



Improving phosphorus availability in Andisols and Oxisols

A thesis submitted to The University of Adelaide
in fulfilment of the requirements for the degree of Doctor of Philosophy

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December 2014

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Abstract

Low phosphorus (P) availability limits plant growth in many soils, particularly in Andisols and Oxisols, due to their large content of minerals that strongly sorb P (e.g. Al/Fe oxyhydroxides, allophane). Because of the strong P retention, P fertilizer requirements are high in these soils. Strategies to increase the efficiency of P fertilizers – and reduce P rates needed to obtain maximal yield – remain key to reducing the pressure on limited rock phosphate reserves. To develop management practices or fertilizer formulations that enhance P availability and fertilizer efficiency in strongly P-sorbing soils, a better understanding of the chemical reactions of P in these soils is needed. This work aimed (i) to examine the chemical behaviour of soil P and added P to plant uptake in strongly P-sorbing soils and (ii) to compare the effect of different P fertilizer types (granular/fluid/nano-sized) as a strategy to increase the efficiency of P fertilizers.

A laboratory incubation experiment was conducted to evaluate the diffusion and lability of P from granular and fluid fertilizers applied to Andisols and Oxisols using the isotopic dilution technique and a novel visualization method. In all soils, fluid fertilizers enhanced P diffusion, but not P lability, i.e. the amount of added P that remained in isotopically exchangeable form. In the Oxisols, a greater percentage of added P remained isotopically exchangeable when added as granular monoammonium phosphate (MAP) (41% labile) than when added as fluid MAP (25% labile). In the Andisols, no significant difference was observed in the percentage of labile P between both fertilizer types (circa 25% labile). Given these results, it was hypothesized that there would be no agronomic benefit from the application of fluid P fertilizer in these soils. A subsequent pot trial was conducted to assess

the uptake of P by wheat (*Triticum aestivum*) from granular and fluid fertilizers using the indirect isotopic dilution method in two Andisols, two Oxisols, and a calcareous soil (where fluid P has been proven more effective). This pot trial indeed showed no significant difference in dry matter yield, P uptake and the percentage of P derived from the fertilizer in the plant (%Pdff) between granular and fluid MAP in the Andisols or Oxisols, while there was a significant increase with fluid fertilizer in the calcareous soil.

Hydroxyapatite nanoparticles ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, n-HAP) were also tested as a potential P fertilizer, based on the hypothesis that nano-sized particles can potentially move in the soil and reach the plant roots through the transpiration flow. Because of the strong adsorption and subsequent fixation of soluble P in this type of soils, nanoparticulate P could potentially have a benefit over soluble fertilizers. Column studies showed some leaching (5%) of n-HAP in the Andisol but very little in the Oxisol. In contrast, bulk-sized HAP did not move in either of the soils. A pot trial using the isotopic dilution procedure evaluated P availability for wheat from n-HAP, bulk-sized HAP, and triple superphosphate. For Andisols and Oxisols, P uptake and %Pdff differed significantly from P treatments as follows: TSP > n-HAP > bulk-HAP. Thus, while sparingly-soluble fertilizer in nanoparticulate form (n-HAP) performed better than its bulk counterpart, it was less efficient than soluble fertilizer (TSP). It was hypothesized that the difference between n-HAP and bulk-HAP was due to the difference in rate of dissolution, but that the n-HAP has no direct effect on the uptake and only contributes *via* dissolution.

The pot trial showed that n-HAP did not have an agronomic benefit over soluble granular fertilizers, but the possible contribution of nanocolloidal P to P uptake was still further investigated in hydroponic experiments. Phosphorus bioavailability is related to its concentration and speciation in the soil solution. Free orthophosphate is the form of P taken up by plants; but colloidal P constitutes an important fraction of total solution P in oxide- or

allophane-rich soils and its bioavailability has not been previously considered. The uptake of P by wheat seedlings was measured from radiolabeled non-filtered (colloid-containing) and 3-kDa filtered (colloid-free) soil-water extracts from Andisols and Oxisols. In the Andisol extracts, P uptake was up to seven-fold higher in the non-filtered solutions than in the corresponding 3-kDa filtered solutions. It is hypothesized that labile humic/fulvic-Fe/Al-P complexes increased the diffusive transport flux of free P to the roots. In the Oxisol extract, no difference in P uptake between both solutions was observed. Also, the diffusional flux of P measured with the diffusive gradient in-thin films (DGT) method was larger in the non-filtered than in the 3-kDa filtered solutions. These results are the first observation that natural colloidal P is not inert and can contribute to plant P uptake.

This work has shown that increasing soil available P and fertilizer efficiency in soils where strong adsorption reactions control P availability is very challenging. However, the observed contribution of colloidal P to plant P uptake for Andisols is a finding that may lead to the development of new management practices to enhance the release of P-containing colloids into solution as a complimentary strategy to P fertilization in these strongly P-sorbing soils. Although in this study hydroxyapatite nanoparticles offered no advantage over conventional soluble P fertilizers for plant growth, this does not imply that nano-sized P fertilizers can be ruled ineffective. The addition of labile nanocolloidal P that is mobile in soil and contributes to P uptake is still a worthwhile fertilizer strategy to investigate.

Declaration

I certify that this work contains no material which has been accepted for the award of any other degree or diploma in my name in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. In addition, I certify that no part of this work will, in the future, be used in a submission in my name for any other degree or diploma in any university or tertiary institution without the prior approval of The University of Adelaide and where applicable, any partner institution responsible for the joint award of this degree.

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Date

Acknowledgments

I would first like to express my deep and sincere gratitude to my supervisors Mike McLaughlin and Fien Degryse for their guidance, support and encouragement during my candidature. Thank you for giving me the freedom and possibility to bring soils from Ecuador, Chile, and New Zealand to carry out my experiments and fulfil my personal interest and desire in learning more about the chemistry of Andisols. I feel very lucky for having the opportunity to work with you.

Outside of my supervisory panel I would like to thank Ron Smernik, who patiently proof-read all my manuscripts and for instilling that writing is as important as doing experiments.

Thanks to Bogumila Tomczak, Colin Rivers, Ashleigh Broadbent, Caroline Johnston, and Gill Cozens for their technical assistance throughout my experiments. Thanks also to Mike Bell, Leo Condrón, Carlos Michiels, and Raul Jaramillo for supplying the soil samples for my studies.

Most importantly I would like to acknowledge The University of Adelaide for providing the financial support for my PhD studies, through the International Postgraduate Research Scholarship (IPRS) and Australian Postgraduate Award (APA). In addition I acknowledge the Adelaide Graduate Centre for the generous DR Stranks Postgraduate Travelling Fellowship that allowed me to spend 5 weeks at the University of Gothenburg in

Sweden to learn about nanoparticle characterization using field-flow fractionation. Special thanks must also go to Geert Cornelis and Martin Hassellöv for hosting me in Sweden.

I would like to express my sincere gratitude to other members of the Soils Group, in particular Cam Grant for his care and support as postgraduate coordinator. Thanks to Lara, Sarah, Courtney, Cuicui, Margaret, Rodrigo and Ros for friendly chats in the lab and in the office. I cannot forget to mention my special gratitude to Sam Stacey who gave me the opportunity to do my PhD at The University of Adelaide and for making sure I was being left in the best hands when he had to leave his position at the University.

I feel truly blessed for having the best companion during my PhD journey. I especially thank my loving husband Diego; this degree would have not been completed without your patience and support.

Finally my most sincere gratitude is reserved to my parents, for their endless love, daily skype calls and continuous support. I felt that you were always close by in spite of being thousands of kilometres away.

List of publications and presentations

Original research articles

1. Montalvo, D., F. Degryse, and M.J. McLaughlin. 2014. Fluid fertilizers improve phosphorus diffusion but not lability in Andisols and Oxisols. *Soil Sci. Soc. Am. J.* 78:214-224.
2. Montalvo, D., F. Degryse, and M.J. McLaughlin. Agronomic effectiveness of granular and fluid phosphorus fertilizers in Andisols and Oxisols evaluated by ^{33}P isotopic dilution technique. (Submitted *Soil Sci. Soc. Am. J.*)
3. Montalvo, D., M.J. McLaughlin, and F. Degryse. Efficacy of hydroxyapatite nanoparticles as phosphorus fertilizer in Andisols and Oxisols. (Submitted *Soil Sci. Soc. Am. J.*)
4. Montalvo, D., F. Degryse, and M.J. McLaughlin. Natural colloidal P and its contribution to plant P uptake. (Submitted *Environ. Sci. Technol.*)

Abstracts from presentations in scientific meetings

1. Montalvo, D., F. Degryse, and M.J. McLaughlin. Colloidal phosphorus and its contribution to plant nutrition. Phosphorus in Soils and Plants, 5th International Symposium, Montpellier, France 26th–29th August 2014. (Oral presentation)
2. Montalvo, D., F. Degryse, and M.J. McLaughlin. The response of wheat grown in Andisols and Oxisols to fluid and granular phosphorus fertilizers. Fluid Forum, Scottsdale, AZ, USA 17th–18th February 2014. (Oral presentation)

3. Montalvo, D., F. Degryse, and M.J. McLaughlin. Potential availability of colloidal phosphorus from the soil solutions of Andisols and Oxisols. ASA-CSSA-SSSA, International Annual Meeting, Tampa, FL, USA 3rd –6th November 2013. (Oral presentation)
4. Montalvo, D., F. Degryse, and M.J. McLaughlin. Lability and diffusion of phosphorus from granular and fluid fertilizers in strongly phosphorus-sorbing soils. SSSA and NZSSS Soil Science Conference, Hobart, TAS, Australia 2nd –7th December 2012. (Poster presentation)

Structure of the thesis

This thesis is presented in publication format and includes papers that have been published or submitted for publication. As a result, there is a degree of unavoidable overlap, especially between the introductory chapters (Chapter 1 and 2) and the introduction sections of the experimental chapters (Chapters 3-6).

Chapter 1 includes the thesis introduction and a general discussion of the importance and limitations of P fertilizer application in strongly P-sorbing soils for adequate crop production. This chapter also outlines the motivations that triggered the development of the present work.

Chapter 2 provides an overview of the literature on the chemical behaviour of soil and fertilizer phosphorus (P) in acidic and strongly P-sorbing soils, and presents the research objectives. This chapter summarizes the key processes that limit the availability of P from water-soluble fertilizers when applied to strongly sorbing soils and highlights the need to improve fertilizer efficiency. This chapter also includes a brief review of the main processes that affect the fate and behaviour of nanoparticles in soils, as it has been suggested that nanotechnology can potentially be used to design more effective fertilizers.

Chapter 3 describes the results from two incubation experiments performed to evaluate the effect of fertilizer type (granular vs. fluid) on the diffusion, lability and solubility of P from a range of P fertilizers applied to acidic and strongly P-sorbing soils.

