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# Soil Phosphorus Tests and Transformation Analysis to Quantify Plant Availability: A Review

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## 1. Introduction

Phosphorus (P) is regarded as the most important soil nutrient after nitrogen (N) for plant growth and development as it plays key roles in plant metabolism, structure and energy transformation. It has also been recognized as a potential pollutant in waters (Anderson, 1980). The P dynamics in soils and cycling in agro-ecosystems are of increased interest due to its contribution to the current environmental, agronomic and economic issues (Sharpley and Tunney, 2000).

Soil P tests involve extraction of P from soils with chemical or ion-sink extractants followed by a quantification of P in the extracting solution. Soil test is expected to determine the amount of P that can contribute to crop growth or water contamination. From the standpoint of availability to plants, soil P can be divided into functional pools of differing bioavailability (Tiessen et al., 1982). The information on soil P transformation between those pools is useful to predict P bioavailability as well as the risk of P transfer from soil to surface waters. However, soil P transformation has received less attention attributable to the difficulties associated with separation of inorganic P ( $P_i$ ) and organic P ( $P_o$ ) fractions and compositional identification of soil  $P_o$  pools. Such investigation is currently possible with an improved sequential fractionation procedure and adoption of advanced techniques such as nuclear magnetic resonance spectroscopy (NMR) and synchrotron-based techniques like X-ray absorption near-edge structure (XANES).

In this chapter, soil P tests with chemical and ion-sink methods and the influences of farming practices on P status and P transformation in soils were summarized. The emphasis was on description of the interrelationships between soil P pools of differing bioavailability. The analytical methods to assess P transformation in soils including advanced techniques such as path analysis, modeling and synchrotron-based techniques were described briefly. The limitations of methodologies of soil P tests and P transformation analyses were discussed and findings from our studies were integrated in this context.

## 2. Soil tests for available P

### 2.1 Conventional chemical extractions

Available P is the amount of P in soils that can be extracted or mined by plant roots and utilized by plant for its growth and development. It is a quantitative (extensive) parameter and is influenced by the prevailing soil conditions at a particular time and the plant's ability to extract P from soil solutions (Raven and Hossner, 1993; Holford, 1997). However, most people often use available P synonymously with P availability, an intensive parameter that does not reflect the amount or concentration of available P (White and Beckett, 1964).

Availability of P for plant utilization is not a function of its concentration in soil, but rather on the rate of its release from soil surface into soil solution (Abdu, 2006). Available P is composed of soil solution P and is replenished by P that enters the solution by desorption or dissolution of  $P_i$  associated with the soil solid phase or by mineralization of  $P_o$  (Hedley et al., 1982). The measurement of available P therefore needs to consider both the amount and rate of release of P from the solid phase. Very few appropriate methods have been developed. Isotopic dilution ( $^{32}P$ ) techniques theoretically permit researchers to quantify the processes of  $P_o$  mineralization, dissolution of insoluble minerals and desorption of aggregate P, and could be likely used for this purpose. But errors involved in the measurement of change rates make it difficult to extrapolate the continuing release (or isotopic dilution) rates to a temporal scale corresponding to cropping seasons and growth cycles under field conditions (Tran et al., 1988; Sharpley et al., 1994). Thus, some limitations have to be overcome to give results that have practical application.

The most widely used soil P tests are chemical extractions that use chemical reagents to extract available P from soils. Water was probably the first extractant used to measure P in soils. The small amounts of soil P extracted by water and difficulties related to chemical analysis limit the use of water as an extractant. Bray and Kurtz (1945) used a combination of HCl and  $NH_4F$  to remove easily acid soluble P forms, largely Al- and Fe-phosphates. In 1953, Mehlich introduced a combination of HCl and  $H_2SO_4$  acids (Mehlich 1) to extract P from soils in the north-central region of the U.S. In the early 1980s, Mehlich modified his initial soil test and developed a multi-element extractant (Mehlich 3) which is suitable for removing P and other elements in acid and neutral soils (Mehlich, 1984). Olsen et al. (1954) introduced 0.5 M sodium bicarbonate ( $NaHCO_3$ ) solution at a pH of 8.5 to extract P from calcareous, alkaline, and neutral soils. The routine soil P tests may not give insight into the level of plant available P as the chemical reagents may solubilize non-labile P. For instance, the acidic Bray and Mehlich I extractants can dissolve Al- and Fe-phosphates, while Olsen extractant removes dissolved and adsorbed P on calcium carbonate and Fe-oxide surfaces (Mallarino, 1997). Moreover, these chemical extractants are not applicable over all soil types, which underscore the use of them for soil P extractions (Myers et al., 2005). Bray and Mehlich-3 extractants were designed to extract P from non-calcareous soils, whereas the Olsen method was meant for non-acidic soils. Furthermore, those conventional soil P tests derived from mineral soils may not necessarily be applicable for organic soils, although some routine soil P tests are being adopted to make agronomic recommendations in muck soils (Castillo and Wright, 2008; Wright, 2009). This, however, is an "alternative-than-never" choice, at this moment without specific test for organic soils available.

