth’s most extremely weathered soils the Ultisols and Oxisols (Richter and Babbar 1991).

This chapter examines rhizospheres and some of their broad biological, physical, and chemical effects on soil formation. In organization, the chapter opens with a discussion of general concepts: of the rhizosphere vs bulk soil dichotomy, of rhizospheres as microsites within soil profiles, and of soil formation including the formation of advanced weathering-stage soils. Subsequently, we evaluate a number of the physical and chemical effects of rooting on the soil. Throughout, the biota’s physical and chemical interactions with soils are seen to be concentrated in the rhizosphere, and over time these interactions transform soils across a wide range of spatial scales, from individual mineral grains to entire soil horizons and profiles. We conclude that rhizosphere processes are instrumental to soil formation including even the earth’s most advanced weathering-stage soils. Throughout this chapter we use data from our long-studied research ecosystem at the Calhoun Experimental Forest in the South Carolina Piedmont and the Duke University Forest (Richter and Markewitz 2001) to support our perspectives of the rhizosphere.

8.2 A REVIEW OF CONCEPTS

RHIZOSPHERE VS BULK SOIL

Plant roots, that is rhizospheres, are networks within the bulk soil, biological hotspots where respiration, gas exchange, nutrient and moisture use, and localized supplies of organic matter are most concentrated (Curl and Truelove 1986). In contrast, the bulk soil is a more oligotrophic environment, especially with respect to supply of root-derived organic matter. More than anything, reactive organic reductants and microbial activity are concentrated near roots compared with the soil as a whole.

By convention (and as an example of Lovejoy's (1936) class concept), the rhizosphere has been characterized as having three components (Clark 1949):

1. *rhizoplane*, the immediate surface of the root,
2. *rhizosphere*, the soil volume surrounding the rhizoplane that is immediately affected by root activity, and
3. *bulk soil*, the soil not directly affected by living roots.

This tripartite construct helps emphasize the special nature of the rhizosphere, but we suggest that it overemphasizes a dichotomy between the rhizosphere and bulk soils. Although the concept of rhizosphere has hardly been monolithic (e.g., Rovira and Davey 1974), a neat division of rhizosphere and bulk soil is difficult to align with our developing understanding of root systems and their effects on soil. High-powered microscopy (e.g., scanning electron microscopy) demonstrates that the rhizoplane is far from a planer surface, and a variety of investigations indicate that the radial influence of the rhizosphere is very ill-defined and that it ranges widely in spatial scale (e.g., Rovira and Davey 1974). Root systems are symbiotic systems in which cells of plants, fungi, and bacteria are intimately associated, both structurally and functionally, so much so that it is difficult to isolate what is plant from what is microbe. The fact that fungi and bacteria colonize root tissues in "endorhizospheres" suggests that concepts of continuity rather than those of class may be in order for how we think of rhizospheres and soil. In place of class concepts of rhizoplane, rhizosphere, and bulk soil, a continuum seems much more pertinent between the following:

- *root-microbe system*, which includes all cells of plant roots, mycorrhizal fungi, and closely associated non-mycorrhizal fungi and bacteria;
- *rhizosphere surrounding these cells*, a volume which is immediately affected by the functioning of the root-microbe system and depends on chemical reaction, chemical element, microorganism, and soil type; and
- *bulk soil*, the soil not immediately affected by the active functioning of roots, but which may be transformed by rhizospheres over pedogenic time.

Much rhizosphere research, however, including our own, relies heavily on a dichotomous contrast of characteristics or processes of the rhizosphere with those of the bulk soil. Whether the variable of interest is microorganism numbers, organic compounds, biological or chemical reactions, or communication-signaling, "rhizosphere effects" are frequently indexed by R/S ratios, that is the ratio of an attribute in the rhizosphere to that in bulk soil (Katznelson 1946). For many soils, R/S ratios for microorganism numbers range from 5 to 20 to

TABLE 8.1 Chemistry and Microbial Properties of Bulk Soil (Conventional 6 cm dia Core Samples) in Four Soil Horizons, and in Rhizospheres (<2 mm Distance from Roots) Sampled at 2–3 m Depth in the Pine-Forest Soil of the Calhoun Experimental Forest. Soil Microbial Data Courtesy of Dr Elaine Ingham, Oregon State University, Corvallis

Soil material	Soil depth (m)	Total carbon (%)	Total bacteria (cells g ⁻¹)	FDA*-active bacteria (cells g ⁻¹)	Total fungi (m g ⁻¹)	FDA-active fungi (m g ⁻¹)
Oe horizon	–	–	1.97 × 10 ⁸	32.9 × 10 ⁶	59160	906
A horizon	0–0.075	0.70	1.44 × 10 ⁸	23.8 × 10 ⁶	18140	653
BE horizon	0.6–1.0	0.24	1.59 × 10 ⁸	1.47 × 10 ⁶	294	5.5
B horizon	2.0–3.0	0.073	1.23 × 10 ⁸	0**	0**	0**
Rhizosphere soil in B	2.0–3.0	0.42	3.17 × 10 ⁸	3.54 × 10 ⁶	1467	65.8

* Fluorescein diacetate stain.

** Detectable concentrations for FDA-active bacteria, total fungi, and FDA-active fungi are < 4 × 10³ units g⁻¹, < 0.3 cm g⁻¹, < 0.3 cm g⁻¹, respectively.

even > 100 (Richter and Markewitz 2001; Anderson *et al.* 2002). Especially deep in the soil, active bacteria and fungi may be prolific in the rhizosphere but approach limits of detection in the surrounding soil (Table 8.1).

Approaches to the rhizosphere based on R/S ratios have been instructive in emphasizing the biological and chemical activity of the habitat of the near-root environment. Unfortunately, R/S ratios suggest a lack of interaction between the rhizosphere and the bulk soils. This is important as several rhizosphere processes significantly interact with bulk soils over pedogenic time.