Chapter 4 presents the results of a pot trial that was conducted to test the hypothesis that fluid P fertilizers do not offer any agronomic benefit over granular P fertilizers in soils where strong adsorption reactions control the availability of P. The isotopic dilution approach was used to assess P uptake by wheat from the P fertilizers. This is a follow-up study to the study presented in Chapter 3.

Chapter 5 describes the results of two experiments conducted to evaluate the potential use of hydroxyapatite nanoparticles as P fertilizer for acidic and strongly P-sorbing soils. In the first experiment, the transport of nano- and bulk-sized hydroxyapatite was evaluated in soil-packed columns. The second experiment was a pot trial where P uptake by wheat from nano- and bulk-hydroxyapatite and a conventional water-soluble P fertilizer was assessed using ^{33}P isotopic dilution.

Chapter 6 presents results of short-term P uptake experiments that were conducted to assess the contribution of colloidal P in soil-water extracts from Andisols and Oxisols to plant P uptake.

Chapter 7 summarizes the principal findings arising from this thesis and includes recommendations for future work.

CHAPTER 1

Introduction

Phosphorus (P) is considered the most important macronutrient after nitrogen limiting plant growth (Holford, 1997). Phosphorus deficiency is a widespread constraint and it has been estimated that in nearly 70% of the world's agricultural soils, the concentration of available P is too low to sustain optimal crop production (Cakmak, 2002). This is certainly the case for highly weathered soils (e.g. Andisols and Oxisols) dominated by Al and Fe oxyhydroxides and allophane, which are minerals known to strongly sorb P (Parfitt, 1989).

Strongly P-sorbing soils are extensively present in subhumid East and West Africa, Central America, South America, and South-East Asia (Fig. 1.1.). Some countries of these regions, especially those in Africa, are constantly being affected by food shortages due to low crop yields, hence it is essential to implement plant nutrient management practices to increase agricultural productivity and ensure food security for the population (FAO et al., 2013; Sanchez, 2010).

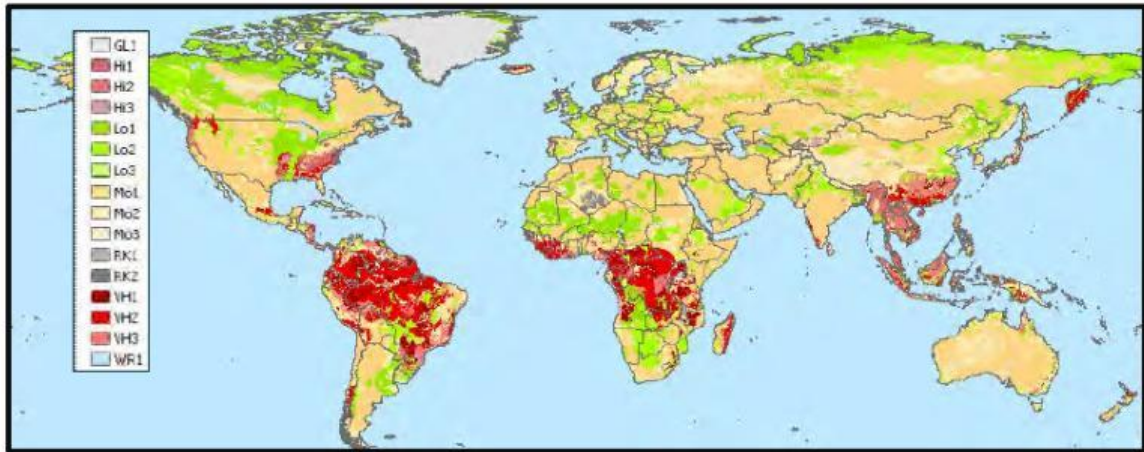


Fig. 1.1. World map of soil phosphorus sorption capacity (area in red corresponds to soils with very high P sorption capacity) (Batjes, 2011).

In order to overcome P deficiency and to increase crop yields, the application of P fertilizers is necessary. However, in strongly P-sorbing soils, P management is challenging because large fertilizer application rates (e.g. $> 300 \text{ kg P ha}^{-1}$) are required to maximize crop yields (Dahlgren et al., 2004; Sanchez and Uehara, 1980). This heavy fertilization is not only economically prohibitive for small farm-holders but can also adversely affect the environment. Furthermore, P fertilizers are produced from rock phosphate, a finite and non-renewable mineral, and it has been speculated that the more accessible reserves will be depleted in the next few centuries (Obersteiner et al., 2013). The continuous and increasing demand for P fertilizers has raised concerns for its long term availability (Scholz et al., 2013).

Management practices designed to improve the efficiency of P fertilizers in strongly P-sorbing soils have been investigated for many decades. Earlier studies suggested that single massive P applications followed by subsequent lower P rates were needed to maximize crop yields and to obtain long-term residual P value (Sanchez and Uehara, 1980; Yost et al., 1979). However, these large P applications do not prevent P from reacting with the soil, so the availability from the remaining fertilizer diminishes with time due to the slow P sorption reactions (Barrow, 1980). The effect of fertilizer placement has also been investigated. In

soils where strong adsorption reactions control soil P availability, banding the fertilizer near the roots has been a better placement option than broadcasting for most crops, as it reduces contact of P with soil resulting in saturation of the sorption sites and hence higher solution concentrations (Havlin et al., 2006; Randall and Hoelt, 1988; Smyth and Cravo, 1990). However, when precipitation reactions are dominant, banding may reduce the efficiency of fertilizer P (McLaughlin et al., 2011).

A strategy with more potential to improve fertilizer P efficiency is the modification of fertilizer formulations (Withers et al., 2014). Ideally, P fertilizers should be designed and/or chosen considering the chemical properties of the soils. The modification of fertilizer formulations that have been investigated to improve fertilizer P efficiency include co-granulating P with other chemical compounds (Bouldin and Sample, 1958; Bouldin et al., 1960), different fertilizer type (Holloway et al., 2001), addition of polymers (Gordon and Tindall, 2006), and recently the use of nanofertilizers has been suggested (DeRosa et al., 2010).

Fluid P fertilizer has been investigated as an approach to improve the efficiency of P fertilizers in calcareous soils. Results from field and pot experiments conducted in Australian calcareous soils have consistently shown higher P uptake, dry matter yield, and grain yield when wheat was fertilized with fluid P fertilizer than with granular P (Bertrand et al., 2006; Holloway et al., 2001). The higher fertilizer efficiency with the fluid form was explained by the enhanced P diffusion resulting in less concentrated P environments and hence less formation of Ca-P precipitates (Lombi et al., 2006). The positive plant response obtained with fluid P in calcareous soils raised interest in the use of fluid P fertilizers in non-calcareous soils. McBeath et al. (2005) evaluated the effectiveness of fluid (phosphoric acid and ammonium polyphosphate) and granular P (triple superphosphate) fertilizers in a collection of Australian soils with soil pH ranging from 5.3 to 8.4. Higher dry matter yield was

measured with fluid P fertilizer in three of the ten acid to neutral soils investigated, in contrast with earlier work where no differences were observed between fluid and granular P fertilizers in acidic soils (Miner and Kamprath, 1971). In a more recent study, Khatiwada et al. (2012) also observed higher resin-extractable P with fluid than with granular P fertilizer applied to an acidic non-calcareous soil. These mixed results indicate no generalizations can be made regarding the efficiency of fluid P fertilizer in acidic soils and more research to better understand its behaviour in non-calcareous soils is still needed.

It has been suggested that implementation of nanotechnology can potentially advance of agriculture and food production through increased efficiency and sustainability (Chen and Yada, 2011; Ghormade et al., 2011; Sekhon, 2014). Nanofertilizers could be designed to release nutrients in a controlled way synchronized with plant demand, or be designed to prevent the immobilization of nutrients in the soil, or could even be directly taken up by the plant and thereby improve nutrient-use efficiency (DeRosa et al., 2010). The potential benefits of nanofertilizers over conventional P fertilizers still need to be explored and hence research in this area is very much needed.

In addition to developing novel more efficient fertilizer formulations, it is important to improve our understanding of soil-plant P dynamics in strongly P-sorbing soils. Plants take up P from the soil solution as free orthophosphate ions (H_2PO_4^- , HPO_4^{2-}) but other P species are also present in the soil solution and their contribution to plant nutrition has been overlooked. For example humic-metal-P complexes can account for an important fraction of solution P in Andisols rich in organic matter and these species may contribute to soil available P as the humic molecules can dissociate to release P (Gerke, 2010).

In summary, the use of P fertilizers for agricultural production is essential but the current management of P fertilizers needs improvement as P will become increasingly expensive in the future. There is a need to develop more effective P fertilizer formulations for

soils that strongly sorb P; however, in order to develop innovative fertilizer technologies it is necessary to better understand the chemical processes that control the fate and availability of added P. Furthermore, P bioavailability also relates to the speciation of P in the soil solution and free orthophosphate is frequently not the dominant P species in the solution of soils, especially in soils rich in Al/Fe oxides. Mobile colloidal P is an important P species in these soils that could potentially contribute to P availability but this has not been yet considered.

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Literature review

Introduction

Phosphorus (P) is an essential element required for plant growth. It participates directly or indirectly in all metabolic processes of plants, as it is a component of key molecules like nucleic acids (RNA, DNA), nucleotides (ATP, ADP), phospholipids, and coenzymes (Raghothama, 2005). Plants suffering from P deficiency exhibit stunted growth and delayed maturity. Purplish coloration of the leaves due to excess anthocyanin accumulation is a characteristic symptom of P deficient plants (Havlin et al., 2006).

There is great awareness on the importance of P to sustain life. In recent years, increasing the efficiency of P fertilizers has gained much interest because of three main reasons as summarized by Johnston et al. (2014). First, inorganic P fertilizers are made from phosphate rock, a finite and non-renewable resource which depletion of easy accessible reserves is a concern. Second, many agricultural soils especially those in developing countries of the tropics are P deficient and therefore application of P fertilizers is indispensable for crop production. Third, inadequate P management and overfertilization especially in developed countries is the main cause for eutrophication of water bodies.

This chapter reviews the literature regarding our current understanding of the chemistry and forms of soil P, the reactions of P fertilizers in soils, and the management practices developed to enhance the efficiency of applied P for strongly P-sorbing soils. Furthermore, since nanotechnology has been proposed as the technology with potential to

improve fertilizer formulations (DeRosa et al., 2010), this chapter includes an overview of the properties and behaviour of nanomaterials in soils and the potential mechanisms by which the efficiency of P fertilizers may be improved with the use of nanotechnology.

