1 General Introduction

1.1 Principal objective of the study

Phosphorus (P) is one of the main limiting nutrients in soils, hence phosphorus fertilization is a common practice with the objective to increase crop production. Concerns are being expressed that due to the limited P resources, lasting only a few more decades, lack of P fertilizers may become a serious problem in the future (Mucchal et al., 1996). Thus more detailed knowledge about long- and short-term P fluxes in soils and P availability to plants is desirable to optimize the use of this scarce resource. The present study therefore intended to contribute to the understanding of P dynamics in soils by studying the flow in and between various P fractions on the basis of long- and short-term plant growth experiments.

1.2 Phosphorus forms in soil

Phosphorus in soils occurs almost exclusively in the form of orthophosphate. The total content is in the range of 0.02 to 0.15% P. Quite a substantial amount of this P is associated with the soil organic matter and in mineral soils the proportion of organic P lies between 20 to 80% of the total-P. For most mineral soils, apatites are believed to be the primary phosphate containing minerals from which the other P containing soil P fractions are derived. In many soils, apatites are the most important inorganic phosphates of the non-labile pool. In addition some Fe and Al phosphates as well as the organic soil P apparently exchange phosphate ions only slowly and thus belong to the non-labile P fraction (Mengel and Kirkby, 1978). Desert soils (Aridisols) typically have low soil organic matter and high pH, and the primary geochemical reservoir of phosphorus is calcium carbonate minerals (Lindsay, 1979; Lajtha and Bloomer, 1988). Soils that dominate humid temperate and tropical regions (Ultisols and Oxisols) are highly weathered, acidic, and dominated by large quantities of sesquioxides. These soils easily adsorb and geochemically fix phosphorus, in many cases leading to phosphorus limitations (Johnson and Cole, 1980; Sanchez et al., 1982; Sollins et al., 1988). Parent material and climate determine the overall weathering rate, and these factors influence the balance between phosphorus loss and retention (Gardner, 1990). Walker and Syers (1976) suggest that the proportion of phosphorus in labile, non-labile, non-occluded, and occluded fractions should vary between soil taxa along a gradient of soil weathering intensity. In ecosystems with young, slightly weathered soils, most of the phosphorus should be found in primary minerals, such as hydroxyapatite. In ecosystems with a moderate weathering regime, most of the phosphorus should be found in organic compounds or adsorbed to secondary clay minerals. And, finally, in ecosystems with highly weathered soils, most of the phosphorus should be in non-labile, occluded, or stable organic forms.

1.3 Phosphorus fixation

When P fertilizers are applied to soils and are dissolved by soil water or are applied as liquid fertilizers, reactions occur among the phosphate, soil constituents, and the nonphosphatic fertilizer compounds which remove P from the solution phase and render the phosphate less soluble. This phenomenon is called P fixation or retention (Sample et al. 1980). Phosphorus ‘fixation’ is, as any sorption process, reversible, and in many weathered soils, Fe- and Al-phosphates are also a potential source of plant available P (Hughes 1982; Hughes and LeMare 1982). LeMare (1982) indicated that particularly organic matter-associated Fe and Al may be involved in the reversible sorption of P. One of the problems in assessing the reversibility of sorption is that sorbed P undergoes further transformations with time (Mattingly 1975, Parfitt et al., 1989). Such processes may involve recrystalisation (Barrow 1983), solid state diffusion (Willett et al. 1988), or multiple P pools which are not in immediate exchange with the solution (Fardeau and Jappe 1980) or which have differing affinities to P (Kanabo et al., 1978). A measurement of available inorganic P therefore needs to consider both the amounts and the rates of release of P from the solid phase.