By broadening perspectives of the rhizosphere, we by no means oppose traditional concepts of the rhizosphere, although we do wish to promote an appreciation for how biological, chemical, and physical activity near roots have profound effects on the whole soil, especially when integrated over pedogenic time. In fact, interactions between the rhizosphere and the whole soil make research on these issues some of the most exciting in all of soil science, biogeochemistry, and ecosystem ecology.

RHIZOSPHERES AS MICROSITES WITHIN SOIL PROFILES

Soil scientists and ecologists have long divided the soil profile into an upper “solum” and the lower “parent material,” in part due to the physical and chemical effects of rooting. The solum is taken to be the O, A, and B horizons, the parent material the C horizon. Rhizosphere densities are much higher in the A and B horizons, but in many soils rhizospheres extend well into the C horizon. The upper soil system – that is the O, A, and B horizons – is characterized

by intense biological activity, a variety of ecological processes, and extensive and thorough rooting (Table 8.1). Roots and associated microorganisms affect much of the physics and chemistry of the upper soil system (Chadwick *et al.* 1990; Brimhall *et al.* 1991; Richter and Markewitz 1995).

With increasing soil depth, concentrations typically diminish of roots, active microbes, organic matter, and bioavailable nutrients. In the soil's lower system, deep within B and throughout C horizons, the near-root environment is nothing less than an oasis of resources compared with the surrounding subsoil. In some respects, rhizospheres in the lower soil system have more in common with the A horizons than they do with the B and C horizons that surround them (Table 8.1). The R/S ratios for biologic and chemical properties may well increase with increasing soil depth (Figure 8.1), a pattern indicative

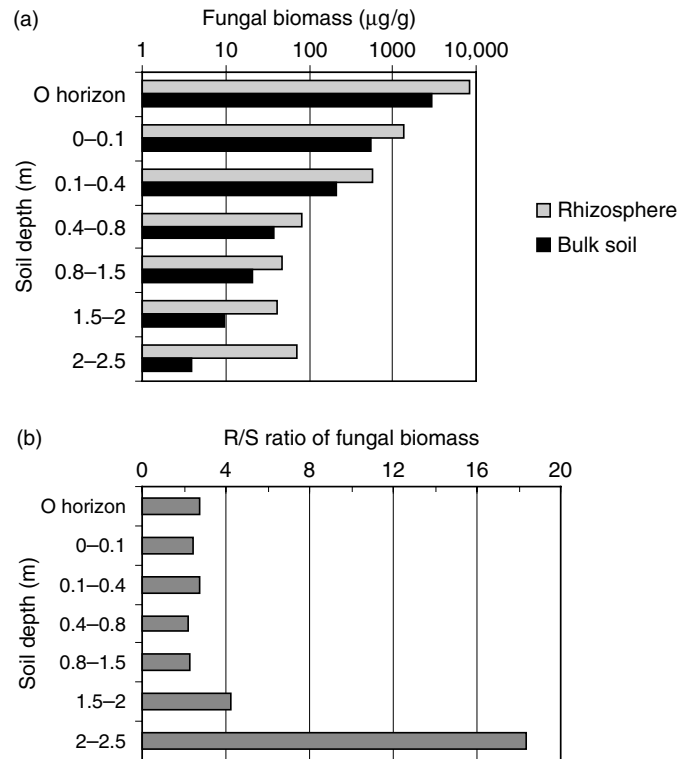


FIGURE 8.1 (a) Fungal biomass in bulk and rhizosphere soil at an Appling soil at the Calhoun Experimental Forest, South Carolina. (b) The conventional R/S ratio for fungal biomass as a function of soil depth. Soil supported a 47-year-old loblolly pine (*Pinus teada*) forest. Fungal hyphae in the rhizosphere soil are illustrated in Figure 8.3. Soil fungal data courtesy of Dr Elaine Ingham, Oregon State University, Corvallis.

of the functioning and structure of rhizospheres in lower soil horizons. For example, in our research site in South Carolina, fungal biomass in bulk soil decreases steadily by three orders of magnitude from the soil surface to 2.5 m depth, whereas fungal biomass in rhizospheres remains relatively constant between depths of 0.4 and 2.5 m.

SOIL FORMATION

Because soils are open thermodynamic systems, soils experience a remarkable set of transformations over time, as energy, chemical elements, and water are processed. Over time, primary minerals are weathered and lost. Although new secondary minerals may be formed during soil development, the soil's primary minerals are decomposed and its acid-neutralizing capacity gradually consumed. If the soil's landform is geomorphically stable, weathering of soils may proceed through a full sequence of weathering as illustrated by Jackson and Sherman (1953) in Table 8.2. Over pedogenic time, weathering consumes even large pools of primary minerals and advanced weathering-stage soils will be formed if hydrologic removals of solutes outpace renewals that can come from weatherable minerals or atmospheric deposition. Our interest in this chapter is in exploring how rhizospheres are involved in the advancement of weathering and soil formation, even including the formation of the earth's most weathered soils, the Ultisols and Oxisols (Richter and Babbar 1991).

TABLE 8.2 Soils are Open Thermodynamic Systems, and Over Time are Transformed, as Energy, Chemical Elements, and Water are Processed. Three General Weathering Stages of Soil Mineral Weathering were Used by Jackson and Sherman (1953) to Illustrate Soil Formation. The Implications of this System Change for Common Soil Minerals and Soil Orders is Illustrated in the Table. This Paper Illustrates the Fundamental Importance of Rhizospheres to the Weathering of Minerals and Formation of Soils

Attribute	Jackson-Sherman (1953) soil weathering stage and soil formation		
	Early	Intermediate	Advanced
Soil Taxonomy orders (Soil Survey Staff 1998)	Entisol Andisol	Inceptisol Mollisol Alfisol	Ultisol Oxisol
Common soil minerals	Gypsum Calcite Olivine Biotite Feldspar	Feldspar Muscovite Vermiculite Smectite	Kaolinite Gibbsite Fe oxide/hydroxides

In humid temperate zones and the tropics, geomorphically stable surfaces can develop enormously deep profiles, sometimes >20 m deep above unweathered bedrock. It is not uncommon that soil weathering exhausts all primary minerals and a number of chemical elements throughout these depths (Figure 8.2). Not atypical in advanced weathering-stage soils is an upper 1–3 m of O, A, and B horizons, below which is the C horizon of highly variable depth, all of which is acidic, extremely low in base cations and phosphorus, and depauperate in primary minerals. Since the original starting materials have been completely transformed by weathering, these soils are composed of only the most insoluble chemical elements and recalcitrant minerals. Only a few chemical elements, such as Zr and Ti, are insoluble enough to resist transportation from weathering environments. It is easy to underestimate the extreme state of weathering exhibited by such soils, and we suggest easy to underestimate the weathering as affected by rhizosphere processes.