Phosphorus in the soil

In soils, P is present in the solid and solution phase. The major processes that control the exchange of P between the solid and liquid phases are dissolution/precipitation of phosphate minerals and adsorption/desorption of P onto soil constituents (Sims and Pierzynski, 2005). Depending on the parent material, soil type, and fertilization practices, the concentration of P in soils can vary from 50 to 3000 mg kg⁻¹ (Sims and Pierzynski, 2005). Although high total P concentrations can be present in soils, the concentrations of P measured in the soil solution are generally low (µM concentrations), especially in highly weathered and oxide rich soils (Johnston et al., 2014).

Soil solution P

Soil solution P represents a minor but critical fraction of total soil P as plant roots take up P as inorganic ions from the soil solution. The speciation of orthophosphate in soil solution is determined by its pH. At pH below 6.5, most orthophosphate is present as H₂PO₄⁻, whereas at a pH higher than 7.5, the dominant P species is HPO₄²⁻. In addition to free orthophosphate, organic P esters (P-O-C bonds) and colloidal P (P associated with Al/Fe oxides and organic matter of size range 1-1000 nm) species can also be present in soil solution (Hens and Merckx, 2002; Shand et al., 2000). Indeed, it has been shown colloidal P can comprise an important fraction of solution P (90%), especially in oxide-rich soils (Haygarth et al., 1997; Hens and Merckx, 2001; Sinaj et al., 1998). Tavakkoli et al. (2013) recently investigated the isotopic exchangeability of colloidal P from filtered soil-water

extracts obtained from neutral and alkaline Australian soils with medium and high organic carbon content. A linear correlation was observed between the concentrations of Al+Fe (related to colloid abundance) and the non-isotopically exchangeable P pool in the soil with medium organic carbon content, whereas in the soil with higher organic carbon content no such relationship was observed (Tavakkoli et al., 2013). Santner et al. (2012) demonstrated that under diffusion-limited P conditions, P associated with Al-oxide nanoparticles enhanced the uptake of P by plants most likely due to P desorption from the nanoparticles near the roots. Since Andisols and Oxisols can have large quantities of soil solution P in colloidal form, the implication of this to plant nutrition needs to be addressed. Furthermore, it has been reported organic P forms can also represent a significant proportion (> 50%) of total P in soil solution (Ron Vaz et al., 1993; Shand et al., 1994); however, its chemical nature and availability to plants has received little attention (Richardson et al., 2005). Using radiolabeled bacterial extracts as organic P sources, Macklon et al. (1997) demonstrated that plants can access orthophosphate-P from dissolved organic P through hydrolysis by root surface phosphatases.

Various analytical methods are available to determine the concentration and speciation of P in solution. Phosphorus measured by colorimetry is usually assumed to correspond to orthophosphate concentration; however, there is ample evidence that other P species (colloidal P and organic P compounds) can hydrolyse during the acidification step and be erroneously detected as orthophosphate by this method (Baldwin, 1998; Sinaj et al., 1998; Van Moorlehem et al., 2011). In addition, membrane filtration, typically over membrane filters with 0.20- or 0.45- μm pore size, has been used to discriminate between dissolved and particulate P in water samples, but this distinction is arbitrary. Small colloidal species can pass through the membrane and be identified as dissolved P. This may give an unrealistic impression of P availability if the P in the small colloids is strongly held and unavailable to

plants. Moreover, filter membranes usually clog during filtration, which can result in a strong reduction of the effective pore size, and hence the pore size of the membrane is not necessarily a good indication of the separation size (Hassellöv et al., 2008). Membranes of smaller pore size (1 kDa ~ 1 nm) have also been used to separate “truly dissolved” P in natural samples (Zhang and Oldham, 2001) but even this kind of separation may still include small colloidal species. Filtration of samples prior to chemical analysis is a standard procedure in laboratories and is justified and encouraged because of its simplicity, the reduction in the chemical complexity of the filtrate, preservation of the samples by removal of bacteria and other microorganisms that can promote biological transformations, and improved data quality obtained with analytical techniques (Doucet et al., 2007). However, filtration also removes the colloidal pool, the importance of which has been recognized as it affects the speciation, bioavailability, and transport of elements in soils (Lead and Wilkinson, 2006).

Soil solid phase P

Most P in soils (> 90%) is present in the solid phase either as adsorbed forms bound to soil particles or organic matter through metal cations, precipitated as phosphate minerals, and as organic forms (Hesterberg, 2010). The main processes that control the distribution of P between solid and liquid phase are adsorption and precipitation. Sorption is a collective term that is used to describe the transfer of P from solution to the solid phase, when the mechanism is unknown (Barrow, 1999). In acidic soils, adsorption is considered the most important mechanism of P sorption. Adsorption can either be non-specific (outer-sphere) or specific (inner-sphere) through ligand-exchange reactions on hydroxylated mineral surfaces (Goldberg and Sposito, 1985; McBride, 1994). It is generally accepted that P sorption in acidic oxide-rich soils occurs primarily by the formation of inner-sphere complexes which are

characterized by strong adsorption forces that are not readily reversible (Fig. 2.1) (Sims and Pierzynski, 2005). The extent of the sorption reactions is determined by the abundance and type of oxide minerals that are present in the soil. For example, amorphous hydrous oxides of Al and Fe are more efficient sorbents than more crystallite forms (Borggaard, 1983; Parfitt, 1979).

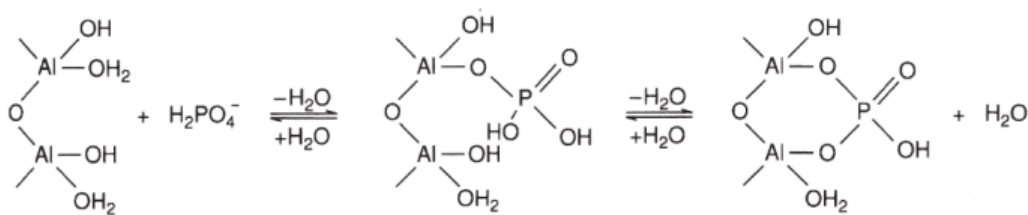


Fig. 2.1 Diagrammatic representation of the adsorption of phosphate to an Al oxide and the formation of the inner-sphere complex (Sims and Pierzynski, 2005).

Precipitation reactions involve the removal of ions in solution to form a new solid-phase compound. Several studies have demonstrated the presence of Ca-P minerals (e.g. hydroxyapatite, octacalcium phosphate) (Beauchemin et al., 2003; Hesterberg et al., 1999; Lombi et al., 2006). It has been suggested that P may also precipitate in acidic soils with Al and Fe to form Al-P and Fe-P mineral phases (Hedley and McLaughlin, 2005; Lindsay et al., 1962). Saturated conditions that facilitate precipitation reactions are expected near the fertilizer application site, but the high concentrations of the ions (Al, Fe and P) are likely to persist only for a short period of time after fertilizer dissolution and hence it is uncertain whether Al/Fe-P minerals (e.g. strengite or variscite) form and/or persist. Earlier work indicated that P in soils was associated with Al, Fe, Si in mixed precipitates more similar to plumbogummite minerals rather than stoichiometrically pure Al-or Fe-phosphate minerals (Norrish and Rosser, 1983). Although it is more widely believed that adsorption is the main sorption mechanism in acid soils (Hesterberg, 2010; Kizewski et al., 2011), recent studies

using x-ray absorption near-edge structure spectroscopy (XANES) have indicated the presence of Al- and Fe-P precipitates in bulk soils (Beauchemin et al., 2003; Khatiwada et al., 2012; Sato et al., 2005) suggesting that precipitation reactions may also play a role in controlling P availability in acidic soils, though it should be kept that differentiation between precipitated Al/Fe-P species or P adsorbed to Al/Fe oxides with spectroscopic techniques is difficult. Moreover, the distinction between adsorption and surface precipitation is not straightforward (Li and Stanforth, 2000).

Availability of P to plants - concepts and measurement

Concepts

From the fertility standpoint, soil P can be conceptualized in a series of forms differing in availability, with the most available forms being termed “labile” and the least available forms termed “non-labile” (Fig. 2.2). Labile P includes orthophosphate-P in the soil solution and the reversibly adsorbed P on the surfaces of the soil components. These two pools are considered in equilibrium, so when P is removed from the solution (e.g. by plant roots), the equilibrium is disturbed and the reversibly adsorbed P desorbs into soil solution. The non-labile P corresponds to P that is not reversibly bound and which is strongly adsorbed to soil particles or in precipitated form. These P forms eventually become available but in a much longer time frame (months, years). Hence, lability as a concept is kinetically defined.

This distribution of P between different pools is often simplified with the Q/I (quantity/intensity) concept. The quantity corresponds to the amount of P in the solid phase that replenishes the soil solution and the intensity to the P concentration in the soil solution. The relationship between quantity and intensity is expressed by the phosphorus buffer capacity (PBC), with a high PBC indicating strong P buffering by the solid phase (Holford, 1997). Phosphorus intensity can be directly measured in the soil solution or estimated by

extraction of the soil with a dilute salt (0.01 M CaCl₂) or water (Ziadi et al., 2013).

Conceptually, isotopic dilution is the most attractive method to determine the quantity or P-buffering pool, but chemical extraction methods are the most common way to estimate the P quantity because of their simplicity (Fardeau, 1995). However, the amount of P extracted is operationally defined by the extractant used, and extracts may mobilize P that is not likely to be plant available in the short term (Demaria et al., 2005).

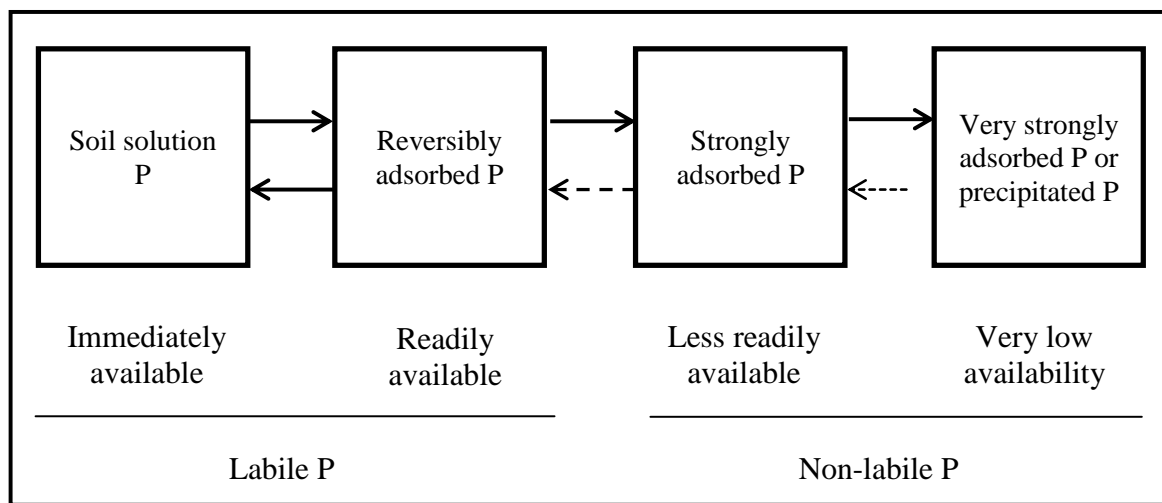


Fig. 2.2 Conceptual diagram for the forms of soil P categorized in terms of plant availability.

