

# 1 Soil Factors Affecting Nutrient Bioavailability

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## 1.1 Introduction

The soil supports plants, is the physical determinant of root growth and extent, and is the main reservoir for plant-available water and nutrients. Therefore, the soil controls the availability of most essential plant nutrients. It regulates availability by means of biophysiochemical processes, which are functions of soil and plant properties. This chapter introduces the concept of soil nutrient bioavailability, and the soil factors that regulate it. It summarizes the processes that control nutrient release and movement in the soil, and points out the importance of selected plant root characteristics in nutrient acquisition.

The soil–plant system’s capacity to supply/absorb nutrients is termed *soil nutrient bioavailability*, and is the ability of the soil–plant system to supply essential plant nutrients to a target plant, or plant association, during a specific period of time as a result of the processes controlling (1) the release of nutrients from their solid phase in the soil to their solution phase; (2) the movement of nutrients through the soil solution to the plant root–mycorrhizae; and (3) the absorption of nutrients by the plant root–mycorrhizal system (Comerford 1998).

Release of nutrients from the solid phase to the soil solution is controlled by the physiochemical processes of desorption and dissolution. It is also a biochemical process by way of mineralization. In both cases, soil and plant root–mycorrhizal characteristics help regulate the expression and dominance of these processes (Table 1.1). The movement of nutrients through the soil solution to the root–mycorrhizal surface is determined by mass flow and diffusion, which in turn are controlled by the interaction of soil and plant characteristics (Table 1.1). Finally, nutrient uptake at the root surface is dependent on the amount of root–mycorrhizal surface and its uptake characteristics.

The following discussion presents the three groups of processes outlined above. It concentrates on delimiting those soil characteristics important to defining nutrient bioavailability. Plant root growth, root function and nutri-

**Table 1.1.** Soil processes and the soil characteristics defining each process, along with a qualitative evaluation of the plant’s influence on the process

Soil process	Defining soil characteristic	Potential plant influence on process
Sorption	Temperature ( $T$ )	Low, shading
	$K_d$ of adsorption, pH	High, root exudates
	Solution ionic strength ( $\mu$ )	None to low
Desorption/ dissolution	$T$	Low, shading
	$K_d$ of desorption, pH	High, root exudates
	$\mu$	None to low
Mineralization/ immobilization	Volumetric water content ( $\theta$ )	High, transpiration
	$T$	High, shading
	Organic matter quality	High
	Enzyme concentration	High, phosphatase exudation
Mass flow	Hydraulic conductivity, $\theta$	High, transpiration effect on $\theta$
	Bulk density ( $\rho$ )	Low to medium, root action
	Pore-size distribution	Low to medium, root action
	Solution concentration ( $C_l$ )	Low to medium, root exudates
Diffusion	Impedance	High, transpiration effect on $\theta$ , root action on soil structure
	$K_d$	Low to medium, root exudates
	$\theta$	High, transpiration
	$\phi$ , pore-size distribution	Low to medium, root action
	$C_l$	Low to medium, root exudates

ent mineralization are covered in other chapters, so their treatment in this chapter will be confined to their influence on plant nutrient bioavailability, and their interactions with other components of the soil bioavailability system.

1.2 Release of Nutrients from the Soil Solid Phase

The key solid phase properties are (1) the quantity of labile nutrients, and (2) the manner of nutrient release to the soil solution. The term labile, in this context, is defined as nutrients in a plant-accessible form during a given time period. Maintenance of the soil solution’s nutrient concentration is a central concept of soil nutrient supply, and will be referred to repeatedly in this chapter. It is central because (1) the quantity of nutrients in solution is low relative to a plant’s demand and, therefore, must be replenished continuously; (2) practically all nutrient uptake occurs from the soil solution; and (3) nutrients must be in solution to move effectively to the plant’s root–mycorrhizal sur-

face, thereby giving the plant a larger soil volume from which it can extract nutrients. The solid phase maintains the soil solution nutrient concentration. Release from the solid phase to the soil solution occurs biochemically (mineralization and immobilization) or physiochemically (adsorption and desorption, and precipitation and dissolution).

Mineralization and immobilization are transformations of nutrients between their organic to inorganic forms. These transformations are functions of the soil temperature regime, soil aeration regime, soil water regime, and the quality of the organic matter from which the nutrient is mineralizing – because these factors control the population and activity of soil organisms (see Chap. 2, this Vol.). However, a subject that is not often considered is the comparative role that mineralization plays in regulating the soil solution concentration of N, P, and S. In extensively managed soil systems, mineralizable nutrients can be the dominant component of the ecosystem's total labile pool, particularly the N pool. However, contribution to the labile pool via mineralization is not necessarily the same as its regulatory influence on the soil solution concentration, especially when considering P and S. This question is crucial for conceptual modeling of the nutrient's soil solution concentration over time.

Reaction of nitrogen with the mineral–organic surface complex of soil is chemically distinct from that of P and S. When nitrate is the primary N species produced by mineralization, mineralization controls the soil solution's nitrate concentration. Since there is little to no sorption of nitrate onto the solid phase, this is the only option. However, ammonium, phosphate and sulfate can sorb to the soil mineral surface subsequent to mineralization. The greater the sorptive capacity of the soil, the greater should be the potential for the mineralized ion to be sorbed onto the mineral surface. Therefore, the role of mineralization should be to (1) control the soil solution concentration directly when the nutrient does not sorb onto the mineral soil, or (2) contribute to the soil solution concentration and to the nutrient concentration on the soil's mineral surface when the soil's sorption capacity is greater than zero. In the latter case, nutrient distribution between the solution and the mineral surface should be related to nutrient affinity for the mineral surface. While it can be shown that mycorrhizal hyphae can intercept mineralized P before other microorganisms, or before sorption to some clays (Joner and Jakobsen 1994), there is little relevant literature directly targeting this topic, even though the interaction between mineralization and sorption is an integral element of modeling bioavailability.