## 2.2 Ion-sink extractions

The ideal soil P test should be able to extract P in a similar manner as plant roots (Abdu, 2006). Ion sink tests have been developed to simulate how plant roots extract available P from soils. Methodologies were detailed in Sibbesen (1978), Schoenau and Huang (1991), Chardon et al. (1996) and Myers et al. (2005).

The ion-sink concept used in P extraction includes ionic exchange resin membranes, resin bags and FeO coated filter papers or strips. The exchange membrane resin is employed with either the batch or miscible displacement techniques. The batch technique involves the use of a wide soil to solution ratio, which varies the P concentration in the solution and the quantity of desorbed P as the reaction proceeds. If there is inadequate mixing of solution with the ion exchanger, a limited rate of reaction may occur (Sparks, 1985). This may also lead to a change in surface chemistry of the colloids and break down of soil particles (Barrow and Shaw, 1977). With miscible displacement technique, there can be error in dilution that leads to error in interpretation by altering the P concentration of soil (Sparks, 1999), which is more pronounced in colloids having low ion absorbing power (Carski and Sparks, 1985). Also, dispersion of soil colloids may not be fully achieved (Sparks, 1999). Even though anion exchange resin extracts more P than the FeO-coated papers, the additional P extracted may not be plant available (Robinson and Sharpley, 1994). Soil particles can contaminate the FeO-coated papers during shaking, which can lead to error in estimating desorbable P (Uusitalo and Yli-Halla 1999). This can, however, be minimized by the use of  $\text{CaCl}_2$  solution as the background electrolyte to minimize soil dispersion (Myers et al., 2005), but reaction with  $\text{CaCl}_2$  may reduce the amount of P extracted (Koopmans et al., 2001).

In spite of the aforementioned disadvantages, ion-sink methods, especially the anion exchange membranes, are still regarded as the most effective method of plant available P extraction. In addition to their capability to extract P from a variety of soil types, regardless of soil properties (Sharpley et al., 1994), the ion-sink methods simulate plant roots and extract P from soil without alteration of the soil chemical and physical characteristics (Raven and Hossner, 1993). Further more, the resin membranes can be re-used several times without losing its extracting power (Schoenau and Huang, 1991). This property makes it relatively cheaper than the FeO-coated papers. The compatibility of resins with soil solution chemistry and pH can be achieved by charging the resins with either  $\text{HCO}_3^-$  or  $\text{Cl}^-$  (Agbenin and Raij, 2001). The use of  $\text{HCO}_3^-$ -resin is more advocated than  $\text{Cl}^-$ -resin, as plant roots accumulate bicarbonate in the rhizosphere, leading to an increase in rhizosphere pH in acid to neutral soils and a decrease in rhizosphere pH in calcareous soils (Sibbesen, 1978), while when  $\text{Cl}^-$ -resin is used, the  $\text{Cl}^-$  accumulated in solution inhibits the exchange reaction (Myers et al., 2005).

## 2.3 Phosphorus determination

Analysis of extracted P is typically done by colorimetry, most notably the Murphy and Riley (1962) method. A specific ion reacts with the color developing reagents to form colorful complex (e.g. blue antimony phospho-molybdate), then light absorption by the formed complex is detected at a specific wavelength. Colorimetric procedures are sensitive, reproducible and enable to automated analysis. In addition, the methods can be accommodated to water samples, digested solutions and extracts (Pierzynski et al., 2008).

Inductively coupled plasma (ICP) spectrophotometry is also now commonly used for P determination, particularly in routine soil P tests offered by public and commercial laboratories. The use of ICP has increased as the use of multi-element soil extractants becomes more popular. Results from ICP are not always directly comparable to those from colorimetric analyses (Pierzynski et al., 2011), as ICP estimates the total P in a solution while the colorimetric procedures measure P that can react with the color developing reagents. Moreover, there are certain limitations that must be considered while evaluating data generated by ICP, such as the matrix effects, spectral interference, etc. (de Boer et al., 1998).

Nuclear magnetic resonance (NMR) is a physical phenomenon based upon the magnetic property of atomic nucleus. It is observed that magnetic nuclei, like  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$ , could absorb radio frequency when placed in a magnetic field with a specific strength, described as the resonance of the nucleus. Different atoms in a molecule resonate at different frequencies at a given field strength. This is a powerful method that allows researchers to determine the structure of chemical compounds. The use of solution  $^{31}\text{P}$  NMR spectroscopy has allowed us to identify P forms in soils and residual materials, and confirm P forms estimated by commonly used chemical extractants, such as sequential fractionation schemes. This technique has enabled more accurate determination of organic forms of P in soils and residual materials (Zhang et al., 1999; Turner and Leytem, 2008). In addition, the use of synchrotron-based techniques (e.g. XANES) has provided insights into both  $\text{P}_i$  and  $\text{P}_o$  forms in soils and residual materials. Descriptions of these approaches were detailed by Beauchemin et al. (2003) and Shober et al. (2006). These analytical advances have been critical in gaining a more detailed understanding of soil P transformation and reaction products following land application of residual materials. This information has helped assess the fate, reactivity, behavior of specific forms of P and the environmental implications of land application of materials such as biosolids and animal manures (Pierzynski et al., 2008).