Reproduced from (Syers et al., 2008).

Measurement

Various soil tests have been developed for measurement of plant available P in soils including chemical extractant methods, ion sink methods, and the ³³P isotopic dilution technique. As previously stated, chemical extraction methods (e.g. Olsen, Melich 3, Colwell) are common routinely used in laboratories and have been calibrated to make P fertilizer recommendations, but there are drawbacks to these methods.

In order to more accurately determine soil available P, anion exchange resin membranes (Saggar et al., 1990), Fe-oxide impregnated paper (Menon et al., 1990), and

diffusive gradient in-thin films (DGT) (Mason et al., 2008) have been promoted as alternative methods. The principle underlying these methods is that they act as a sink for P and potentially mimic the uptake of P by plant roots. The main advantage of these methods is that the extraction of available P occurs without chemical alteration or change in the pH of the soil, as opposed to the chemical extracts. Recently, Six et al. (2012) showed that in acidic oxide-rich soils conventional soil extracts including, oxalate, Olsen, Colwell, Bray-1, and Mehlich 3 and even the anion exchange membranes measured significant amounts of P that was not accessed by plants (as determined through isotopic dilution), whereas the DGT technique sampled only from the plant-accessible P pool.

The isotopic dilution principle is a widely accepted method that allows discriminating between labile and non-labile soil P pools. In this method, radioactively labelled orthophosphate (^{33}P or ^{32}P) is added to a soil suspension (water or dilute salt extract) and set to an equilibration time to allow exchange of the radioisotope with the most accessible phosphate ions in the soil. In laboratories, operationally defined equilibration times between 1 and 7 days are employed. The isotopically exchangeable P is a function of time, and hence it increases with the exchange time (Fardeau, 1995), but the changes in the amount of available P pool are usually small (Buhler et al., 2003; Pypers et al., 2006). The isotopically exchangeable P (E-value) is then determined by measuring the specific activity (ratio of radioactive P over stable P) of P in the solution. Alternatively, the labile pool can also be determined by measuring the specific activity of P in plants grown in a radiolabeled soil (L-value) (Larsen, 1952; Russell et al., 1954). E- and L-values usually agree (Frossard et al., 1994); however, differences have been reported when L-values were determined with plants that can access non-isotopically exchangeable P likely by secretion of organic acids that can solubilize P from the non-labile pool (Hocking et al., 1997).

Isotopic methods have also been used to measure the fraction of P taken up by plants from fertilizer (Pdff) (Morel and Fardeau, 1991). Two approaches can be used: i) direct labeling in which the P source (e.g., fertilizer) is radiolabeled (tracing) and ii) indirect labeling in which the soil is labelled (isotopic dilution). In the latter approach, the Pdff is calculated from the specific activity of the plants grown in soil with and without added P. This indirect approach has been used to determine Pdff from water-soluble fertilizers and sparingly soluble P sources (Bertrand et al., 2003; Kato et al., 1995; Zapata and Axmann, 1995).

Strongly P-sorbing soils: Andisols and Oxisols

Although P retention is not a criterion for the classification of soils according the Soil Taxonomy, there are soil orders which are characterized by their high P retention capacity, specifically Andisols and Oxisols. Andisols cover about 1% of the world's land area, of which 60% occur in tropical countries (Takahashi and Shoji, 2002). Andisols are dominated by short-range-order aluminosilicate clay-size minerals (allophane, imogolite) and Al/Fe-humus complexes (Buol et al., 2011). Allophane and imogolite are characterized by small particle size (3–6 nm in diameter), high specific surface area (700–1500 m² g⁻¹), permanent and variable charge, and strong affinity for anions such as phosphate (Parfitt, 2009).

Although allophane and imogolite are most commonly found in soils derived from volcanic ash, they can occur in any environment where sufficient Al and Si exist in solution for precipitation and formation of these noncrystalline minerals (Harsh et al., 2002). For management purposes, Andisols can be distinguished as allophanic (dominated by allophane and imogolite) and non-allophanic forms (dominated by Al-humus complexes and 2:1 layer silicates) (Dahlgren et al., 2004). Non-allophanic Andisols are formed preferentially under more acidic conditions (pH < 5) and in an abundance of organic matter (Dahlgren et al.,

2004). It has been observed that allophanic Andisols sorb less P than the non-allophanic Andisols that contain large amounts of Al/Fe-humus complexes (Matsuyama et al., 1998).

Oxisols occupy approximately 8% of the world's land and the largest extents of land containing Oxisols are found in South America and parts of Central Africa (Buol and Eswaran, 1999). Oxisols are formed under processes of intense weathering and leaching that caused disilication and accumulation of Al and Fe oxides. The clay fraction of Oxisols is primarily dominated by 1:1 type silicate minerals (kaolinite), gibbsite ($\text{Al}(\text{OH})_3$), hematite (Fe_2O_3), goethite (FeOOH), and other Al/Fe (hydr)oxides (Buol and Eswaran, 1999).

As previously stated, the Al/Fe compounds found in Andisols and Oxisols are mainly responsible for the sorption of phosphate. It is generally accepted that phosphate is adsorbed by initial adsorption reactions through ligand exchange, followed by further slow reactions. In the case of (hydr)oxides, this slow reaction has been attributed to migration of the phosphate ion further into the particles or within the pore spaces of aggregated small particles (Willett et al., 1988). In the case of allophanes, the slow reaction has been linked to the disruption of the allophane structure exposing more reactive sites and possible precipitation of aluminium phosphates (Parfitt, 1989; Rajan, 1975).

Because of the high capacity of these soils to sorb P through adsorption or precipitation reactions, soil available P is very low and should be supplemented by the use of P fertilizers. Given that Andisols and Oxisols are extensively present in regions with limited access to P fertilizers (e.g. countries of Africa), agronomic management practices (e.g. fertilizer placement or the use of crops tolerant to low P soils) have been investigated and implemented to improve the efficiency of added P and to reduce the application rates (Sanchez and Uehara, 1980). These practices are discussed in the next section.

Management of P in strongly P-sorbing soils

Increasing the efficiency of added P has been for long time the main goal of nutrient management research. The main approach to improve fertilizer efficiency has been the implementation of best management practices for fertilizers - the 4Rs principle - that involves the use of right rate, right source, right time, and right place (IPNI, 2014). However, for strongly P-sorbing soils, integrating plant species that are tolerant to low levels of soil P is also an important strategy to enhance P use efficiency (Sanchez and Uehara, 1980).

Plant mechanisms to improve P acquisition

Plants that are genetically adapted to low P soils are often characterized by low P requirement and/ or increased efficiency in taking up P from the soil (Rao et al., 1999). A key trait to efficiently acquire P from the soil is the enhancement of the root system through greater root growth, modification of root architecture and development of root hairs (Lynch and Brown, 2008). There is evidence that plants that are able to produce more roots and more root hairs are likely to be better adapted to grow in soils with low P status (Gahoonia and Nielsen, 1998; Vandamme et al., 2013). Indeed, this is a desirable phenotypical trait for selecting genotypes in breeding programs (Lynch and Brown, 2008).

Another adaptive response of certain plants to P deficiency is the exudation of low-molecular weight organic acids especially malic and citric acids from the root into the rhizosphere (Jones, 1998; Vance et al., 2003). Hocking et al. (1997) showed that white lupin and pigeon pea grown in a P-deficient Oxisol accessed soil P from a pool that was inaccessible to other species (e.g. wheat) most likely by the ability of these species to secrete organic acids that can solubilize inorganic bound P.

Management practices to improve fertilizer efficiency

Selecting right place

Broadcast and banding are fertilizer placement options that have been investigated for enhancing plant response to added P. In strongly P-sorbing soils, banding of the P fertilizer near the root zone is in general a more efficient placement option than broadcasting application (McLaughlin et al., 2011; Randall and Hoefl, 1988). Banding concentrates the fertilizer in a small volume of soil resulting in saturation of sorption sites and therefore higher P solution concentrations for plant uptake (Havlin et al., 2006). In a long term field study, Smyth and Cravo (1990) reported greater yields for initial corn and cowpea grown in an Oxisol, when triple superphosphate was banded than when applied broadcast at equal P rates. Conversely, in calcareous soils where precipitation reactions most likely control P availability banding may reduce fertilizer P efficiency (McLaughlin et al., 2011).

Given that added P can react with the soil components and be transformed into forms no longer available to the plants, applying P to the leaves may be an option to enhance fertilizer efficiency (Fernández and Brown, 2013; McLaughlin et al., 2011). A recent review by Noack et al. (2010) on research on foliar P fertilization found that mixed results have been reported on literature regarding the effectiveness of foliar P on grain yield. Variables such as soil P level, soil water status, crop type, fertilizer formulation and climatic conditions may influence a response to foliar P application (Noack et al., 2010).

Selecting right source

The most common inorganic P fertilizers are water-soluble ammonium phosphates and superphosphates and sparingly soluble reactive phosphate rock (see further). The selection of the right fertilizer source will depend on the soil chemical properties (e.g. pH, P sorption capacity), crop type, and the environmental conditions. For example, slow release P fertilizers

such as the sparingly soluble P sources may be preferred P fertilizers where P is susceptible to loss by leaching (Hart et al., 2004). Fluid P sources have been reported to be more effective than granular P fertilizers in calcareous soils (Holloway et al., 2001) (see further).

Behaviour of P fertilizers in soils

The chemical characteristics of the soil and the form of P applied determine the reactions that occur when fertilizer is added to soil, which ultimately determine the availability of P to the plants. When granular P fertilizers are applied to the soil, the first process that takes place is wetting of the granule mostly by mass and capillary flow of water from the moist soil toward the hygroscopic granule, forming a saturated phosphate solution at the granule surface (Lawton and Vomocil, 1954; Williams, 1969). Opposite to this movement of water, there is outward movement of P from the saturated solution to the soil by an osmotic pressure gradient which continues as long as the concentrated salt remains (Hedley and McLaughlin, 2005). The initial high P concentrations around the fertilizer granule may favour P precipitation reactions.

Benbi and Gilkes (1987) conceptualized three zones that form adjacent to a fertilizer granule as it dissolves, which are represented in Fig. 2.3 (as revised by Hedley and McLaughlin, 2005).

