1.1 Phosphorous

Phosphorus exists in soils in organic and inorganic forms. Organic forms of P are found in humus and other organic material. Phosphorus in organic materials is released by a mineralization process involving soil organisms. Inorganic phosphorus which will be focused on in this study is negatively charged in soils. Almost all phosphorus is taken up by plants as either of two orthophosphate ions of $H_2PO_4^-$ and HPO_4^{2-}. Phosphorous is a major or even the prime limiting factor for plant growth (Hinsinger, 2001). After N, P is the second most frequently limiting macronutrient for plant growth. Phosphorus is a key element in many physiological and biochemical processes. It is an essential part of sugar phosphates; it is involved in respiration and energy transfer via adenosine triphosphate (ATP); and is a part of ribonucleic acid (RNA), deoxyribonucleic acid (DNA), and membrane phospholipids. Phosphorus is also involved in controlling key enzyme reactions and in the regulation of metabolic pathways (Theodorou and Plaxton, 1993). In addition, phosphorylation and dephosphorylation of proteins are crucial for signal-transduction pathways in plants (Raghothama and Karthikeyan, 2005).

1.2 Phosphorus availability in soil

Phosphorus (P) availability is one of the major constraints to plant growth. Phosphate in the soil solution P pool is immediately available but its amount is very small in comparison to the amount needed by plants and to the total P in soils. Although P ions can reach larger concentrations in highly fertilized soils, in many soils indeed, the P concentration in the soil solution is in the micro-molar range (between 0.1 and 10 μM). These are rather low compared with the adequate P concentrations for optimal plant growth (external P requirement) which can reach values of several *µ*M or tens of *µ*M for the most demanding crop species (Hinsinger, 2001). In addition, plants can suffer from P deficiency even though the total P content of the soil appears more than adequate. The reason for this apparent discrepancy is that the concentration of soluble P is often very low (<5 µmol L^{-1}) compared to the total amount of P bound to soil minerals and charged sites or fixed into organic forms that are inaccessible to plants. The availability of soil phosphorus for plant uptake is affected by its chemical availability, which is related to the concentration of inorganic phosphate in solution. Also soil physical factors are important in P availability, because they determine the rate of phosphate transport. In addition, plant properties play an important role in P acquisition from soil. Together, soil chemical, soil physical and plant factors affect the plant uptake of soil phosphorous.

1.2.1 Phosphorus chemical behaviors in soil

Phosphorus is affected by some chemical properties in soil. The effect of pH changes on P availability in soils and P uptake has been discussed by some researchers (Nye, 1981; Gahoonia et al., 1992; Thomson et al., 1993). However, for different soil constituents the relation between pH and P in soil is different; decreasing pH in alkaline soils causes increased P uptake by plant due to the dissolution of P minerals, whereas in acid soils an increase in pH increases P uptake because of desorbing P from metaloxids (Gahoonia et al., 1992). The pH effect on P availability is not target point in our study.

In many agricultural systems in which the application of P to the soil is necessary to ensure plant productivity, the recovery of applied P by crop plants in a growing season is very low, because in the soil more than 80% (Holford, 1997) or 90% (Mengel and Kirkby, 1982) of the P becomes immobile and unavailable for plant uptake because of adsorption, precipitation, or conversion to the organic form.

Due to the particular chemistry of P in soil it reacts readily with positively charged oxides of Fe or Al, and calcium (Ca) ions to form relatively insoluble substances. This fraction can be described as non-labile P (Mengel and Kirkby, 1982). Although the total amount of P in the soil may be high, it is often present in unavailable forms or in forms that are only available outside of the rhizosphere, where there is no root (Schachtman et al., 1998).

The availability of P to plants is limited, to a large extent, by the rate of the reactions that replenish the pool of soluble P (Ryan et al., 2001; Randall et al., 2001).