### 3. Soil P transformation

#### 3.1 Soil P fractionation

From the standpoint of availability to plants, soil P is divided into three functional fractions each including both  $\text{P}_i$  and  $\text{P}_o$  forms: (1) readily labile P pools, (2) moderately labile P pools and (3) sparingly soluble P pools (Tiessen et al., 1982). Due to the technical difficulties involved in isolating specific P compounds from soils, the financial, practical and safety limitations of using P radioisotopes, and limited access to NMR spectroscopy and synchrotron-based techniques, most of field studies on P transformation in soils must rely on alternative methods of measuring changes in soil P fractions. One technique is to sequentially separate soil P into various  $\text{P}_i$  and  $\text{P}_o$  fractions based on their bioavailability and biological associations, by first removing labile P, then more stable forms. This sequential extraction method was originally presented by Chang and Jackson (1957) and was later modified by Petersen and Corey (1966) and Williams et al. (1967). Briefly, this soil P sequential procedure uses  $\text{NH}_4\text{Cl}$  to extract labile  $\text{P}_i$ ,  $\text{NH}_4\text{F}$  to dissolve specifically Al-associated  $\text{P}_i$  followed by  $\text{NaOH}$  to extract Fe-bound  $\text{P}_i$  and by dithionite-citrate for reductant-soluble or 'occluded'  $\text{P}_i$  forms. The  $\text{HCl}$  dissolved Ca-bound  $\text{P}_i$  and the final residue is analyzed by  $\text{Na}_2\text{CO}_3$  fusion for total P. However, the procedure presents many interpretational problems. Since  $\text{P}_i$  reprecipitates during the fluoride extraction, the separation of Al- and Fe-associated  $\text{P}_i$  is not reliable and the reductant-soluble or 'occluded'  $\text{P}_i$  is an ill-defined pool. Furthermore, the  $\text{P}_o$  fraction is ignored (Williams et al. 1967).



An improved P fractionation scheme was developed by Hedley et al. (1982). This sequential extraction aimed to quantify labile  $P_i$ , Ca-associated  $P_i$ , Fe- and Al- associated  $P_i$ , as well as labile and more stable forms of  $P_o$ . With this improved procedure, soil P is initially extracted with an anionic-exchange resin (resin-P), and then with  $\text{NaHCO}_3$  ( $\text{NaHCO}_3\text{-}P_i/P_o$ ). Resin-P and  $\text{NaHCO}_3\text{-}P$  are assumed to be the readily plant-available fractions and generally regarded as P that is sorbed on carbonates, sesquioxides or crystalline minerals (Mattingly, 1975). Moderately labile P, sorbed on amorphous Fe and Al minerals and the 'protected P' that is occluded or contained within aggregates, is then extracted with NaOH ( $\text{NaOH-}P_i/P_o$ ). The sparingly soluble apatite-type P minerals are extracted with HCl ( $\text{HCl-P}$ ), and the residual P is dissolved by a  $\text{H}_2\text{O}_2$  (or  $\text{K}_2\text{S}_2\text{O}_8$ )- $\text{H}_2\text{SO}_4$  digestion (residual  $\text{H}_2\text{SO}_4\text{-}P$ ). The  $\text{H}_2\text{SO}_4\text{-}P$  fraction, chemically stable and not readily available to plants, may consist of either  $P_o$  or  $P_i$ , or both. This approach is currently the only one to evaluate both available  $P_i$  and  $P_o$  in soils with moderate success (Tiessen and Moir, 1993), although modifications to the procedure are often study-specific, for example, the use of de-ionized water instead of anionic-exchange resins to extract readily labile P. It was proven useful for establishing the effects of long-term cropping practices on  $P_i$  and  $P_o$  fractions and transformation (O'Halloran et al., 1987a; Paniagua et al., 1995; Richards et al., 1995; Tran and N'dayegamiye, 1995; Zhang and Mackenzie, 1997a, 1997c; Zhang et al., 2004; Zheng et al. 2001, 2002, 2004a) and for assessing soil P status in field soils (Simard et al., 1995; Beauchemin and Simard, 2000; Zheng et al., 2004b). It was also valuable for quantifying changes in soil P fractions in short-term incubations (Hedley et al., 1982; Iyamuremye et al., 1996) and from greenhouse experiments (Ivarsson, 1990). In addition, it offers a useful index of the relative importance of P cycling by biological versus geochemical processes in soils at different stages of development (Cross and Schlesinger, 1995).