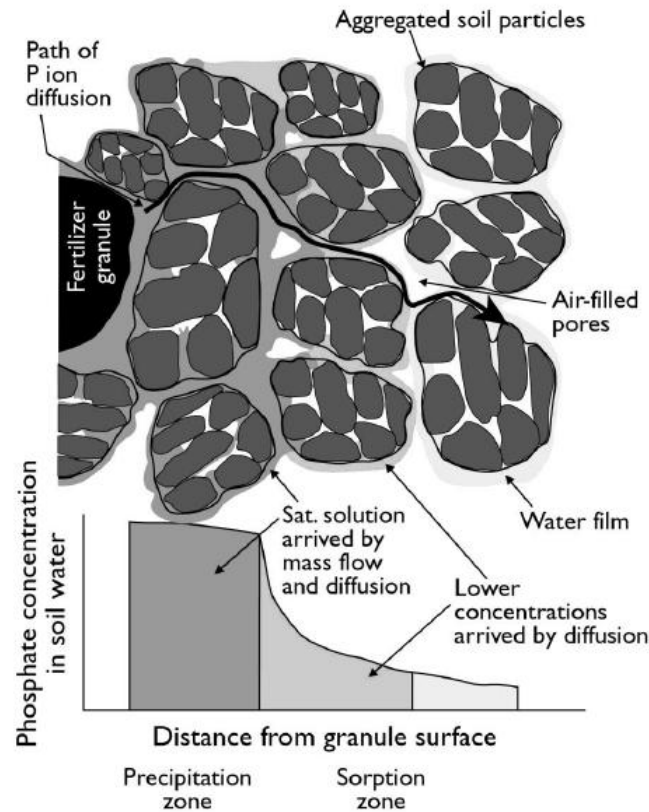


Fig. 2.3 Diagrammatic representation of the movement of phosphate by mass flow and diffusion from the granule of water-soluble P fertilizer, figure not to scale. (Hedley and McLaughlin, 2005).

The first zone is the immediate fertilizer-soil interface and residual granule. In this zone the amount and type of P compounds that form depends primarily on the chemical form of P applied. For example, when monocalcium phosphate is applied to the soil it dissolves forming a saturated solution that Lindsay and Stephenson (1959) described as having similar Ca and P concentrations to the metastable triple point solution they obtained in a pure system. As the solution moves away from the granule, precipitates of dicalcium phosphate dihydrate and anhydrous dicalcium phosphate remain at the granule site (Lehr et al., 1959). Experimental studies have indeed shown that some P is retained at the site of application and does not move into the soil. For instance, Lombi et al. (2004) showed that about 12% of P

applied as monoammonium phosphate (MAP) in a calcareous soil remained in the granule after 5 weeks of incubation. Based on results of X-ray diffraction analysis, these authors concluded that the incomplete dissolution of the granule occurred in part because of the presence of insoluble crandallite-like minerals $[\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot (\text{H}_2\text{O})]$ in the granule, and in part because *in situ* precipitation of Ca-P compounds probably due to Ca diffusion from the soil into the granule.

The second zone corresponds to P-saturated soil next to the granule where precipitation reactions control the fate of P. In this zone, the pH of the saturated solution and the concentration of P and of the accompanying cation control the reaction with the soil. For example, the saturated solution of the monocalcium phosphate fertilizer is strongly acidic (pH 1.5) and in acid and neutral soils can cause the dissolution of aluminosilicates and hydrous oxides of Al and Fe, increasing the concentration of Al and Fe in solution and causing its co-precipitation with the saturated P solution as Al-P or Fe-P (Hedley and McLaughlin, 2005; Lindsay, 1979). In contrast, the saturated P solution of diammonium phosphate with a pH of 8 may cause less solubilisation of Al and Fe, but can favour the precipitation of Ca and Mg phosphates (Moody et al., 1995). Direct evidence that precipitation is an important process that may control P availability in the vicinity of the fertilizer site has indeed been found for calcareous soils. Lombi et al. (2006) reported that octacalcium phosphate (OCP) and apatite-like minerals were the predominant P reaction products when MAP was applied in granular form, whereas forms similar to monocalcium phosphate (more soluble than OCP and apatite) were reported when P was applied as fluid MAP. In contrast, few spectroscopic studies have reported on the presence of Al/Fe-P precipitates in soils (Kizewski et al., 2011) suggesting that precipitation of P with Al and Fe is generally not an important process, but that adsorption reactions are more likely to control P solubility in acidic soils.

The third region corresponds to the unsaturated P zone, where principally soil properties affect fertilizer P availability. In this zone, adsorption processes dominate as the P sorption maximum is not exceeded and the concentrations of P and other ions do not exceed the solubility product of possible mineral phases (Hedley and McLaughlin, 2005). The extent of P sorption is usually related to the abundance and nature of Al/Fe oxyhydroxides in acidic soils (McLaughlin et al., 1981), whereas in alkaline soils the presence of carbonates and Fe oxides may control P retention (Ryan et al., 1985). Benbi and Gilkes (1987) reported less P sorption and greater mobility of P out of the zone near the fertilizer granule in a soil with 2% sesquioxides than in a soil with 60% sesquioxides. The generally higher P sorption capacity of Andisols than of Oxisols has been related to the presence of allophane and imogolite and organometallic complexes which sorb more P than the Al/Fe oxides from the Oxisols (Parfitt, 1989; Sanchez and Uehara, 1980; Violante and Pigna, 2002).

Phosphorus fertilizers

Current P fertilizer formulations

In soils with low status of available P, the application of P fertilizers is necessary for optimal crop production. Water-soluble P fertilizers such as superphosphates and ammonium phosphates are the dominant P sources used in agricultural production systems worldwide (Table 2.1). The superphosphates include: single superphosphate (SSP, 9%P, 19%Ca, 11%S) and triple superphosphate (TSP, 20%P, 15%Ca), which are produced by the reaction of rock phosphate with sulphuric acid to obtain SSP, or by reaction of phosphoric acid with rock phosphate for TSP. The ammonium phosphates, monoammonium phosphate (MAP, 22%P, 11%N) and diammonium phosphate (DAP, 20%P, 18%N), are produced by the reaction of phosphoric acid with anhydrous ammonia. Because transportation, handling, and storage can constitute a relatively high fraction of the final fertilizer cost, the phosphate fertilizer industry

mainly produces these high analysis P fertilizers (Leikam and Achorn, 2005). Currently, about 75% of the phosphate rock produced worldwide is used to produce phosphoric acid as this is the precursor for production of high analysis fertilizers (e.g. ammonium phosphates) (Van Kauwenbergh, 2010).

Table 2.1 Global use of common phosphate fertilizers (Hedley and McLaughlin, 2005).

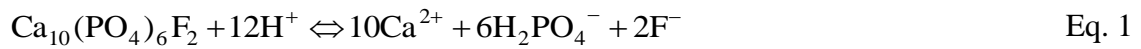
Product	Typical %P	% of fertilizer used	
		1973/1974	1998/1999
Phosphate rock direct application	9-15	5.5	1.7
Single superphosphate	7-10	24.6	20.9
Triple superphosphate	20	11.1	6.5
NPK mixtures		34.6	20.9
Ammonium phosphates	20-23	13.8	42.2
Other NP compounds†		3.2	4.7
Others†		7.3	3.0

†Other NP compounds include nitrophosphates and ammonium phosphates other than monoammonium phosphate (MAP) and diammonium phosphate (DAP).

Phosphorus fertilizers are available in granular or fluid form. Granular P forms constitute the most commonly used fertilizer type, but fluid P is the preferred option in certain agricultural systems due to ease of handling and versatility of application (Havlin et al., 2006).

Direct application of phosphate rock has been used as an alternative to supply P to acidic soils in low-input agricultural systems as this is a cheaper P source than manufactured fertilizers (Hammond et al., 1986; Rajan et al., 1996; Sanchez and Salinas, 1981). Phosphate rock is sparingly soluble, hence the potential to supply plant available P is determined by the rate of dissolution in soils. As described in the reaction for fluorapatite (Eq. 1), the supply of

protons favors the congruent dissolution of phosphate rock (Hammond et al., 1986; Khasawneh and Doll, 1979):



The rate of dissolution can be enhanced by reducing the particle size of the phosphate rock as this ensures more surface area is in contact with the soil (Hedley and McLaughlin, 2005; Khasawneh and Doll, 1979). This is demonstrated by data from pot and field trials where plant dry matter and P uptake increased when the applied phosphate rock was ground to finer particle sizes (Alston and Chin, 1974; Cooke and Widdowson, 1959). However, grinding to a particle size less than 150 μm was observed to offer little further advantage (Kanabo and Gilkes, 1988; Khasawneh and Doll, 1979).

Despite its lower price, phosphate rock is not widely used as a P source to fertilize soils (Table 2.1). Phosphate rock is a less efficient P fertilizer than water-soluble P sources because of the slow rate of dissolution (Bolland and Gilkes, 1990; Hammond et al., 1986) which makes it unsuitable for short-term crops with an initial high demand of P, but it is potentially more appropriate for perennial crops and pastures (Bolan et al., 1990; Hedley and McLaughlin, 2005).

Modifying current fertilizer formulations to improve fertilizer P efficiency

A potential strategy to reduce P sorption by soils and thereby improve the efficiency of P fertilizers is through the modification of fertilizer formulations. The strategies that have been evaluated and/or suggested include altering the soil pH near the fertilizer granule (Owino-Gerroh and Gascho, 2005), the use of polymers and organic chelating agents (Gordon and Tindall, 2006; Urrutia et al., 2014), and the use of fluid P fertilizers (Holloway et al., 2001; Khatiwada et al., 2012). More recently, it has been suggested that the use of nanofertilizers may have potential for improving fertilizer efficiency (DeRosa et al., 2010).

The selection of the most appropriate technology will depend on the particular chemical properties of the soils.

Because soil pH can affect P retention reactions, methods have been developed to modify soil pH near the fertilizer application point to enhance P solubility (McLaughlin et al., 2011). Owino-Gerroh and Gascho (2005) reported for instance that the application of sodium silicate to an acidic Ultisol significantly increased the shoot P concentration from 0.55 mg g⁻¹ to 0.91 mg g⁻¹. The authors concluded that sodium silicate increased the soil pH and most likely the solubility of added P was enhanced as precipitation reactions of P with Al and Fe were diminished.