1.4 Phosphorus transformation and availability in soils

Roots take up P from the soil solution, which is the immediate nutrient source for plants. While solution P constitutes only a minor fraction of total soil P, it is constantly replenished by the hydrolysis of labile inorganic P (P_i) or by mineralization of organic P (P_o). These fractions, in turn, are in exchange with more stable P compounds through slow reactions. Therefore, the P supply to vegetation depends on the quantities of labile P_i, the rate of transformations between labile and more stable P_i, and the size and rates of P transformation of the mineralisable P_o pool in the soil (Tiessen et al., 1984). Both geochemical and biological processes regulate the availability of P in soils. In most natural ecosystems, geochemical processes may also determine the long-term distribution of phosphorus in soils, but in the short-term, biological processes influence P distribution because most of the plant-available P is derived from soil organic matter (Ballard, 1980; Wood et al., 1984, Smeck, 1985; Tate and Salcedo, 1988; Walbridge, 1991; Walbridge et al., 1991). Walker and Syers (1976) suggest that the proportion of total-phosphorus held in various forms changes as soils develop. The weathering of primary minerals supplies phosphate to the plant-available pool in the soil. Bacteria, fungi, and higher plants incorporate phosphate into biomass, initiating the biological cycle. Decomposition and mineralization return inorganic P to the soil solution. Over time, both biological and geochemical processes transform inorganic phosphorus into stable forms of organic and inorganic phosphorus in soil (Tiessen et al., 1984; Sharpley et al., 1987).

1.5 Phosphorus fractions defined by the extractants

A potentially available P pool, analogous to the mineralisable N or S pools measured with incubation and leaching techniques (Ellert and Bettany, 1988) is not feasible, because of the reactivity of solution P with the soil mineral phase. The sequential extraction of Chan and Jackson (1957) attempted to separate chemically identifiable forms of Pi, but problems of reprecipitation of extracted P, and the similarity in the solubility of Fe and Al associated P limited its success (Williams et al. 1967; Williams and Walker 1969). A sequence of alkaline followed by acid extracts, which forms part of the Chang and Jackson scheme gives a reliable distinction between Al and Fe and Calcium-associated P_i (Kurmies, 1972).

In most unweathered soils P occurs predominantly in the form of apatites, calcium phosphates containing carbonate, fluoride, sulfate, hydroxide, and a number of different cations, or in primary minerals where P substitutes isomorphously for silicate in crystal structures. Weathering and leaching reduce total-P contents, and cause the formation of secondary Fe and Al phosphates with low solubilities. At the same time, the accumulation of organic matter in the soil as a result of the establishment of vegetation is accompanied by the formation of organic P (P_o) pools.

The Hedley fractionation procedure (Hedley et al., 1982) was based on these concepts and in their P fractionation, phosphate ions from the soil solution are removed by anion exchange resins and other forms of labile, non-labile, non-occluded, and occluded inorganic and organic phosphorus are removed sequentially with a series of successively stronger agents. The Hedley fractionation procedure has been used with some success in temperate (Hedley et al., 1982) and tropical (Tiessen et al., 1991; Araújo et al., 1993) soils to study the distribution and transformations of inorganic and organic P forms. Various interpretations for phosphorus fractions to plant availability suggested by different authors have been summarized by Cross and Schlesinger (1995). The terminology that relates to P found in soil extracts to plant availability has been interpreted in various ways in the literature. The interpretation of P fractions is based on an understanding of the action of the individual extractants, their sequence and their relationship to the chemical and biological properties of the soil (Tiessen and Moir, 1993).

According to Tiessen and Moir (1993), resin P is reasonably well defined as freely exchangeable P_i, since the resin extract does not chemically modify the soil solution. They also considered that bicarbonate extracts a P_i fraction which is likely to be plant available, since the chemical changes introduced are minor and somewhat representative of root action (respiration). This fraction is not comparable to the widely used available P test after Olsen (Olsen et al., 1954) because the resin-extractable pool has been removed at this point. Labile-P_o is easily mineralized and contributes to plant available P (Bowman and Cole 1978). More stable forms of P_o involved in the long-term transformations of P in soils are extracted with hydroxide (Batsula and Krivonosova, 1973). Hydroxide-extractable P_i has lower P availability (Marks, 1977) and is thought to be associated with amorphous and some crystalline Al and Fe phosphates. The dilute HCl-P_i is clearly defined as Ca-associated P, since Fe- or Al-associated P, that might remain unextracted after the NaOH extraction, is insoluble in acid. There was rarely any P_o in this extract. The hot concentrated HCl is a very stable residue P pool and P_o extracted at this step may simply come from particulate organic matter, but may be easily bio available. The residue-P is highly recalcitrant P_i. Cross and Schlesinger (1995) reported in their survey of literature regarding Hedley fractionation that in general, labile P is thought to be available to microbial and vegetation communities in the short term, because it rapidly desorbs from the surface of soil particles. Non-labile P fractions are thought to be tightly bound to soil particles, and unavailable to plants. The non-occluded phosphorus, including phosphorus that is extracted with NaOH, is considered to be biologically available only on a long-term basis.