Several calculations help emphasize the extreme state of weathering represented by such soils. In our long-term research site at the Calhoun Experimental Forest in the Piedmont of South Carolina, unweathered granite and gneiss underlies A, B, and C horizons in soil profiles that may total up to 25 m of unconsolidated material over actively weathering bedrock. The pH of ground samples of pulverized but unweathered bedrock is 7.9 in water, yet the pH of the soil sampled throughout at least the upper 8 m of A to C horizons

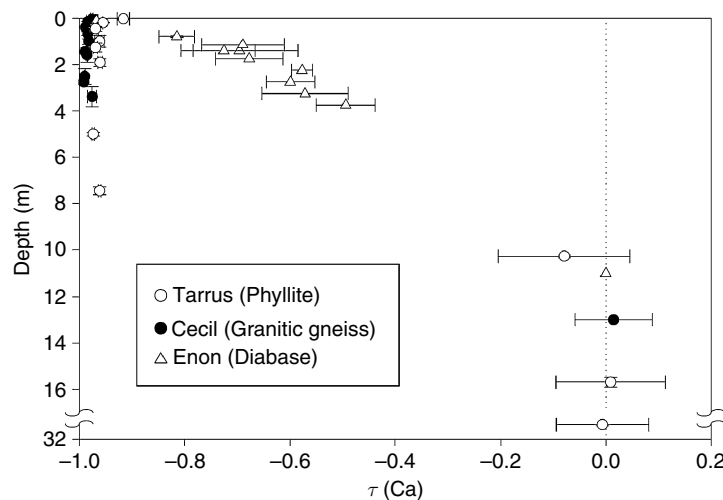


FIGURE 8.2 Calcium loss from three deep soil profiles (Tarrus and Cecil are Ultisols, Enon is an Alfisol). Tau expresses the estimate of the original Ca that has been lost during soil formation (e.g., -0.6 indicates that 60 percent of the Ca in the primary minerals has been lost to weathering).

ranges from 3.8 to 4.2 in 0.01 M CaCl₂. Exchangeable acidity (with 1 M KCl) totals about 4000 k molc ha⁻¹ in this 8 m soil profile, an enormous quantity of acidity. Even more impressive, however, is the quantity of acid that has been consumed during weathering of granitic-gneiss into the kaolinite-dominated Ultisol. Transforming granitic-gneiss into 1 m of kaolinite is estimated to require (i.e., to consume) on the order of 100,000 k molc ha⁻¹ of acid (Richter and Markewitz 1995, 2001). Weathering 10 m of granitic gneiss to kaolinite thus requires about 10⁶ k molc ha⁻¹. This extreme acidification raises questions about the sources and rates of acid inputs that have so thoroughly weathered these Ultisols, much less advanced weathering-stage soils overall. In the next section of our chapter, we examine how the rhizosphere is responsible for a considerable fraction of the weathering that over pedogenic time leads to such advanced weathering-stage soils.

8.3 RHIZOSPHERES: WHERE ECOSYSTEMS CONCENTRATE BIOLOGICAL INTERACTIONS WITH SOIL MINERALS

The extreme acidification and weathering state of Ultisols and Oxisols raise questions about the mechanisms by which these soils are transformed over time. Since rooting affects both physical and chemical weathering in soils and rocks, in this section, we examine some mechanical effects of rooting on the soil environment, and subsequently examine prominent sources of rhizosphere acidity that stimulate weathering and soil formation.

THE PHYSICAL ATTACK

Growing roots and their mycorrhizal hyphae follow pores and channels that are generally not less than their own diameters (Figure 8.3). As tree roots grow, they expand in volume radially, and exert enormous pressures on the surrounding soil by cylindrical expansion. Even relatively consolidated, unweathered rocks are susceptible to physical effects of roots. Rock wedging results when growing roots expand rocks' planes of weakness in joints or fractures. Over generations of trees, root growth and tree uprooting facilitate mechanical weathering of minerals in A and B horizons, accelerating chemical weathering by increasing minerals' surface area that is contacted by microbes, organic compounds, electrons, and protons.

The pressure of growing roots can be so great that roots can fracture and decompose minerals by exerting pressures on individual mineral grains or whole soils, that is across spatial scales that range from sub-micrometers to