Adsorption–precipitation and desorption–dissolution reactions regulate the removal of nutrients from, or release into, the soil solution. Adsorption–desorption reactions are classified as either outer sphere or inner sphere (Soil Science Society of America 1996), which for the most part differentiates between cations (outer sphere) and anions (inner sphere), notably phosphate and sulfate. Anions participate in outer sphere reactions when the soil has a

positive charge. Except for specific circumstances, however, this does not add much to our understanding of their bioavailability.

An outer sphere reaction is an electronegative attraction of charged nutrients to the exchange complex of the soil surface. Cation exchange is the sorption process when cations are involved, and anion exchange is the process when anions are concerned. Outer sphere reactions are rapid, have comparatively weak bonding between the nutrient and the soil surface, and do not have kinetic limitations for equilibrium. An inner sphere reaction occurs when the solute becomes part of the soil mineral surface, such as during ligand exchange. In this case, the bond is covalent, can exhibit strong hysteresis between sorption and desorption, and is considered not to have kinetic limitations to equilibrium, unless the time frame is on the order of minutes to hours.

Both sorption (adsorption–precipitation) and desorption are key to nutrient cycling in soils. They help describe the fate of nutrients added by mineralization and fertilization, and their subsequent influence on the soil solution concentration. Numerous studies describe sorption, while fewer studies address desorption (Singh and Jones 1976; Peaslee and Phillips 1981; Colombo et al. 1994; McDowell and Condron 2001; Koopmans et al. 2004), and even fewer detail the effect that desorption has on the soil solution concentration (Brewster et al. 1975; Raven and Hosner 1994; Bhatti and Comerford 2002; Barros Filho et al. 2004). This is regrettable, given the importance of desorption in understanding bioavailability. The problem is further complicated by the consensus that sorption and desorption are hysteretic, particularly for inner sphere reactions. Clearly, better understandings of desorption and the hystereses between desorption and sorption are required (Barros Filho et al. 2004).

Recognizing that desorption is a key to bioavailability, how is desorption best described? Unlike kinetically dynamic mineralization, desorption is described as an equilibrium or quasi-equilibrium reaction through the use of desorption isotherms. Remembering that the soil solution concentration is a key component to defining a nutrient's bioavailability, the most useful soil property derived from isotherms is the partition coefficient ( $K_d$ ):

$$K_d = dC_s/dC_l \quad (1.1)$$

$C_s$  is the concentration of the labile nutrient on the solid phase, and  $C_l$  is the nutrient concentration in the soil solution.  $K_d$  is the rate of change of the labile nutrient on the solid phase with respect to the soil solution concentration, and is the first derivative of the adsorption or desorption isotherm. It describes the distribution of the labile form of the nutrient between the solid and solution phases, relates to the soil's ability to buffer a nutrient's solution concentration, and is key to describing a nutrient's ability to move in the soil solution (see below).

$K_d$  is a function of the quantity of nutrient on the sorption complex, the pool size of the sorption complex, and the affinity of the nutrient for the sorption complex. Barros Filho et al. (2004) showed that, for soils with similar clay mineralogy,  $K_d$  can be predicted from the amount of nutrient sorbed and the clay content. The sorption complex is the cation exchange complex for outer sphere reactions, and the anion sorption complex for inner sphere reactions. For outer sphere reactions,  $K_d$  depends on the makeup of the other exchangeable cations on that complex, while release from the inner sphere depends on having anions with a higher affinity for covalent bonding with the soil surface (Fox et al. 1990; Lan et al. 1995).

Determining the quantity of mineralizable organic N, P, and S is covered in Chapter 2 (this Vol.), but note that the estimate is dependent on the time frame chosen. The quantity of labile inorganic nutrients has historically not been measured directly, but indexed by standardized soil extractions using acidic or basic solutions. These often correlate well with response to fertilization, or growth over a continuum of nutrient deficiency to sufficiency, but do not measure the total pool of labile inorganic nutrients.

The difficulty in estimating the quantity of labile inorganic nutrients differs between outer and inner sphere ions. For outer sphere inorganic nutrients, the amount of exchangeable cations can be a good first-order estimate, particularly if (1) the time frame is not too long, or (2) clay mineralogy does not promote rapid movement of interlayer solutes to the exchange complex. For example, exchangeable potassium is a good estimate of total labile potassium, unless (1) the clay mineralogy of soil allows for the presence of significant non-exchangeable K (Guzel et al. 2001), or (2) root chemistry dissolves interlayer aluminum compounds, releasing potassium tied up or occluded with the interlayer aluminum (Comerford et al. 1990).

In contrast, labile inner sphere nutrients are difficult to measure, since their release can also be a function of root chemistry. One labile pool of inorganic P available to all plants is that removed by simple equilibrium exchange. All that is necessary to promote P desorption is its removal from solution by uptake or leaching. Unfortunately, this is not a large component of the bioavailable pool. Ligand exchange and congruent dissolution are two ways by which inorganic P is released to solution beyond simple equilibrium exchange, but these require the chemical action of plant roots (see below).

### 1.3 Nutrient Movement Through the Soil Solution

Nutrients move to roots through the solution phase. Movement occurs by mass flow or diffusion, or both. These processes are soil state-dependent (Table 1.1). Mass flow ( $Q_{MF}$ ) is defined as the quantity of nutrient flowing to the root system with the transpiration stream, or:



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