It has been also suggested that cation-chelating compounds may reduce P sorption because of complexation of the P-sequestering cations Ca, Al, and Fe (Gordon and Tindall, 2006). An example of a product with such properties is maleic-itaconic acid copolymer which has been marketed as an enhancer of P fertilizers (Gordon and Tindall, 2006). In a laboratory study, Degryse et al. (2013) evaluated the effect of coating granular MAP with the copolymer. The authors concluded that even at very high (unrealistic) application rate (100%) of the copolymer little effect on P diffusion was observed in a strongly P-sorbing Oxisol. These results are consistent with evidence from a large number of field trials where the response of plant yield to the copolymer was 1.2% ± 1% relative to the control treatment. This lack of effect is also expected based on theoretical calculations, and such compounds should hence not be recommended as an approach to increase the efficiency of fertilizer added P (Chien et al., 2014).

Another approach that has been investigated is the use of fluid P fertilizers instead of solid granular forms. Earlier studies that compared the effectiveness of fluid and granular P fertilizers in acidic to neutral soils did not find differences in plant response (Miner and Kamprath, 1971; Rhue et al., 1981; Subbarao and Ellis, 1975). However, in these studies

comparisons were made between fertilizers containing different chemical compounds (e.g. polyphosphate vs. orthophosphate), which may have confounded the results (Engelstad and Terman, 1980). As previously mentioned, the effectiveness of fluid fertilizers in calcareous alkaline soils of Australia was investigated in field and greenhouse studies. Higher plant P uptake and dry matter yield were observed when P was applied in fluid than in granular form for fertilizers of the same chemical composition (granular MAP vs. fluid MAP) (Bertrand et al., 2006; Holloway et al., 2001). The higher fertilizer efficiency with the fluid form was explained by the enhanced P diffusion resulting in less concentrated P environments and hence less formation of Ca-P precipitates (Lombi et al., 2006). A recent study in a non-calcareous soil (pH 5.9) also reported greater available P measured by a resin exchange membrane technique with fluid than with granular MAP (Khatiwada et al., 2012). There has been little evaluation of the effect of fertilizer type (fluid or granular) on P diffusion and bioavailability in strongly P-sorbing acidic soils (Andisols and Oxisols).

High expectations have been placed on the potential use of nanotechnology in fertilizer development. In nanofertilizers, nutrients (e.g. N, P, K) can be encapsulated in nanotubes or nanoporous materials, or coated with a thin protective polymer film, or delivered as nanoparticles or emulsions (DeRosa et al., 2010). To date, nanofertilizers have been mainly prepared for the slow-release of nutrients and various materials have been investigated (Gogos et al., 2012). For example, Corradini et al. (2010) explored the use of chitosan nanoparticles obtained by polymerizing methacrylic acid for the incorporation of N, P, K nutrients as a potential slow release fertilizer. In another study, Kottegoda et al. (2011) investigated the release of nitrogen (N) from urea-modified hydroxyapatite nanoparticles encapsulated into the cavities of soft wood *Gliricidia sepium*. The authors reported that the nanofertilizer exhibited a sustained slow-release of N that continued even 60 days after the application in the soil, in contrast to the conventional urea fertilizer that released an initial

large quantity of N. In another study, zeolite NaP1/hydroxyapatite composites containing ammonium, potassium and phosphate ions were prepared and claimed as a novel slow-release N, P, K nanofertilizer (Watanabe et al., 2014). Recently Liu and Lal (2014) investigated in a pot trial the potential use of hydroxyapatite nanoparticles (15 nm) as a novel P fertilizer of enhanced efficiency and of lower eutrophication risk than conventional water-soluble calcium dihydrogen phosphate. The authors concluded the plants that received the nanofertilizer produced greater plant biomass and soybean seeds yield compared to the plants fertilized with the regular water-soluble P source, though their statistical tests showed no significant differences between the treatments.

Nanomaterials

General properties

Nanomaterials are commonly defined as particulate material with at least one dimension that is smaller than 100 nm (Borm et al., 2006; Christian et al., 2008). Nanoparticles are widely present in the environment derived from natural sources (e.g. colloids in soil and aquatic systems, aerosols from volcanic eruptions) or as a consequence of anthropogenic activities (e.g. industrial emissions, vehicle exhausts). In recent years, there has been much interest in manufactured nanoparticles which are intentionally produced and have increasingly been used in commercial applications (Navarro et al., 2008; Tourinho et al., 2012). The unique characteristics of very small particle size and hence high surface area to volume ratio provide the nano-sized materials with unique physico-chemical properties that make them suitable for numerous applications (Christian et al., 2008; Handy et al., 2008). Manufactured nanoparticles are mainly used in the fields of electronics, pharmaceuticals, energy, medicine, and environmental remediation (Nowack and Bucheli, 2007). Recently it

has been proposed nanotechnology can be used as a tool to enhance crop yield while reducing the negative environmental effects of agricultural production (Chen and Yada, 2011).

Behaviour of manufactured nanoparticulate nutrients in soils

The fate and behaviour of manufactured nanoparticles when released to the environment depend on the intrinsic properties of the particle (e.g. size, surface charge and coating) and the physico-chemical properties of the surrounding media (e.g. pH, ionic strength, organic matter) (Petosa et al., 2010). If nanoparticulate nutrients are intended to be used as fertilizers, soils and plants will be the direct exposure pathway, either through direct application to the soil or as foliar fertilizers to the plants. Soils are complex media that provide a large sink of reactive surfaces that may interact with the applied nanoparticles influencing their mobility and bioavailability (Batley and McLaughlin, 2010). The key processes that affect nanoparticle fate and bioavailability in soils are aggregation, dissolution, transport, direct uptake, and bioaccumulation (Fig. 2.4) (Klaine et al., 2008).

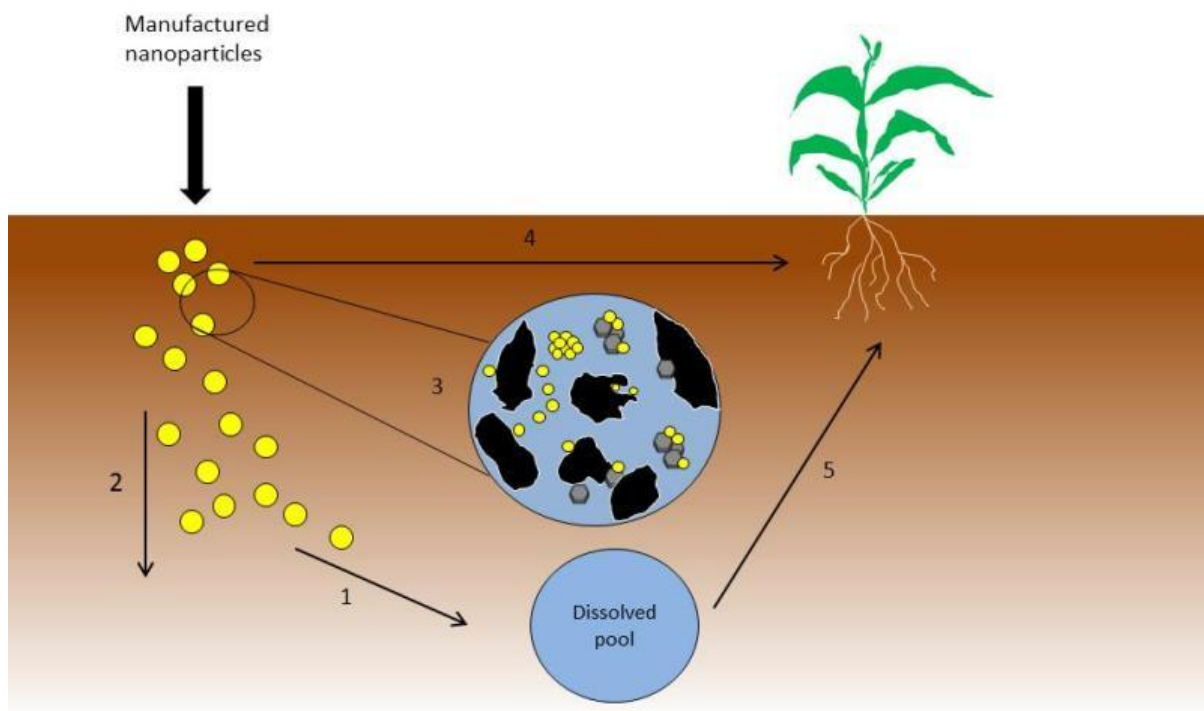


Fig. 2.4 Key processes affecting nanoparticle fate and bioavailability in soils: (1) Dissolution; (2) Transport; (3) Aggregation; (4) Particle direct uptake; (5) Plant/soil biota bioaccumulation. Reproduced from Klaine et al. (2008)

Aggregation

Nanoparticles in suspension move randomly by Brownian motion, but eventually collisions between particles can occur resulting in aggregation (Hotze et al., 2010). In soils, aggregation of manufactured nanoparticles may occur as homoaggregation by attachment of similar particles and heteroaggregation by attachment of dissimilar particles (e.g. manufactured nanoparticles attached to natural colloids) (Cornelis et al., 2014). Coating the surface of the nanoparticles with polymers or surfactants is a common approach to prepare stable (i.e. not aggregating) nanoparticle suspensions, as these compounds can provide an electrostatic or steric barrier that prevent nanoparticles aggregation (Lin et al., 2010). However the stabilizing effects may be reduced as some capping compounds can be easily degraded in soils (e.g. organic acids) (Cornelis et al., 2014).

The soil properties that mainly affect aggregation of nanoparticles are ionic strength, pH, and organic matter content (Hotze et al., 2010). For example, a higher ionic strength in the soil solution reduces the thickness of the electrostatic double layer and hence promotes nanoparticle aggregation (Handy et al., 2008; Jiang et al., 2009). Natural colloids, like Al and Fe oxyhydroxides which are commonly present in soils, have a relatively high point of zero charge ($\text{pH}_{\text{PZC}} = 7-9$) (Qafoku et al., 2004); therefore at soil pH values below their isoelectric point the positively charged surfaces will provide favourable electrostatic conditions for attachment of negatively charged nanoparticles (i.e. heteroaggregation). However, the presence of organic matter may enhance nanoparticle stability by masking the charges of soil minerals that would otherwise facilitate attachment (Wang et al., 2012a).

Dissolution

Particle dissolution kinetics are size-dependent, consequently nanoparticles are expected to dissolve faster than larger particles of the same material (Borm et al., 2006), as has been experimentally shown in pure systems (Ma et al., 2011; Zhang et al., 2010). However, despite this faster dissolution, nanoparticles may not necessarily behave differently from their bulk counterpart. For instance, Milani et al. (2012) studied the dissolution kinetics Zn from MAP coated with ZnO nanoparticles or bulk ZnO and found that there was no difference in the dissolution rate, likely because in both cases the ZnO had transformed to the same chemical form.