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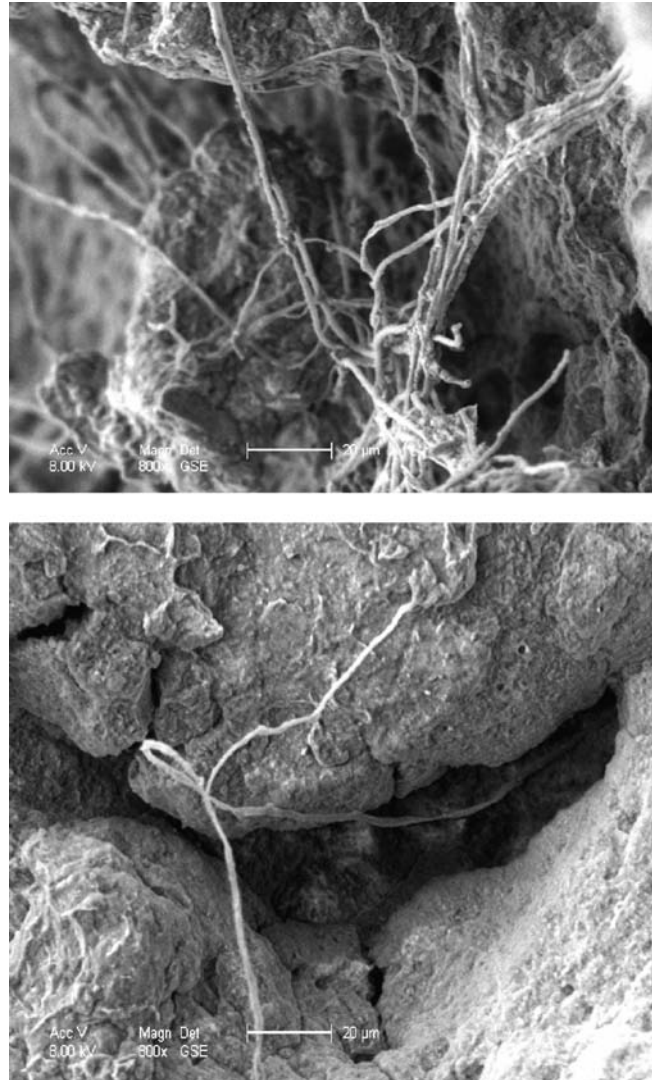


FIGURE 8.3 ESEM images (8.0 kV, 20 μm on horizontal scale) of rhizospheres at 1.5 m depth in Appling soil B horizon at the Calhoun Experimental Forest, SC. Rhizospheres are of basidiomycete hyphae of the genus, *Rhizopogon*.

many decimeters and even meters (Dexter 1987; Misra *et al.* 1987; April and Keller 1990; Richter *et al.* submitted).

In A horizons, growing roots can displace soil upward. Surrounding the root collars of large trees, for example, surface soils are uplifted considerably

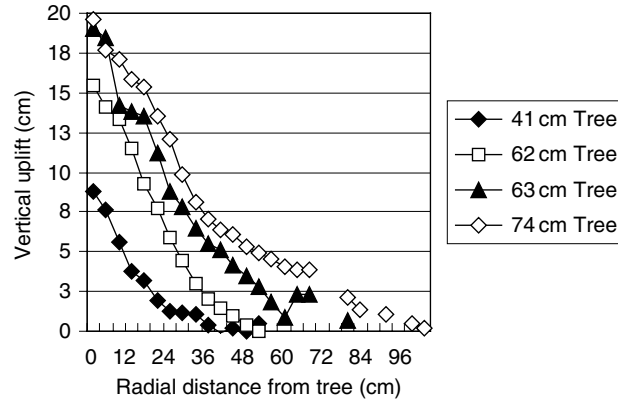


FIGURE 8.4 Soil microtopography surrounding four 70-year-old loblolly pine (*Pinus taeda*) trees in the Duke Forest, North Carolina. Diameters are given for each of the four trees.

in the surrounding rhizosphere (Figure 8.4). Over time, the uprooting of trees especially during windstorms causes particle abrasion and mixing of the upper soil system, increasing the soil's surface area that is subject to chemical weathering.

In contrast to A horizons, root growth pressures cannot be relieved by upward displacement in B and C horizons. Pressures of growing roots are relieved by soil consolidation, as taproots establish anchorage by expanding radially in a process that has severe physical effects on individual soil particles, soil structure, and overall soil architecture. In the Duke Forest, bulk densities of B horizons adjacent to tap roots of 70-year-old trees exceeded 1.9 mg m^{-3} , a consequence of tap roots consolidating soil for up to 50 cm radial distance from the growing root (Figure 8.5). These rhizosphere effects no doubt cause severe abrasion and disintegration of individual soil particles, reduced porosity, hydraulic conductivity, and aeration, and greatly altered biogeochemical functioning. Such effects accumulate over time and may represent a significant, understudied process affecting biogeochemistry of forests. Such mechanical processes have impacted forested Ultisols and Oxisols on numerous occasions, given these soils' relatively great age.

THE CHEMICAL ATTACK

Rhizospheres not only physically alter soil minerals from individual grains to whole horizons, they chemically interact with soils at a wide range of spatial scales as well. Here, we focus on four rhizosphere processes that affect soil

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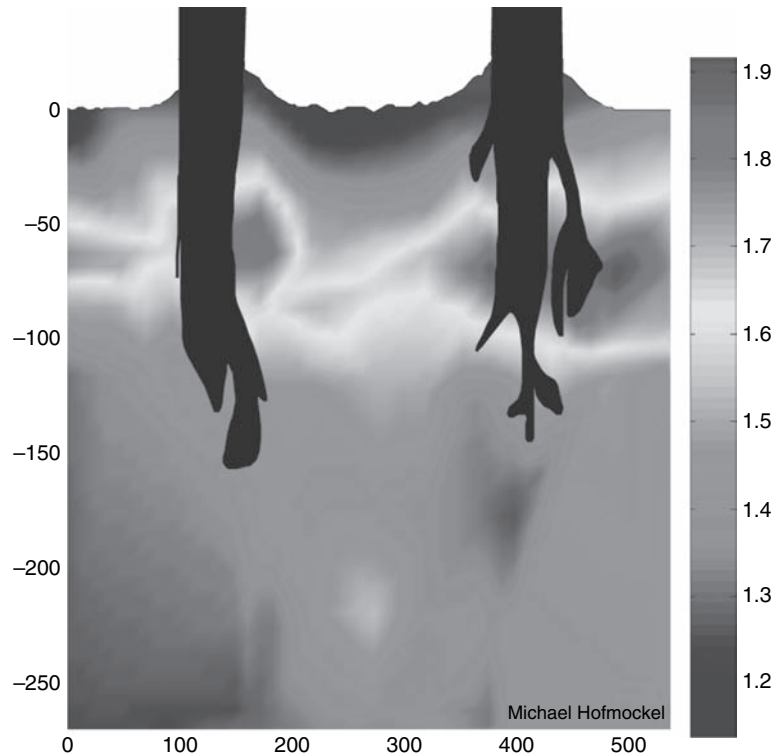