### 3.2 Conceptual model of soil P transformation

The P transformation in soils involves complex mineralogical, chemical and biological processes (Fig. 1). The P cycle in soil is a cohesive dynamic system under the influence of long-term chemical transformations and short-term changes due to plant uptake or cropping. The leaching of bases, the removal of carbonates and the increasing Fe and Al activity that accompany the development of soils cause a shift from primary to secondary  $P_i$  forms and also influence the stabilization of organic matter and its associated  $P_o$  (Walker and Syers, 1976). The abundance and activity of various  $P_i$  forms and the turnover of  $P_o$  in soils control the replenishment of labile solution P following plant uptake. Surface associated or amorphous  $P_i$  replenishes the labile P pool while more stable crystalline species act as a sink as well as long-term reservoir of P, depending on other soil properties such as pH (Murrman and Peech, 1969). In this way, hydroxide or acid extractable  $P_i$  ( $\text{NaOH-}P_i$  or  $\text{HCl-P}$ ) may act as the quantity factor that buffers the more labile P forms. The  $P_o$  may perform a similar function through controlled mineralization-immobilization processes (McGill and Cole, 1981). Soil organic carbon has a major role of promoting processes involved in P transformation, through its contribution as energy source for microbial activity (Stevenson, 1986). Microbes are heavily involved in P transformation in three ways: (1) by decomposition of  $P_o$  compounds, with release of available  $P_i$ ; (2) by immobilization available P into cellular material; and (3) by promoting the solubilization of fixed or insoluble mineral forms of P, such as through the production of chelating agents (Stevenson, 1986; Frossard et al., 2000).

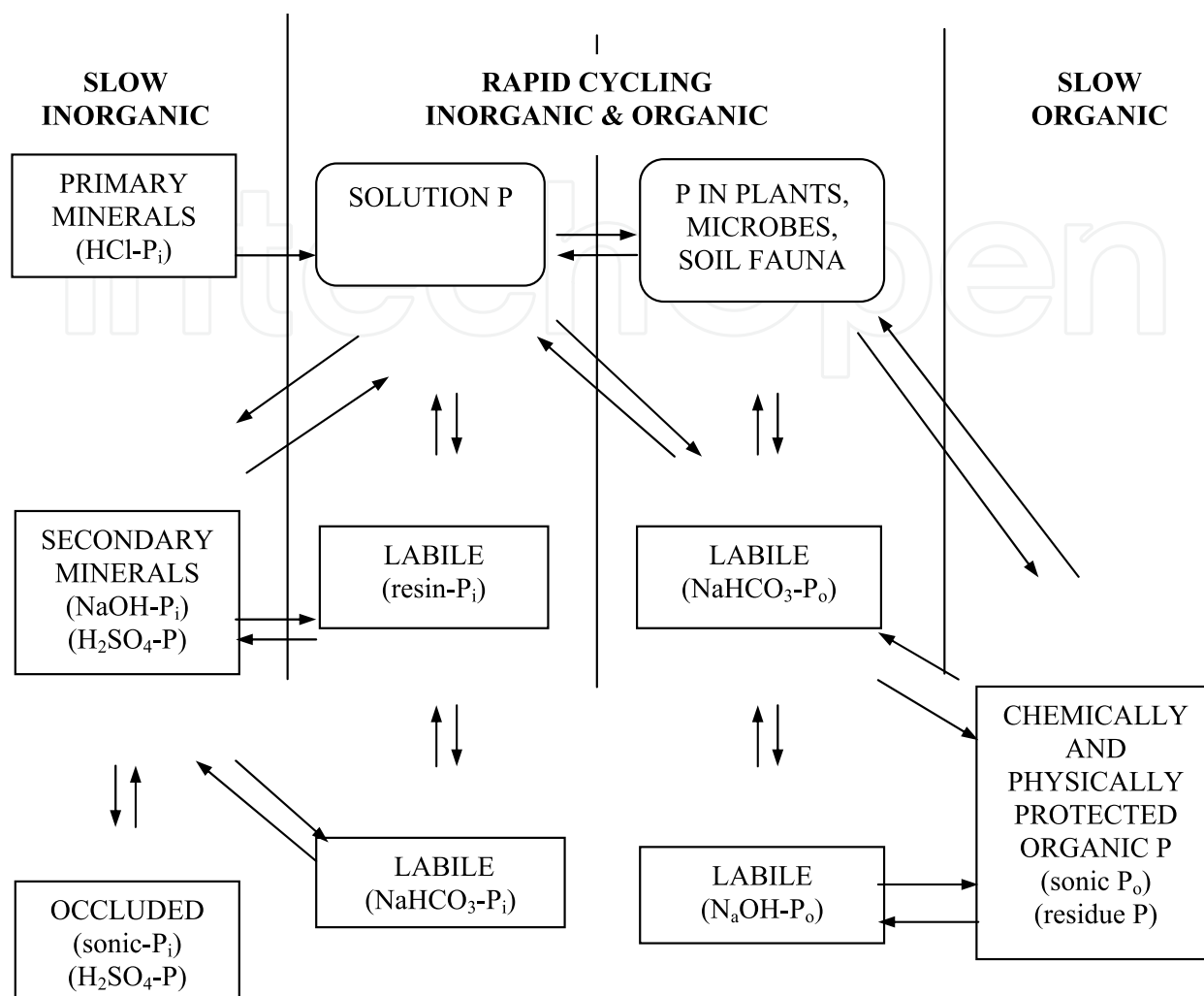


Fig. 1. A conceptual model of soil phosphorus transformation with its measurable components (Source: Tiessen et al., 1984)