1.6 General hypothesis and objectives of the study

Accumulated soil P in surface soils from long-term and continuous agricultural fertilization is a major source of soluble and particulate forms of P contained in runoff that is entering water resources and degrading water quality (Daniel et al., 1998). However, more information regarding long–term effects of different cropping systems and fertilization practices on inorganic and organic P depletion or accumulation in soil depending on specific conditions is still much in need. Because much of the total soil P is unavailable for immediate plant uptake, several attempts have been made to quantify the relative changes in soil organic and inorganic pools after long-term cultivation using sequential P fractionation procedure (e.g., Hedley et al. 1982; Tiessen at al., 1984; Beck and Sanchez, 1994). In sequential P fractionation procedure (Hedley et al., 1982), labile inorganic P (P_i) and organic P (P_o) forms are removed first, followed by more stable P forms removed with stronger agents. The relative distribution of soil inorganic and organic P pools may be influenced by initial soil characteristics as a result of soil type (Tiessen et al., 1984), climate, and management practices. The primary advantage of the Hedley fractionation scheme is that information can be obtained about short- and long-term P availability by quantifying various P fractions (including organic) of varying degrees of availability to plants.

Schmidt et al. (1996) indicated that inorganic P extracted in the resin, $NaHCO_3$, and NaOH fractions for two Ultisols from North Carolina, USA, and organic P in the NaOH fraction of one of these soils represented the biologically dynamic P.

Beck and Sanchez (1994) investigated soil inorganic and organic P pools in a highly weathered soil in Peru which had been cultivated for 18 years and found that the NaOH-extractable inorganic P pool acts as a sink for fertilizer P but that organic P pools were the primary source of plant–available P in the non-fertilized systems. They also found that crop yields were positively related to levels of available P measured by anion exchange resin and by NaOH-extractable organic P. NaOH-extractable organic P contains P associated with humic compounds and P adsorbed to Fe and Al oxides and, although it is more stable than bicarbonate extractable organic P, it can be an important P source when the amount of labile inorganic P is small (Buresh et al. 1997). Traditional methods of measuring plant-available P are inadequate for low-to no-input systems (Beck and Sanchez ,1994). Iron oxide paper is a sink like anion resin acting more or less analogous to the withdrawing behavior of a plant root. Iron oxide strip P and bicarbonate extracted P were highly correlated with plant P uptake in various studies (Bowman et al., 1978; Sharpley, 1991). Both Fe-strip P and the $NaHCO_3$-Pi in medium P sorption soils responded similarly to plant-available P removal (Guo et al., 2000).

Guo et al. (2000) have examined the changes in P fractions under exhaustive cropping with 14 crops on eight soils ranging in weathering from Vertisols and Molisols to Ultisols and Oxisols amended with $Ca(H_2PO_4)_2 \cdot H_2O$. They found that the Fe-impregnated strip and $NaHCO_3$-P_i decreased the most in response to plant P uptake in all soils. The NaOH-P_i also declined with plant P uptake in all soils. The HCl-P and residual P seemed to act as a buffer for strip-P and $NaHCO_3$-P_i in the slightly weathered soils whereas NaOH-P_i seemed to act as buffer for the same P fractions in the highly weathered soils. $NaHCO_3$-P_o and NaOH-P_o fractions were no significant contributors to available P in these soils that received high levels of inorganic P.

The plant species can actively improve their acquisition of P in several ways. Access to total soil P resources can be improved by increasing the absorbing area of the root system (Barber, 1995), through increased root length, decreased root diameter (Marschner, 1986) and increased association with micorrhizae (Joner and Jakobsen, 1995). Alternatively, plants can actively increase the availability of recalcitrant P resources by altering the chemistry and/or biochemistry of the rhizosphere. Plants can achieve this by altering pH and thus P solubility (Gahoonia et al., 1992b; Zoysa et al., 1998), exuding phosphatase which catalyses the mineralization of organic P (Helal, 1990; Helal and Dressler, 1989; Perez-Corona et al., 1996). For the purpose of this, the plant species can help sustain production in the tropical regions where the availability and use of mineral fertilizers is limited (Sanchez et al., 1997). Novais and Kamprath (1978) observed depletion of P from Al- and Fe-phosphate species in a green house study using soils that previously received heavy P fertilization.