FIGURE 8.5 Bulk density of soil surrounding two 70-year-old loblolly pine trees. Bulk density in g/cm^3 (scaled in color in key to right of figure). Depth and horizontal distances are in cm (on y - and x -axis respectively). Bulk densities were obtained with conventional slide hammer for 180 samples on the face of the excavation. Isolines of densities were obtained using Matlab's interpolation via a shading function ("INTERP"). See Plate 2.

acidification and weathering, and thereby promote soil formation including that of advanced weathering-stage soils. The four rhizosphere processes that directly affect acid production include the following:

- Root nutrient-ion uptake;
- Organic acid production;
- Redox-reactions of metals;
- CO_2 production.

Remarkably, each of these sources of acidity result from the vegetative production and decomposition of photosynthetically derived organic matter. Although other biogenic acid systems can affect soil acidification and weathering dissolution (e.g., oxidation reactions involving nitrogen and sulfur), we

focus on these four as widespread sources of protons across a wide range of rhizospheres.

Root Uptake of Nutrient Ions

A major source of soil acidity is derived from the uptake of nutrients by vegetation. Root uptake of nutrient cations and anions directly affects the soil's acid-base status because the physiological process of nutrient-ion uptake is electroneutral: that is the uptake of cations and anions is balanced by the release of H^+ and OH^- , respectively, into the rhizosphere. If roots take up more nutrients as cations than anions, plant accumulation of nutrients acidifies soil. A large collection of scientific literature describes soil acidification by "excess cation uptake" in terrestrial ecosystems, including cultivated field crops, aggrading secondary forests, and old-growth forests (Pierre *et al.* 1970; Sollins *et al.* 1980; Ulrich 1980; Driscoll and Likens 1982; van Breemen *et al.* 1982; Binkley and Richter 1987; Johnson and Lindberg 1992; Markewitz *et al.* 1998).

Plant species exert differential effects on soil acidity due in part to plant-nutrient uptake requirements. Many oak and hickory species (*Quercus* and *Carya* spp.) have calcium uptake that is two- to fivefold greater than many pines (*Pinus* spp.), and thus have much more potential to promote acidity throughout the rooting zone. Alban (1982) demonstrated this with comparisons of acidity in soils that supported tree species with a wide range of cation uptake, and we hypothesize that such species differences are expressed most greatly in rhizospheres. Richter (1986) estimated H^+ budgets of five forest stands and illustrated a manyfold variation in cation uptake and potential for soil acidification.

Within the rhizosphere, very low pH has been measured with plant systems having large net cation uptake (Lynch 1990). As much as two pH-unit depressions have been measured in rhizospheres compared with bulk soil, conditions that will affect not only cation exchange in the rhizosphere, but dissolution of weatherable minerals as well (April and Keller 1990).

Organic Acid Production

Organic acids play significant and varied roles in rhizosphere acidification and mineral weathering, contributing protons and serving as ligands that complex metals (Boyle and Voigt 1973; Duchaufour 1982; Brimhall *et al.* 1991; Qualls and Haines 1991; Buol *et al.* 1997). Organic acids can also promote redox reactions with electron-deficient metals (a rhizosphere-promoted process considered in the next section on redox cycling). A wide variety of organic compounds have acid functional groups, mainly carboxylic or phenolic, and these originate not only from products of decomposition and carbon oxidation

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but also as exudates from plant roots and associated microbes (Lapeyrie *et al.* 1987; Herbert and Bertsch 1995). Organic acids range widely in molecular weight from relatively small compounds such as oxalic and citric acids to much larger humic compounds with enormous numbers of carboxylic and phenolic functional groups.

Organic acids are weak acids with pKa values that range widely from as low as 3 (carboxylic) to as high as 9 (phenolic). Many carboxylic functional groups have a relatively low pKa, with oxalic, citric, malic, and formic acids, as representative low-molecular weight organic acids (Fox and Comerford 1990), all possessing pKa < 4.0. Such acids readily contribute protons to the soil system under a wide range of pH conditions. In addition to being a source of protons, many organic acids are effective ligands that complex metal cations such as Al and Fe, greatly facilitating mineral dissolution and metal translocation within soils, thereby enhancing weathering processes.

In general, organic acids are typically highest in concentration in O horizons and decrease sharply with depth into the mineral soil (Fox and Comerford 1990; Herbert and Bertsch 1995; Richter and Markewitz 1995b). For example, in our Calhoun Experimental Forest, collections of soil water from lysimeters in soil profiles that support pine forests have soluble organic acids that decrease from about 115 $\mu\text{molc/L}$ in water that drains the O horizon to 73 $\mu\text{molc/L}$ in waters draining the A horizons, and are below detection at 60 cm and deeper (Markewitz *et al.* 1998). This decrease in organic concentrations with soil depth masks the significance of organic acids' effects on weathering in the lower soil system. Rhizospheres in lower soil systems develop in macropores, solution channels, and fracture zones and other planes of weakness (Herbert and Bertsch 1995), all of which as microenvironments that can experience relatively high concentrations of organic acids given the presence of active roots and associated microbiota.