### 3.3 Impacts of farming practices on soil P fractions and transformation

#### 3.3.1 Effects of fertilization

Numerous studies have investigated the effects of fertilizer additions on P fractions and transformation. Generally, resin-P,  $\text{NaHCO}_3\text{-P}_i$  and  $\text{NaOH-P}_i$  reflect the difference between fertilizer P and crop P removal. Stable fractions are less affected by inorganic fertilizer P or manure application (O'Halloran, 1993; Richards et al., 1995; Tran and N'dayegamiye, 1995; Zhang and MacKenzie, 1997a, 1997c). The  $\text{P}_o$  fraction is either unaffected by excess inorganic fertilizer P (McKenzie et al., 1992a, 1992b; Zhang and MacKenzie, 1997a; Zheng et al., 2001) or increased with high rates (Schmidt et al., 1996), but it increases when inorganic fertilizer is combined with farmyard manure (O'Halloran, 1993; Tran and N'dayegamiye, 1995; Zhang and MacKenzie, 1997a). The  $\text{P}_o$  is a source of P to plants when fertilizer P is

inadequate to meet crop P requirements (Zhang and MacKenzie, 1997a, Zheng et al., 2001, 2004b). In many cases, the readily labile P increases more when the two P nutrient sources are applied together than when only one is applied (Paniagua et al., 1995). Consequently, the effects of P fertilization on different P pools in soils depend on nutrient sources and rates of P applied as chemical fertilizer or manure (O'Halloran, 1993; Zhang and MacKenzie, 1997a, 1997b; Zheng et al., 2001, 2002).

Long-term organic residues or manure application increases microbial activity and potential mineralization of soil organic matter (N'dayegamiye and Angers, 1990). Consequently, it may induce transformation of soil  $P_o$  to  $P_i$  fractions and increase the available P in surface and subsurface soil horizons (Sharpley et al., 1984; Tran and N'dayegamiye, 1995, Zheng et al., 2002, 2004a). This mineralization of  $P_o$  during the growing season is very important for P availability to plants. Nevertheless, the excessive application of manure or of P-rich organic amendments plays a significant role in decreasing the P sorption capacity in soils (Sharpley et al., 1993; Simard et al., 1995; Beauchemin et al., 1996; Zheng et al., 2001). Decreased P sorption capacities might increase the risk of contamination of the receiving water bodies.

### 3.3.2 Effects of tillage

The impacts of tillage on P forms and availability have been the subject of many investigations. There was an increase in total and labile P contents in surface soil layer due to no-till operations (Cruse et al., 1983; Weill et al., 1990; Selles et al., 1997). This was attributed to the enhanced microbial activity and mineralization of soil  $P_o$  (Follett and Peterson, 1988) or to a lack of soil mixing with fertilizer P thus reducing P fixation by soil colloids (Sweeney, 1993; Selles et al., 1997, 1999). As a result, extractable P in surface soils is increased in no-tillage compared to conventional tillage. Soil  $P_o$  is generally increased near the bottom of plow layer by tillage due to the incorporation of crop residues (Dick, 1983, Weill et al., 1990). Nevertheless, O'Halloran et al. (1987a) did not observe a significant difference in the size of soil P fractions except for NaOH- $P_o$  between stubble mulch, bare sod and no-till practices in a grassland soil. On the other hand, Sharpley et al. (1993) found that no-till plots tended to have higher soil moisture content and lower temperature, which resulted in more dissolved P in the runoff than conventionally tilled plots. Blevins et al. (1990) observed that movement of P was reduced using a system of chisel plowing compared to direct seeding or conventional plowing. The chisel plowing was associated with a reduced runoff following the spreading of fertilizers on the soil surface. Therefore, as with fertilization, tillage can alter distribution of P fractions and affect the transformation and transfer of P in soils.

### 3.3.3 Effects of cropping systems

Cropping systems also have major effects on changes in P fractions in soils. As cropping systems change from less intensive systems (i.e. crop-summer fallow) to more intensive cropping sequences (i.e. continuous wheat and wheat-wheat-fallow), soil P availability and transformation become less predictable due to larger  $P_i$  and  $P_o$  components from greater residue and litter which are maintained on soil surface (O'Halloran, 1987a, b). Wagar et al. (1986) found a buildup of  $P_o$  occurred with and without added P fertilizer when cropping