Transport

The mobility of nanoparticles in soils is affected by its interaction with the soil matrix. Aggregation is the main process that restricts the transport of nanoparticles in soils. For example, homoaggregation leads to particle entrapment in soil pores if these are smaller than

the size of the aggregates. Darlington et al. (2009) found that aluminium oxide nanoparticles of different sizes (50, 80, and 120 nm) had similar, limited mobility in saturated soil columns because of nanoparticle aggregation. Heteroaggregation may also lead to reduced nanoparticle mobility in natural soils. Cornelis et al. (2013) studied the transport of polyvinylpyrrolidone coated-silver (Ag) nanoparticles of particle size 40 nm in flow-through column experiments in 11 soils. In all soils, the mobility of Ag nanoparticles was restricted as evident from the low mass recovery of Ag in the leachates (0.2 – 9%). Attachment of the negatively charged Ag nanoparticles to the positively charged soil colloids was most likely the reason for the low mobility.

Potential mechanisms to improve fertilizer efficiency with nanotechnology

The potential mechanisms by which nanofertilizers may enhance nutrient uptake is through the controlled release of nutrients to synchronize with crop uptake, enhanced transport through the soil potentially reaching plant roots, or even direct uptake by the plant (DeRosa et al., 2010).

Direct uptake by plants

Direct uptake of nanofertilizers by plant roots can occur if the nanoparticles are very small, as the pore diameter of plant cell walls (5–20 nm) limits the uptake of large particles (Nair et al., 2010). A few studies have indeed reported direct uptake of nanoparticles by roots of plants grown in nutrient solutions (Lin and Xing, 2008; Wang et al., 2012b; Zhu et al., 2008) and even in soil (Zhao et al., 2012a). For example, Wang et al. (2012b) exposed maize seedlings for two days to a solution containing copper oxide (CuO) nanoparticles of size range 20–40 nm and showed, using transmission electron microscopy (TEM) that the CuO nanoparticles were not only present inside the root cell wall, but also in the intercellular space

and the cytoplasm of the cortical cells. In a similar way, ZnO nanoparticles were observed in the root epidermis and cortex and within the xylem cells of soil-grown plants (Zhao et al., 2012a). It is not very well established which route plants use for nanoparticle uptake as there are examples in the literature that support both apoplastic (Wang et al., 2012b; Zhao et al., 2012a; Zhao et al., 2012b) and symplastic (Lin et al., 2009; Zhao et al., 2012a) pathways. Translocation from the root to the shoot may occur through translocation of the nanoparticle itself or because of dissolution of the nanoparticle inside the root and subsequent translocation of the ionic element. Translocation of particles was reported by Zhu et al. (2008) who used magnetization to determine the presence of iron oxide (Fe_3O_4) nanoparticles in roots and shoots of *Cucurbita maxima* (pumpkin) grown in solution culture. However, no magnetic signals in the shoots were detected when the plants were grown in soil (Zhu et al., 2008).

Direct uptake of nanofertilizers is also possible through foliar application; in which case nanoparticles may enter through the stomatal openings or through the bases of trichomes and then be translocated to various tissues (Nair et al., 2010). Few studies have reported foliar uptake of engineered nanoparticles (Birbaum et al., 2010; Corredor et al., 2009; Wang et al., 2013). Corredor et al. (2009) investigated the penetration and transport of iron-carbon nanoparticles in pumpkin plants by injecting the nanoparticle suspension into the pith cavity of the leaf petiole and by placing droplets on the leaf surface close to the insertion point of the petiole. Electron microscopy results showed intracellular localization of the nanoparticles and displacement from the application point possibly through the vascular system. In another study, Wang et al. (2013) reported aerosolized nanoparticles sprayed onto leaf surfaces of watermelon plants were able to penetrate the stomata *via* gas uptake translocated through the phloem and reach the roots. However, other studies reported no translocation of the nanoparticles in the plants after incorporating into the leaves (Birbaum et al., 2010). It is

likely that the particle size and number concentration are important factors for the translocation of nanoparticles inside the plants (Wang et al., 2013).

Enhanced transport through the soil

Provided that nanoparticles are not retained in the soil's solid phase, nanoparticles in the soil solution can potentially reach plant roots through mass flow as a result of transpirational water uptake by the plant (Asli and Neumann, 2009). In this case, nanoparticles can be directly taken up by the roots of the plants. Furthermore, transport of the nanoparticles with mass flow could potentially be a strategy to fertilize impoverished subsoils. Studies on semiarid cropping systems of Australia showed significant increments in crop yields with deep placement of P fertilizers, but this is an expensive practice. Fertilizing subsoils with mobile nanoparticles may be an economically sound alternative.

Aim and specific objectives of this thesis

The aim of this work was to investigate possible strategies to improve the efficiency of added P and soil P in Andisols and Oxisols.

Specifically, the objectives of this thesis were:

1. to investigate the effect of fertilizer type (granular vs. fluid) on the chemical processes that control the fate of fertilizer P when applied in acidic and strongly P-sorbing soils;
2. to evaluate the agronomic effectiveness of granular and fluid P fertilizers for wheat grown in Andisols and Oxisols;
3. to evaluate the potential use and efficiency of hydroxyapatite nanoparticles as P fertilizer in Andisols and Oxisols; and
4. to evaluate the contribution of colloidal P from the soil-water extracts of Andisols and Oxisols to plant P nutrition.

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CHAPTER 3

Fluid fertilizers improve phosphorus diffusion but not lability
in Andisols and Oxisols

Statement of Authorship

Title of Paper	Fluid fertilizers improve phosphorus diffusion but not lability in Andisols and Oxisols
Publication Status	<input checked="" type="radio"/> Published, <input type="radio"/> Accepted for Publication, <input type="radio"/> Submitted for Publication, <input type="radio"/> Publication style
Publication Details	Montalvo, D., F. Degryse, and M.J. McLaughlin. 2014. Fluid fertilizers improve phosphorus diffusion but not lability in Andisols and Oxisols. Soil Sci. Soc. Am. J. 78(1): 214-224. doi:10.2136/sssaj2013.02.0075

Author Contributions

By signing the Statement of Authorship, each author certifies that their stated contribution to the publication is accurate and that permission is granted for the publication to be included in the candidate's thesis.

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Contribution to the Paper	Performed analysis on all samples, interpreted data, wrote the manuscript and acted as corresponding author.		
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Contribution to the Paper	Supervised development of the work, helped with data interpretation and manuscript evaluation.		
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Signature		Date	

Montalvo, D., Degryse, F. & McLaughlin, M.J. (2014). Fluid fertilizers improve phosphorus diffusion but not lability in Andisols and Oxisols. *Soil Science Society of America Journal*, 78(1), 214-224.

NOTE:

This publication is included on pages 49 - 59 in the print copy of the thesis held in the University of Adelaide Library.

It is also available online to authorised users at:

<http://dx.doi.org/10.2136/sssaj2013.02.0075>

CHAPTER 4

Agronomic effectiveness of granular and fluid phosphorus fertilizers in Andisols and Oxisols evaluated by ^{33}P isotopic dilution technique

Statement of Authorship

Title of Paper	Agronomic effectiveness of granular and fluid phosphorus fertilizers in Andisols and Oxisols evaluated by ³³ P isotopic dilution technique		
Publication Status	<input type="radio"/> Published, <input type="radio"/> Accepted for Publication, <input checked="" type="radio"/> Submitted for Publication, <input type="radio"/> Publication style		
Publication Details	Submitted for publication Soil Science Society of America Journal		

Author Contributions

By signing the Statement of Authorship, each author certifies that their stated contribution to the publication is accurate and that permission is granted for the publication to be included in the candidate's thesis.

Name of Principal Author (Candidate)	Daniela Montalvo Grijalva		
Contribution to the Paper	Performed analysis on all samples, interpreted data, wrote the manuscript and acted as corresponding author.		
Signature		Date	

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Contribution to the Paper	Supervised development of the work, helped with data interpretation and manuscript evaluation.		
Signature		Date	

Name of Co-Author	Mike J. McLaughlin		
Contribution to the Paper	Supervised development of the work and manuscript evaluation.		
Signature		Date	

Name of Co-Author			
Contribution to the Paper			
Signature		Date	

Montalvo, D., Degryse, F. & McLaughlin, M.J. (2015). Published as 'Agronomic effectiveness of granular and fluid phosphorus fertilizers in Andisols and Oxisols'. *Soil Science Society of America Journal*, 79(2), 577-584.

NOTE:

This publication is included on pages 63 - 86 in the print copy of the thesis held in the University of Adelaide Library.

It is also available online to authorised users at:

<http://dx.doi.org/10.2136/sssaj2014.04.0178>

CHAPTER 5

Efficacy of hydroxyapatite nanoparticles as phosphorus
fertilizer in Andisols and Oxisols

Statement of Authorship

Title of Paper	Efficacy of hydroxyapatite nanoparticles as phosphorus fertilizer in Andisols and Oxisols
Publication Status	<input type="radio"/> Published, <input type="radio"/> Accepted for Publication, <input checked="" type="radio"/> Submitted for Publication, <input type="radio"/> Publication style
Publication Details	Submitted for publication Soil Science Society of America Journal

Author Contributions

By signing the Statement of Authorship, each author certifies that their stated contribution to the publication is accurate and that permission is granted for the publication to be included in the candidate's thesis.

Name of Principal Author (Candidate)	Daniela Montalvo Grijalva		
Contribution to the Paper	Performed analysis on all samples, interpreted data, wrote the manuscript and acted as corresponding author.		
Signature		Date	

Name of Co-Author	Mike J. McLaughlin		
Contribution to the Paper	Supervised development of the work and manuscript evaluation.		
Signature		Date	

Name of Co-Author	Fien Degryse		
Contribution to the Paper	Supervised development of the work, helped with data interpretation and manuscript evaluation.		
Signature		Date	

Name of Co-Author			
Contribution to the Paper			
Signature		Date	

Montalvo, D., Degryse, F. & McLaughlin, M.J. (2015). Efficacy of hydroxyapatite nanoparticles as phosphorus fertilizer in Andisols and Oxisols. *Soil Science Society of America Journal*, 79(2), 551-558.

NOTE:

This publication is included on pages 89 - 112 in the print copy of the thesis held in the University of Adelaide Library.

It is also available online to authorised users at:

<http://dx.doi.org/10.2136/sssaj2014.09.0373>

CHAPTER 6

Natural colloidal P and its contribution to plant P uptake

Statement of Authorship

Title of Paper	Natural colloidal P and its contribution to plant P uptake
Publication Status	<input type="radio"/> Published, <input type="radio"/> Accepted for Publication, <input checked="" type="radio"/> Submitted for Publication, <input type="radio"/> Publication style
Publication Details	Submitted for publication Environmental Science & Technology

Author Contributions

By signing the Statement of Authorship, each author certifies that their stated contribution to the publication is accurate and that permission is granted for the publication to be included in the candidate's thesis.