Redox Cycling of Electron-Deficient Metals

Redox cycling in rhizospheres of relatively well-aerated soils is a little-studied process with considerable potential impact on soil acidity. The presence of oxygen in relatively well-aerated soils ensures a low level of chemically reactive electrons and a preponderance of metal ions in higher valence, electron-deficient oxidation states. Contrary to the bulk soil environment with generally abundant O₂, rhizospheres can be reducing environments due to the turnover of decomposable organic compounds that are regularly added by roots (e.g., see Chapter 2). Because oxygen is actively consumed in the rhizosphere due to microbial decomposition and root respiration, steep redox gradients can develop between the near-root environment and the surrounding soil. One

TABLE 8.3 Two Symbolic Representations of Reductive Dissolution and Oxidative Precipitation of Iron in Soils

Reductive dissolution	Oxidative precipitation
<i>Amorphous Fe(OH)₃</i>	
$\text{Fe(OH)}_{3(s)} + \frac{1}{4}\text{CH}_2\text{O} + 2\text{H}^+ \rightarrow$	$\text{Fe}^{2+} + \frac{1}{4}\text{O}_2 + 2\frac{1}{2}\text{H}_2\text{O} \rightarrow$
$\text{Fe}^{2+} + \frac{1}{4}\text{CO}_2 + 2\frac{3}{4}\text{H}_2\text{O}$	$\text{Fe(OH)}_{3(s)} + 2\text{H}^+$
<i>Goethite (FeOOH)</i>	
$\text{FeOOH}_{(s)} + \frac{1}{4}\text{CH}_2\text{O} + 2\text{H}^+ \rightarrow$	$\text{Fe}^{2+} + \frac{1}{4}\text{O}_2 + 1\frac{1}{2}\text{H}_2\text{O} \rightarrow$
$\text{Fe}^{2+} + \frac{1}{4}\text{CO}_2 + 1\frac{3}{4}\text{H}_2\text{O}$	$\text{FeOOH}_{(s)} + 2\text{H}^+$

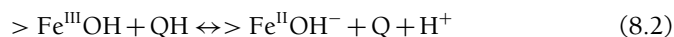
visible outcome can be rhizosphere-induced mottling: that is where rhizospheres reduce Fe, potentially mobilizing Fe^{II} to more oxidized zones nearby. The consequences for the soil's acid budget are hypothetically enormous: approximately two moles of H⁺ are produced or consumed for every mole of Fe oxidized or reduced, respectively (Table 8.3).

Such redox reactions have fascinating correlates in anaerobic soils subject to regularly high-water tables (e.g., Brinkman 1970; van Breemen 1988; Van Ranst and De Coninck 2002). In regularly anaerobic soils, roots are often the main local sources of oxygen, as many wetland plants transport O₂ to their roots to keep them alive and active. As a consequence, iron-oxidizing bacteria precipitate Fe plaque as oxidized coatings on root surfaces (Emerson *et al.* 1999; Weiss *et al.* 2003, 2004). In seasonally waterlogged soils such as paddies and other wetlands, redox cycles of reductive dissolution and oxidative precipitation are separated in time: during wet seasons and high-water tables, Fe^{III} is reduced and acidity consumed; during dry seasons, Fe²⁺ is oxidized and acidity produced. Brinkman (1970) described the consequences of these redox cycles on acidity and weathering of Pakistani wetlands and named this Fe-redox cycling "ferrolysis."

Few studies have considered how these redox processes of wetlands may be related to redox processes in generally well-aerated soils that typically experience high redox potential. Nonetheless, in relatively well-aerated soils, two processes facilitate rhizosphere-induced mottling: the ready supply of organic reductants from root and microbial activity, and the consumption of O₂ by respiration in the near-root environment. Both combine to reduce Fe^{III}: organic reductants can be adsorbed to oxide/hydroxide surfaces which facilitate Fe^{III} reduction in surface chemical reactions; if rapid rhizosphere respiration is accompanied by sluggish O₂ resupply, redox potential can potentially plummet. Under these conditions, Fe^{II} hypothetically enters a soluble phase and is transported out of the rhizosphere following a sequence of reactions outlined by Stone (1986): (1) initial adsorption and complex formation

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of organic reductant (QH_2) and oxide surface; (2) electron transfer; and (3) dissolution.



where the symbol > represents bonding to surface metals in the oxide lattice, and QH_2 , QH, and Q are hydroquinone reductant, semiquinone, and quinone, respectively. The impact of these reactions on Fe mobility is hard to overestimate. Reduction of Fe^{III} increases iron solubility with respect to oxide/hydroxide phases by as much as eight orders of magnitude (Stumm and Morgan 1996; Stumm and Sulzberger 1992).

Reductive dissolution of Fe^{III} consumes protons in the rhizosphere but upon translocation of Fe^{II} to adjacent but more oxidized microsites, Fe^{II} encounters soluble O_2 and is oxidatively precipitated. The oxidation is likely driven microbially and also produces protons which facilitate cation exchange and mineral weathering via surface chemical reactions in the bulk soil environment (Figure 8.6). Reaction kinetics of adsorbed Fe^{II} at $\text{pH} < 5$ is relatively rapid compared to aqueous Fe^{II} (Wherli 1990), and we hypothesize that oxidation of adsorbed Fe^{II} rapidly yields co-adsorbed H^+ , which protonate cation exchange and pH-dependent sites on oxides and stimulate mineral weathering. Thus, rhizosphere-induced mottling may affect great changes in acid–base status and

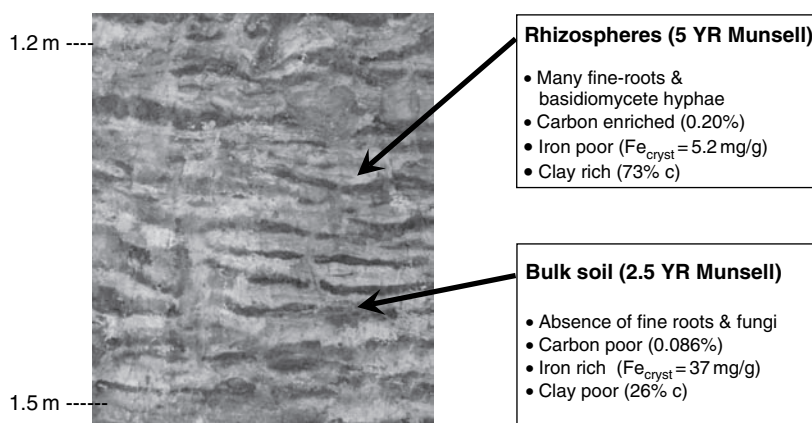


FIGURE 8.6 Pronounced rhizosphere-initiated redoximorphic features that demonstrate effects of Fe-redox cycling in B horizons at Calhoun Experimental Forest, SC. The close-up photo is of a soil excavation at 1.2–1.5 m depth. See Plate 3.

mineral weathering in soils due to steep redox gradients and spatial separation of microsites of relatively high and low redox potential.