systems changed from conventional winter wheat-fallow to more intensive rotations. Bowman and Halvorson (1997) observed that a change from wheat-fallow to continuous wheat cropping produced a significant increase of labile P fractions in 0-5 cm surface soils. Zheng et al. (2001) observed that forage-forage-barley rotation produced larger labile P fractions than barley monoculture in the 30-60 cm layer in a Labarre silty clay after 10 years of cultivation. Recently, Zhang et al. (2006) investigated the P status after 45 years of consistent cropping practices under three cropping systems of continuous corn, rotation corn and continuous bluegrass. Compared to the adjacent native soil in forest ecosystem, the study showed that continuous cropping without P fertilization decreased all P forms significantly except for water extractable  $P_o$ , with the largest decrease in labile  $P_i$  and moderately labile  $P_o$ ; continuous cropping with fertilization resulted in comparable total P concentrations in the continuous corn and rotation corn systems and increased total P in the continuous bluegrass sod. The study also indicated that long-term cropping significantly enhanced the rate of moderately labile  $P_o$  mineralization, regardless of P fertilization, especially for continuous corn cropping system. However, compared to monoculture, crop rotations showed no effect on nutrient contents in the 0-20 cm soil layer in an experiment with soybean, corn and wheat in an Oxisol and in a Rhodic Ferralsol (DeMaria et al., 1999).

### 3.4 Soil texture effects on soil P fractions and transformation

Soil texture can be related to changes in P fractions and transformation. O'Halloran et al. (1985) found that up to 90% of the spatial variability in total P content of a Mollisol was explained by texture. A similar study showed that significant proportions of variability of all P fractions, except for  $H_2SO_4$ -P in a Brown Chernozemic loam, could be attributed to changes in sand content (O'Halloran et al., 1987b). Increasing silt plus clay content has been significantly correlated with larger soil resin-P,  $NaHCO_3$ - $P_i/P_o$  and  $NaOH$ - $P_i/P_o$  pools.  $HCl$ -P was positively correlated with sand content (O'Halloran et al., 1987b). There is evidence that P transformation in soils were closely linked to microbial activity and C dynamics, which affect P mineralization and immobilization (Hedley et al., 1982). For example, a loam soil supported higher microbial biomass than the sandy loam and sandy soils (Cooper and Warman, 1997). Huffman et al. (1996) indicated that soil texture had a greater effect on P transformation than did the combined effects of residue addition, residue placement and nutrient addition, because soil texture affected the labile  $P_i$ , labile  $P_o$ , and microbial P pools. Therefore, among those factors, the particle size of soil fractions tends to account for larger proportion of variability in soil P fractions. Those findings emphasize the importance of considering soil texture when planning studies of the effects of cropping practices on P fractions and transformation.

### 3.5 Profile-wise distribution of soil P fractions

Much effort has been devoted to investigate the vertical changes in forms and distribution of soil P as influenced by cropping practices. These changes in P forms were mainly limited to the top of 30 cm (O'Halloran, 1993; Sharpley et al., 1993; Bowman and Halvorson, 1997; Selles et al., 1997), or to depths of 65 cm (Reddy et al., 1980; Mozaffari and Sims, 1994; Richards et al., 1995), with a few studies extending to depths  $\geq 90$  cm (Chang et al., 1991;

Simard et al., 1995; Beauchemin et al., 1996; Zheng et al., 2001). These studies suggested that the impacts of cropping practices on soil P fractions extended deeper in soil profile than the depth distributed by primary tillage, and P profile-wise distribution was often complicated by P downward movement. The  $P_o$  movement in soils was greater than that of  $P_i$  (O'Halloran, 1993; Richards et al., 1995). This may be due to the fact that  $P_o$  was not retained as strongly as  $P_i$  by sorbing components of solid phase, or perhaps that  $P_o$  movement was driven by mineralization process. The  $P_o$  migrated to subsoil can be mineralized, since  $P_o$  was used by microorganisms as an energy source for their metabolism in reduced layers of poorly drained soils (Zheng et al., 2001).

The downward migration of P is associated with changes in soil P sorption capacity (Reddy et al., 1980). Simard et al. (1995) found that P sorption index ( $P_{si}$ ) in agricultural soils was markedly decreased in all three horizons compared with forest soils from a watershed in Quebec. Accumulation of added P has led to an increase in total labile P pool in the A horizon (0-30 cm), while resilient P pools were the major sinks for mobile P in the B (30-60 cm) and C (60-90 cm) horizons in agricultural soils (Simard et al., 1995; Beauchemin et al., 1996; Zheng et al., 2001). This finding was in line with previous studies suggesting that repeated additions of manure decreased P sorption capacity of soils and accelerated P downward movement (Reddy et al., 1980; Sharpley et al., 1993; Mozaffari and Sims, 1994).