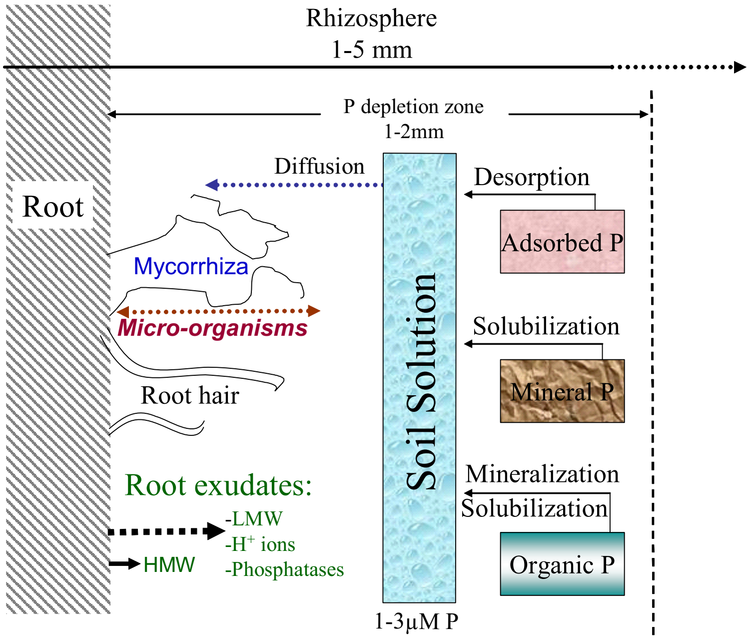

Figure 1: Diagram of processes affecting P availability in the rhizosphere (modified after Ae et al., 2001).

Figure 1 shows processes and factors related to P availability in the rhizosphere. Speciation, precipitation-dissolution and adsorption-desorption of P are the major factors and processes governing the mobility of P ions in soils that determine the bioavailability of inorganic P (Hinsinger, 2001). Different from orthophosphate ions, P can also occur as a range of negatively and positively charged or uncharged species in the soil solution, the distribution of which is much dependent on the pH and on the concentration of metal cations such as Ca, Fe and Al and organic and inorganic ligands. As most P species present in soil solution are negatively charged the major P sorbents are those soil constituents that bear positive charges. These comprise various variable charge compounds that contain hydroxyl (Fe and Al oxides), carboxyl (organic matter) or silanol (clays) groups; silanols are compounds containing silicon to which hydroxy substituents bond directly. The oxides are present not only in ferralsols from tropical regions that are known for their properties being largely influenced by Fe and Al oxides, but also in soils in the alkaline pH range such as calcareous soils (Samadi and Gilkes, 1998; Hinsinger, 2001). The precipitation–dissolution equilibria that govern the solubility of P minerals are under the direct dependence of the pH and the concentration of P and that of the considered metal cation. Phosphate ions readily precipitate with metal cations, forming a range of P minerals. Hence, in neutral to alkaline soils, P ions will rather precipitate as Ca phosphates: dicalcium or octacalcium phosphates, hydroxyapatite and eventually least soluble apatites. In contrast, under acidic conditions P ions will precipitate as Fe and Al phosphates such as strengite, vivianite, variscite and various minerals of the plumbogummite group (Lindsay et al., 1989; Hinsinger, 2001). Major processes that control solution P concentration in soils are adsorption onto and desorption from various soil constituents. Phosphate ions are bound on edges of clay mineral and, more importantly, on the surface of iron and aluminum oxides and hydroxides. The surface charge of metal (hydr)oxides depends on the pH and composition of the electrolyte solution. The sorption of phosphate on metal (hydr)oxides surface is done via non-specific adsorption (electrostatic) and/or specific adsorption (ligand exchange). Non-specifically bound ions, so-called ion pairs, are placed at the head end of the diffuse double layer. Specifically bound ions share ligands with the surface and approach the surface more closely than ion pairs (inner sphere complexes) (Geelhoed, 1998). Phosphorous uptake by plants was shown to be related to P sorption and to the amount of extractable Fe and AL in both acid and calcareous soils, indicating phosphate desorbed from metal (hydr)oxides is an important source of P for plant growth (Soils and Torrent, 1989a,b). Desorption of sorbed P will occur mostly via a ligand exchange reaction, which means that a decrease in the concentration of P ions in the soil solution and an increase in the concentration of competing anions will both shift the adsorption– desorption equilibrium towards enhanced desorption (Hinsinger, 2001).