The close correspondence of rhizospheres and soil redoximorphic features (Fimmen 2004) is observable in many soils, which supports a hypothesis that rhizosphere-stimulated Fe-redox cycling significantly controls soil acid-base reactions. In humid climates, all but the most well-drained soils experience at least temporary periods of saturation during which electron-deficient Fe and Mn oxides and hydroxides can function as electron acceptors in microbially mediated reactions. In the southern Piedmont of the southeastern North America, a region nearly 20 million hectares in area, more than half of the mapped soil series have official descriptions that indicate redoximorphic features in B horizons.

Estimates of rates of Fe cycling are not well quantified, although the significance of such redox reactions to soil acidification and mineral weathering can be readily demonstrated with chemical data from Ultisols at the Calhoun Experimental Forest. In this soil's B horizon, the total content of KCl-exchangeable acidity per 1 m of B horizon is on the order of $500 \text{ k molc ha}^{-1}$ and the BaCl_2 -TEA exchangeable acidity (buffered at pH 8.2) is about double or triple that, to as much as $1500 \text{ k molc ha}^{-1}$, again per 1 m of B horizon. We have previously estimated that to create 1 m of kaolinite-dominated B horizon at the Calhoun from the original bedrock of granite gneiss requires the consumption of about $100,000 \text{ k molc ha}^{-1}$ of acid-neutralizing capacity in granite-gneiss (Richter and Markewitz 2001). In other words, to create 1 m of kaolinitic B horizon requires $100,000 \text{ k molc ha}^{-1}$ of acidity to have reacted with and consumed the acid-neutralizing capacity of the parent geologic material. Remarkably, only about 0.5–1.5 percent of that acidity still resides on the B horizon's cation exchange sites. We can use these data to evaluate the significance of redox cycling of Fe by estimating the content of Fe^{III} that coats the surfaces of the kaolinite, quartz, and other particles in B horizons. Dithionite-citrate-bicarbonate extractions of the B horizon recover between about 25 and $200 \text{ cmolc kg}^{-1}$ of Fe which if taken to be Fe^{III} could represent $50\text{--}400 \text{ cmolc kg}^{-1}$ of H^+ generation equivalent to about $7500\text{--}60,000 \text{ k molc ha}^{-1}$ of the total $100,000 \text{ k molc ha}^{-1}$ that has reacted with the parent rock to form the kaolinite-dominated soil. Rhizosphere effects on redox cycling of Fe requires much greater study with regard to its impact on mineralogy, acidification, weathering, and soil formation. These calculations reinforce the importance of conceiving of the rhizosphere broadly in space and time.

Carbonic Acid System

Respiration is a central process of ecosystems, and organic-matter decomposition and plant-root respiration elevate belowground CO_2 greatly. Soil's

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elevated CO_2 stimulates carbonic acid weathering with mineral surfaces and thus significant cation exchange and weathering dissolution (Reuss and Johnson 1986; Amundson and Davidson 1990; Richter and Markewitz 1995b; Oh and Richter 2004). Carbonic acid weathering involves all three phases of the soil system: CO_2 in the gas phase, carbonic acid and associated ions in the liquid phase, and in the solid phase, protons and carbonates interact with cation exchange, mineral surfaces, and mineral structures. Since partial pressures of CO_2 typically increase with soil depth, B and C horizons are subject to the main brunt of the carbonic acid system's attack. Moreover, since rhizospheres are the main sources of CO_2 in the subsoil, we expect that carbonic acid weathering is most greatly elevated in subsoil rhizospheres. Sorensen (1997) illustrated that respiration depleted O_2 in the near-root environment, we can assume this pattern is coupled with a marked increase in CO_2 .

Since H_2CO_3^* (the sum of dissolved and hydrated CO_2) is a very weak acid with a $\text{pK}_{\text{a}1}$ of 6.36 (Stumm and Morgan 1996), the carbonic acid weathering system is widely conceived to be self-limiting in its effects on soil acidification and weathering (Reuss and Johnson 1986). However, H_2CO_3^* can be an effective acidifying agent even at relatively low pH, as pure H_2CO_3 (hydrated CO_2) is a much stronger acid than H_2CO_3^* , and has even been estimated to have a $\text{pK}_{\text{a}1}$ of about 3.8 at 25°C (Snoeyink and Jenkins 1980). The little appreciated, relatively strong acidity of H_2CO_3 may be a critical feature of the chemistry of soil carbonic acid, especially because CO_2 ranges commonly between 1 and 10 percent in bulk soil atmospheres. Elevated partial pressure of soil CO_2 ensures relatively high concentrations of H_2CO_3^* in solution and ensures that protons of even a small fraction of H_2CO_3^* will dissociate, despite low pH, due to the low $\text{pK}_{\text{a}1}$ of pure H_2CO_3 . Equilibrium calculations indicate that in situ pH is depressed from 5.65 (at atmospheric CO_2) to 4.9 and 4.4 in dilute soil waters at equilibrium with 1–10 percent CO_2 , respectively (Table 8.4), and that HCO_3^- will increase from 3 to 15 and $46\ \mu\text{molL}^{-1}$ in dilute soil water. These values are very close to what is measured by titration

TABLE 8.4 Solution pH of Low Ionic Strength Solutions in Equilibrium with CO_2 at Different Partial Pressures. The Soil Atmosphere at >1 m Depths of Many Soils Ranges up to 5–10 percent CO_2 , and in Atmospheres of Rhizospheres may Exceed 10 percent

CO_2 (%)	pH	HCO_3^- (mmolL^{-1})
0.036	5.65	0.0029
1.0	4.9	0.0145
5.0	4.6	0.036
10	4.4	0.046
100	3.9	0.145

in soil–water collections from 2 to 6 m depth in the extremely acid Ultisols of the Calhoun forest (Markewitz *et al.* 1998). Although CO₂ may rarely lower soil solution pH below 4.5 and will not rapidly mobilize much Al from soil profiles to stream and river waters (Reuss and Johnson 1986), elevated subsoil and rhizosphere CO₂ ensures that carbonic acid stimulates mineral dissolution and creates Al-saturated soils once weatherable minerals are consumed.