## 4. Analysis of P transformation in soils

### 4.1 Path analysis of soil P transformation

Path analysis is a statistical technique used to examine interrelationships among variables that are often illustrated by a path diagram. It provides not only plausible explanations of observed correlations by constructing the cause-and-effect model, but also allows decomposition of observed correlations into direct and indirect effects (Johnson and Wichern, 1988). Path analysis was useful in linking changes in soil P fractions and clarifying concepts of P transformation in soils (Tiessen et al., 1984; Beck and Sanchez, 1994; Zhang and MacKenzie, 1997a; Zheng et al., 2002, 2004a). Using path analysis, Tiessen et al. (1984) found that in Mollisols, much of resin- $P_i$  was derived from  $NaHCO_3-P_i$  and  $NaOH-P_i$  fractions, and in more weathered Ultisols, 80% of variability in labile P was accounted for by  $P_o$  forms. Beck and Sanchez (1994) showed that the  $NaOH-P_i$  fraction acted as a major sink for fertilizer P in soils and  $P_o$  was a major primary source of plant-available P in unfertilized soils of Peru. Zhang and MacKenzie (1997a), using the same approach for soils receiving manure and fertilizer P, indicated that  $P_o$  accumulated as  $NaOH-P_o$  through  $NaHCO_3-P_i$ . The  $NaHCO_3-P_i$  and  $NaOH-P_i$  were major sinks for added P. When mineral fertilizer was the only source of P, most  $NaHCO_3-P_i$  was directly supplied from fertilizer P through  $NaOH-P_i$ . Zheng et al. (2002, 2004a) investigated the P transformation in a Labarre silty clay as affected by nutrient sources and cropping systems in a long term study and showed that the roles of  $P_o$  pools were more important than  $P_i$  pools for P transformation and  $NaHCO_3-P_o$  was sensitive to P source and was likely acted as a transitory pool rather than as a sink or source of soil P (Fig. 2). Thus, path analysis can reflect the changes in P transformation depending on soil type, climatic conditions and cropping practices.

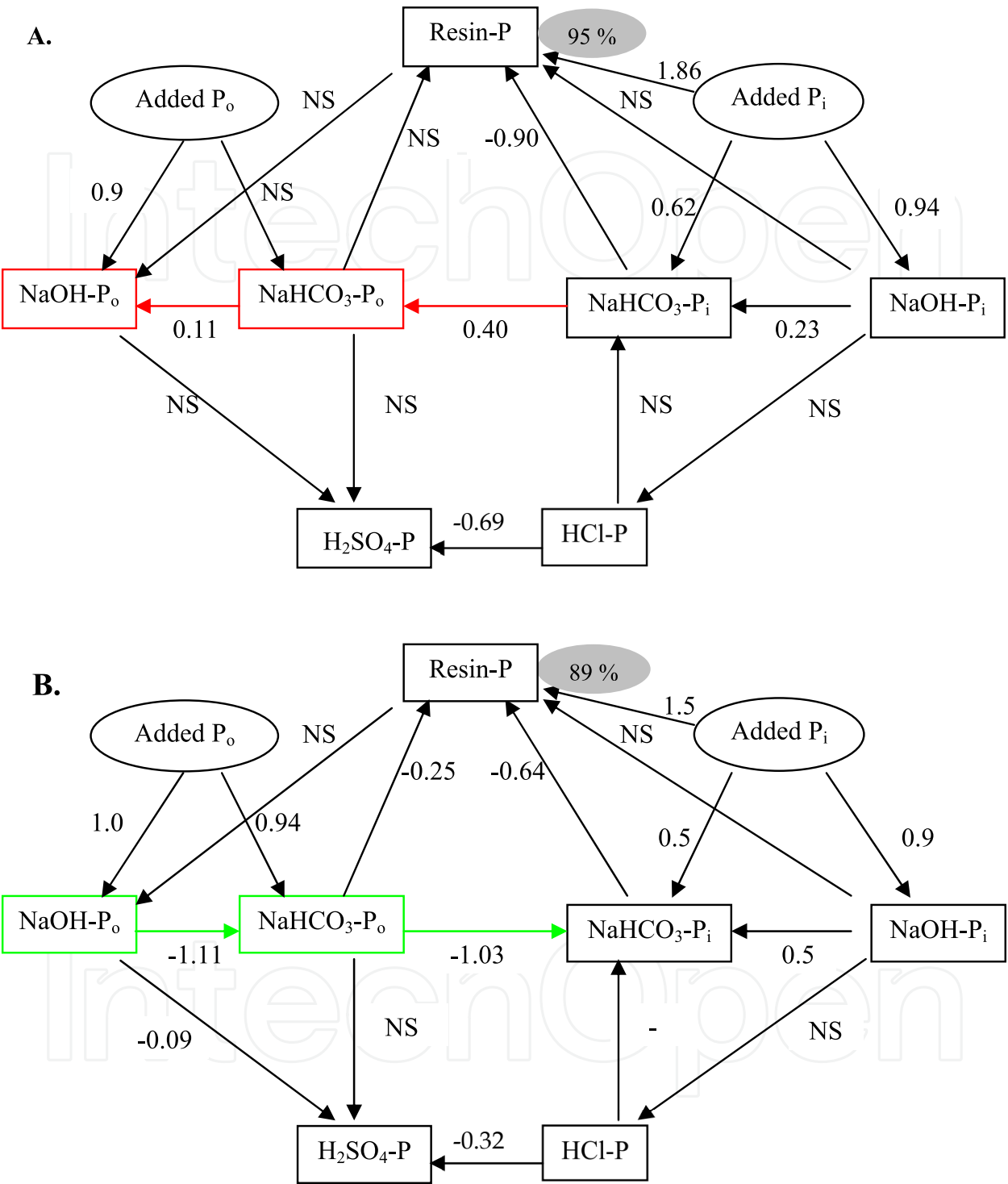


Fig. 2. Pathways of P transformation after 10 annual applications of mineral fertilizer (A) and liquid dairy manure (B) in the 0-15 cm soil of a Labarre silty clay under barley monoculture. The percentage value indicates the partial correlation between assed  $P_i$  and resin-P; numbers are path coefficients; NS, not significant at  $P \leq 0.05$  (Source: Zheng et al., 2004a)