1.2.2 *Phosphorus transport in soil*

The movement of nutrient from the soil toward the root is a result of interaction between plant roots and some physical factors in soil. Because of strong retention of P ions onto their solid constituents, the mobility of P in soil is low and only a marginal proportion of inorganic P is present as phosphate ions in the soil solution. Hence, physical factors in soil are important for transport toward the root particularly under low P conditions. Therefore, P transport in soil is one important factor to assess P availability in soil.

The total flux (the amount of ions or molecules crossing a unit area per unit of time) of P from soil to root is the sum of mass flow and diffusion. The major part of total P taken up by crop plants, about 95%, reaches the roots by diffusion. The principles of diffusion were established by Fick (1855). Fick's first law states that the flux by diffusion (F_D) is proportional to the concentration gradient ($\frac{\partial C}{\partial x}$ or $\frac{\Delta C}{\Delta x}$). With replacing the effective diffusion coefficient, D_e, Fick's first law can be shown as

$$F_D = -D_e \frac{\Delta C}{\Delta x} \qquad (1)$$

C is the concentration of ions per volume of soil that participate in diffusion. These include the ions in the soil solution plus those ions on the solid phase that may be released into the soil solution. According to Nye (1966) D_e is given by:

$$D_e = D_L \Theta f \frac{1}{b} \qquad (2)$$

Where, D_e is the effective diffusion coefficient, D_L is the diffusion coefficient in water, Θ is volumetric soil water content, f is impedance factor or tortuousity factor which indicates that the diffusion path of ions in soil is longer than the straight line between two points, b is soil buffer power which allows for the fact that not all ions but only the fraction of the ion in solution is actually diffusing (Jungk A, Claassen N. 1997). The volumetric soil water content, Θ, is expressed in volume of water per volume of soil. It can affect nutrient supply of plants. With increasing Θ effective diffusion coefficient and diffusion is increased; for example, effective P diffusion coefficient was increased by factor 25 within the range of Θ which may be found in a Luvisol (Bhadoria et al., 1991b). Understanding the diffusive transport of ions from soil to plant roots requires knowledge of the impedance or tortuosity factor**.** When ions diffuse in soil, the effective pathway is therefore longer than the straight line between two points; it is often defined by

$$f = \left(\frac{L}{L_e}\right)^2 \qquad (3)$$

Where L is the straight-line distance between two points, and L_e is the actual or effective distance of solute movement through the soil between the same two points. The buffer behavior is important for diffusion of nutrient ions in a soil and their mobility toward plants (Aharoni et al., 1991). The equilibrium between solution and solid phases causes at least part of ions bound to the solid phase to be released into the solution. With reestablishing the equilibrium, it can thus be said that the solution concentration of the ion is buffered. Soil buffer power is defined by

$$b = \frac{\Delta C}{\Delta C_L} \qquad (4)$$

C is the total amount of ion participating in diffusion, i.e., the ions in solution plus those bound to solid phase that can be released into ambient solution, and C_L is the concentration of the ion in soil solution.

As a result, the concentration of a nutrient in soil solution, the volume of soil that is filled with water, the geometry of soil pore system and the capacity of soil to retain ions are major physical factors in soil affecting diffusibility of ions in soil (Jungk and Claassen, 1997).

When the availability of nutrients such as P in the soil is low, uptake is limited by the transport rate of nutrient to the root (Nye and Tinker, 1977). With absorbing P by roots the concentration of P near the root surface is decreased and a depletion zone is created around the roots. The extension of the depletion zone can be estimated by equation (5):

$$\Delta x = \sqrt{\pi D_e t} \qquad (5)$$

Δx is the extension of the depletion zone which is the distance to the point on the curve where the concentration of diffusing P is decreased by 20% of the total decrease at the root surface (Jungk and Claassen, 1997). With decreasing P concentration near to the root, a P concentration gradient is established toward the roots. The concentration gradient of P in soil is increased either by (a) stronger decrease of the concentration at the root surface, (b) increase of the soil solution concentration or by both of them (Claassen, 1992).