Two lines of evidence support this perspective of the potency of carbonic acid. A first line of evidence comes from laboratory studies (Oh and Richter 2004) in which solutions equilibrated with varying pressures of CO₂ were used to extensively leach soils that had a range of cation exchange capacities and weatherable minerals. Cation exchange was the dominant mechanism supplying cations to solution in these leaching studies which greatly diminished soil base saturation. Carbonic acid leaching displaced nearly all exchangeable base cations from two of three soils tested, and in one Ultisol, even 1 percent CO₂ displaced all exchangeable base cations and even elevated Al in soil solution.

Second, many Ultisols and Oxisols are underlain by deep saprolites or extremely acidic C horizons that represent soil conditions pushed to an extreme state of weathering (Richter and Markewitz 1995). Some of these geomorphically stable profiles are 10s of meters in depth. Given that most subsoil CO₂ originates from the rhizosphere respiration, rhizosphere processes must be recognized to affect enormous volumes of bulk soil. Of the acid-producing ecological processes that can potentially acidify such enormous volumes of C horizons, rhizosphere-initiated carbonic acid and Fe-redox cycling are likely the major candidates.

8.4 OVERVIEW OF THE RHIZOSPHERE'S WEATHERING ATTACK

Whether the perspective is one of mechanics or of chemistry, the rhizosphere represents a highly significant interface between biology and geology, an interfacial environment with broad consequences for earth's biogeochemistry and soil formation.

We started this chapter by noting that the scientific literature on the rhizosphere has historically been narrowly focused in space and time. While the focus of the rhizosphere as microsite has helped us understand how actively growing roots create special habitats for roots and microbes, rhizospheres also have much larger scale effects on soil formation and biogeochemistry.

We conclude with a summary for considering how rhizospheres drive much of the mechanical and chemical mineral weathering and the direction of soil formation. To describe this broad rhizosphere concept, we divide the soil profile into upper and lower soil systems (Brimhall *et al.* 1991;

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Richter *et al.* 1995b) because rhizosphere effects differ greatly as a function of soil depth:

- an upper soil system that includes the traditional *solum*, the O, A, E, and B horizons, and
- a lower soil system that mainly includes the C horizon or saprolite.

Over millennial time scales, the upper soil system is mechanically mixed by bioturbation, a mixing that is broadly rhizospheric affected. Root pressures abrade and shatter primary particles and secondary aggregates; root balls and root plates disturb soil horizons in tip-up mounds of wind-toppled trees. Below the B horizon, however, the C horizon is more sedentary due in part to less root penetration. The mechanical mixing and pressures of growing roots accelerates rhizosphere that are chemically derived.

The chemical attack of ecosystems on soil minerals is strongly mediated by rhizospheres. In upper soil systems, rhizospheres extensively affect acidity due to root uptake of nutrient ions; in the lower system such uptake effects are highly localized within rhizospheres. Rhizosphere production of organic acids is patterned similarly to that of nutrient uptake: broadly extensive in the upper system, more spatially explicit in the lower system. Organic acids, derived from rhizodeposition and from oxidative products of decomposition, weather minerals via proton-exchange reactions, by complexing metal cations such as Al and Fe, or by serving as electron sources for the redox-cycling of electron deficient metals.

In addition to organic acids, a variety of organic compounds are added to rhizospheres by roots and microbes, many of which can facilitate reduction of metals, especially Fe and Mn, which are mobilized out of the rhizosphere only to precipitate and oxidize on contact with soluble O₂. This redox-cycling phenomenon is likely further promoted by consumption of O₂ via rhizosphere respiration. Redox-cycling of Fe and Mn affects major fluxes of protons and given the spatial separation of reduced and oxidized microsites, such acid-base dynamics may exert strong control over mineral weathering and cation exchange throughout the soil profile.

Lastly, carbonic acid, which often increases with soil depth, is likely to be greatly elevated in rhizospheres as well, given that rhizospheres are microsites of concentrated root and microbial respiration. Carbonic acid is especially important in lower soil systems and concentration gradients of CO₂ are often steep from subsoil to the soil surface and from rhizospheres to the bulk soil itself. Recent evidence suggests that the potential for carbonic acid to weather minerals and acidify even already acidic soils cannot be underestimated.

In concert, a variety of rhizosphere processes alter mineral surfaces, attack mineral structures, and over time consume weatherable soil minerals, all

helping to direct soil formation. Chemical elements are released by the combined effects of mechanical and chemical weathering, taken up by plants and microbes to meet nutritional requirements, adsorbed to organo and mineral surfaces, recombined into secondary clay minerals, and leached to groundwaters, rivers, lakes, and eventually to the ocean. Over pedogenic time, on stable landforms, the ultimate soil products of such rhizosphere-assisted weathering are advanced weathering-stage soils, such as Ultisols and Oxisols. Few chemical elements are insoluble enough to resist transformations and transportation by weathering environments, due not in small part to the intense physical and chemical effects of the rhizosphere.

The concept of the rhizosphere has been significant to ecological, biological, agronomic, and forestry sciences in its first 100 years of its use. During its second century of use, the dynamics of rhizosphere response to environmental change will become a focus of intense study as the concept of rhizosphere as continuum is enriched by details of how rhizospheres interact with the whole soil profile.

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