## 4.2 Modeling of soil P transformation

The P concentration in soil solution is in turn controlled by P transformation processes such as mineralization, precipitation and adsorption. The complexity of interactions among these processes has led to the use of both descriptive and mechanistic mathematical models to describe them. The interpretation of changes in P concentrations in soil solution has been modeled using a variety of approaches, such as adsorption model, sorption-transport model and multi-reaction model. Most of earlier simulations of P adsorption have been based on simple rate constants (Jones et al., 1984), such as Langmuir (Enfield et al., 1981), Freundlich (Shaviv and Shacher, 1989) and Elovich equations (Chien and Clayton, 1980). A few studies have used kinetic equations such as first- or second-order reaction rates to describe the P sorption in soils (Bowden et al., 1980; Beauchemin et al., 1996). Nevertheless, adsorption models did not fully describe the mechanisms of P transformation in soils, and hence were unlikely to be generally applicable. Van de Zee and Gjaltema (1992) proposed a sorption-transport model in which both sorption reversibility and precipitation irreversibility were taken into account, but reaction rates remained uncertain.

A mechanistic multi-reaction model was conceived to represent P concentrations under dynamic boundary conditions, and to explain temporal and spatial P distribution among water soluble and resin-,  $\text{NaHCO}_3$ -,  $\text{NaOH}$ -, and  $\text{HCl}$ -P fractions (Grant and Heaney, 1997; Grant et al., 2004). The model describes adsorption-desorption, precipitation-dissolution and ion pairing. The model can explain the temporal and spatial distribution of soluble and solid fractions under specified changes in boundary conditions in different soil types. However, the model requires more detailed, explicit information about soil chemical composition, which may not be readily available in routine fashion for many soils. Thus, where necessary, some assumptions must be made. To date, despite several P transformation models have been developed to describe certain processes, the majority of existing models need to be verified in heterogeneous soils under field conditions. Furthermore, it is unlikely that one model can kinetically represent all processes involved in P transformation.

## 5. Summary

Phosphorus is an essential element for plant growth and development, as it plays key roles in plant metabolism, structure and energy transformation. It is also a potential pollutant of water. The P dynamics in plant-soil-water systems is of increased interest due to its importance for environmental, agronomic and economic issues.

Soil P test involves P extraction from soils followed by a quantification of the nutrient in the extracting solution. The most widely used soil P tests are chemical extractions, such as Bray 1 & 2, Olsen, Mehlich I & III methods. Those chemical extractants are not applicable over all soil types, which is a limitation for soil P extraction. The ion-sink extractions, including ionic exchange resin membranes, resin bags,  $\text{FeO}$  coated filter papers or strips, simulate plant roots to extract P from soils without alteration of soil characteristics and have the advantage of extracting P from variety of soil type regardless of soil properties. The mainstay of P determination is the use of colorimetric procedures, most notably Murphy and Riley (1962). Inductively coupled plasma (ICP) spectrophotometry is becoming more popular for multi-element determination. The isotopic dilution ( $^{32}\text{P}$ ) techniques, the  $^{31}\text{P}$  NMR solution and the synchrotron-based techniques can provide insights into P chemistry and forms in soil and

residual materials. Although these advanced analytical techniques are capable of gaining more detailed understanding of P dynamics in soils, unfortunately not all researchers have access to the required instrumentation.

Based on its availability to plants, soil P can be divided into functional groups of readily labile P pools, moderately labile P pools and sparingly soluble P pools, each includes both  $P_i$  and  $P_o$  forms. The P transformation in soils plays important roles in P bioavailability and mobility from soil to water, and was intensively affected by cropping practices, i.e. fertilization, tillage and cropping systems. It involves complex chemical, mineralogical and biological processes. The complexity of interactions among these processes has led to the use of both descriptive and mechanistic mathematical models to describe them. Path analysis is powerful in plausibly explaining interrelationships among P pools of differing bioavailability and clarifying changes in P fractions and transformation in soils. Mechanistic multi-reaction models that describe transformation processes of mineralization-mobilization, adsorption-desorption, precipitation-dissolution and ion pairing are available to interpret the temporal and spatial distribution of P fractions in soils. However, the models require more detailed, explicit information on soil chemical composition that are not routinely available for many soils. Furthermore, most mechanistic models need to be verified in heterogeneous soils under field conditions.

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