Name of Principal Author (Candidate)	Daniela Montalvo Grijalva		
Contribution to the Paper	Performed analysis on all samples, interpreted data, wrote the manuscript and acted as corresponding author.		
Signature		Date	

Name of Co-Author	Fien Degryse		
Contribution to the Paper	Supervised development of the work, helped with data interpretation and manuscript evaluation.		
Signature		Date	

Name of Co-Author	Mike J. McLaughlin		
Contribution to the Paper	Supervised development of the work and manuscript evaluation.		
Signature		Date	

Name of Co-Author			
Contribution to the Paper			
Signature		Date	

Montalvo, D., Degryse, F. & McLaughlin, M.J. (2015). Natural colloidal P and its contribution to plant P uptake.

Environmental Science and Technology, 49(6), 3427-3434.

NOTE:

This publication is included on pages 115 - 138 in the print copy of the thesis held in the University of Adelaide Library.

It is also available online to authorised users at:

<http://dx.doi.org/10.1021/es504643f>

Conclusions and future outlook

Phosphorus is the main nutrient that limits productivity in Andisols and Oxisols. In these soils, where strong adsorption reactions control P availability, enhancing the availability of fertilizer P or of P already present in the soil is very challenging. Current management practices have mainly focused on increasing the levels of soil P through large fertilizer applications which is certainly an unsustainable practice in the long term. Even though there is no doubt that P fertilizers will continue to be indispensable for modern agricultural production, the selection and application of P fertilizers needs to be more targeted and should consider the physical and chemical properties of the soils. However, in order to develop new management practices and fertilizer formulations to increase the availability of soil and added P, it is necessary to better understand the chemical behaviour of P in these soils. This thesis represents a substantial contribution in this direction. The main conclusions that can be drawn from this thesis are detailed below:

1. Fluid fertilizers enhanced P diffusion but not lability in Andisols and Oxisols.

A significantly greater diffusion of P was observed with fluid MAP than with granular MAP in the four strongly P-sorbing soils that were used in this study (two Andisols and two Oxisols). Differences in the physical and chemical processes that occur after the application of either fertilizer type mainly explain these results. In the case of granular fertilizers, the diffusion of P outward from the point of application is restricted by the movement of water

from the soil toward the hygroscopic granule by mass and capillary flow (Lawton and Vomocil, 1954). Such an event does not occur with the fluid source but only an outward mass flow of the solution (Miner and Kamprath, 1971). The greater diffusion of P in the soil with the fluid fertilizer also reduces the formation of highly P concentrated zones, where P availability can be reduced due to precipitation reactions. This has been identified as the main reason why fluid P fertilizers are more effective than granular forms in calcareous soils (Hettiarachchi et al., 2006; Lombi et al., 2004).

In terms of lability (i.e. the amount of P from the fertilizer that remained isotopically exchangeable after 24 h of equilibration time), a greater percentage of added P remained labile when added as granular MAP (41% labile) than when added as fluid MAP (25% labile) in the Oxisols. In the Andisols, no significant difference was observed in the percentage of labile P between the two fertilizer types (circa 25% labile). These results suggest that in soils where strong adsorption rather than precipitation reactions limit P availability, the greater diffusion of fertilizer P in the soil with the application of fluid forms does not reduce – and may even enhance – the transformation of P to less available forms. The dilution effect of P with the fluid fertilizer is therefore counterproductive in strongly P-sorbing soils as P is in contact with more adsorption sites with high energies of bonding.

2. The application of fluid P fertilizer to Andisols and Oxisols did not provide any additional agronomic benefit over conventional granular P fertilizer.

Results from the plant growth experiment showed no significant differences in plant dry matter yield, shoot P concentration or P uptake between fluid or granular MAP applied to Andisols and Oxisols. In contrast, significantly higher plant growth was observed with fluid MAP than with its granular counterpart in the calcareous soil, in agreement with previous work (Bertrand et al., 2006; McBeath et al., 2005). The results from the pot trial are also in

line with the results from the incubation experiment, where a similar or even lower amount of P remained in labile form when added as fluid fertilizer than as granular fertilizer in the Andisols and Oxisols, in contrast with the calcareous soil where a higher proportion of P remained in labile form with the fluid fertilizer.

The isotopic dilution approach was used to calculate the percentage of P in the shoots that was derived from the applied fertilizers (%Pdff). In general, the %Pdff values were relatively high for Andisols and Oxisols and ranged from 65% up to 88%. No significant difference was observed in the %Pdff between fluid and granular MAP applied to Andisols and Oxisols, while the %Pdff was significantly higher for fluid than for granular MAP in the calcareous soil. These data indicate that in soils where adsorption reactions control P sorption, fluid fertilizers have no agronomic benefit over granular fertilizers. Furthermore, due to the very low soil-available P in Andisols and Oxisols, plants rely mainly on added P; however, because of the very low fertilizer P efficiency, much effort needs to be put in the development of new fertilizer formulations and management practices for these strongly P-sorbing soils.

3. *Nanohydroxyapatite was a more efficient P source than bulk hydroxyapatite for wheat grown in Andisols and Oxisols, but water-soluble P fertilizer was still more efficient.*

Nanohydroxyapatite (n-HAP) was evaluated as P fertilizer based on the hypothesis that the nano-sized particles can potentially move in the soil and reach the roots of the plants through the mass flow produced by the transpiration of the plants. Once close to the roots, P depletion could promote the dissolution of n-HAP or if the particles are very fine they could even be directly taken up by the roots. The advantage of n-HAP over conventional water-soluble P fertilizers would be less contact of free orthophosphate with the soil, thus minimizing opportunities of P being strongly adsorbed to the soil.

Results from the column experiment conducted to evaluate the transport of nanoparticles showed some movement (5%) of n-HAP in the Andisol, but very limited transport of the nanoparticles was observed in the Oxisol (0.4%). The limited transport of the nanoparticles in both soils might be related to aggregation of the nanoparticles in the soil. Indeed one of the main challenges of working with nanoparticles is to keep the nanoparticles dispersed in suspension by inhibiting aggregation. The greater mobility of n-HAP in the Andisol could be related to the higher organic C content that may have acted as an electrostatic barrier hindering the attachment of the negatively charged n-HAP particles to the soil particles. Alternatively, the greater mobility of n-HAP in the Andisol could also be due to that soil's higher porosity. In contrast to the n-HAP treatment, practically no movement of bulk hydroxyapatite (HAP) particles was observed in either of the soils.

Results from the pot experiment showed higher plant P uptake from the n-HAP than the bulk HAP in the Andisols and Oxisols, most likely due to faster dissolution of the nanoparticles. In all the soils, the highest plant P uptake was observed with the water-soluble P fertilizer. It can be concluded from the results of this study that n-HAP was a more effective P source than bulk HAP in Andisols and Oxisols, but water-soluble P fertilizer was still more effective.

4. Colloidal phosphorus from Andisols contributes to P uptake by plants

The effect of natural colloidal P to plant P uptake was investigated in short-term hydroponic experiments using radiolabeled non-filtered and filtered soil-water extracts from the Andisols and Oxisols. Wheat seedlings were exposed to non-filtered solutions (containing colloidal P) and to 3-kDa-filtered solutions (colloid-free). For the Andisols, the ^{33}P activity in the plant was significantly higher when the plants were exposed to the non-filtered solutions than to the 3-kDa filtered solutions. In contrast, no significant difference was observed for the

Oxisol. Quantitative analysis indicated the contribution of the colloids relative to that of the free ion was approximately 10%, but because of the high abundance of colloidal P relative to P present as the free ion, the flux was increased up to seven-fold.

Possible reasons for the contribution of colloidal P to plant P uptake could be i) direct uptake of the colloid and ii) enhanced P diffusion. In the first scenario, the colloids would have to be small due to the very fine pore size diameter of the plant cell wall. Analysis of the particle size of the colloids using a high speed disk centrifuge showed that the size of the colloids was between 30 to 240 nm for the Andisols and 10 to 60 nm for the Oxisol. It was not possible to determine the size of the colloids that contributed most to the uptake, so the possible contribution of very small colloids through direct uptake cannot be disregarded. Nevertheless, it seems more likely that the higher P uptake in the non-filtered solutions was mainly due to enhanced diffusion. The calculated thickness of the diffusion layer (~ 1000 μm) in the 3-kDa filtered solutions fell within the range for diffusion-limited uptake (100-1000 μm) (Santner et al., 2012). In case of diffusion-limited uptake, P will desorb from labile colloids (i.e. colloids from which P can easily be released) within the diffusive boundary layer, thus enhancing the diffusive supply of free orthophosphate to the plant roots. This hypothesis was supported by the fact that diffusion fluxes as measured with the DGT technique were higher for the non-filtered than for the 3-kDa filtered solutions.

The differences in the contribution of colloidal P in the Andisols and Oxisols may be related to the different nature of the colloids. The P-containing colloids in the Oxisols are likely most (hydr)oxide particles. In Andisols rich in organic matter, P bound to humic-Al/Fe complexes is often an important species (Buol et al., 2003; Gerke, 2010) and it can be speculated that the colloid-enhanced uptake in the Andisols was related to this type of colloid. The results from this study provide clear evidence that natural colloidal P from the Andisols are not inert and can contribute to plant P uptake. This is an interesting finding for

the area of plant nutrition that may open new possibilities to enhance soil P management in these problematic soils.

Future outlook

Enhancing the availability of soil P and the efficiency of fertilizer P in Andisols and Oxisols is very challenging and difficult to address, as proven in the present work as well as from previous research on this topic. There is no doubt that P fertilizers will continue to be an essential component for agricultural production to maximize crop yields. However, to enhance the efficiency of applied P, fertilizers should be designed considering the soil chemical properties, crop type and environmental conditions. The development of new fertilizer formulations is therefore a strategy where much work is still needed and which can possibly bring more positive outcomes.

In strongly P-sorbing soils, complexed P could be a more efficient P source than free orthophosphate because complexed P is protected from fixation. For example, humic-metal-phosphate complexes could be a new type of P fertilizer for these soils (Urrutia et al., 2014). Research is needed to design stable humic-metal-P complexes that can easily diffuse through the soil pores and from which P can be desorbed for plant uptake. Moreover, nanotechnology may also provide numerous possibilities for creating fertilizers where P is maintained in an available form. In this work, nanohydroxyapatite was not a more effective P source than conventional soluble fertilizer, but the idea of applying nanoparticulate P instead of free orthophosphate in strongly P-sorbing soils still merits further investigation. One of the challenges of working with nanoparticles is their inherent propensity to aggregate; therefore research is needed to design capping agents that can maintain the nanoparticles stable in suspension. These dispersion agents should also be non-toxic and degradable as they will be

released widely into the environment. In this context, research is also needed to evaluate the consequences of exposing soil microorganisms, microfauna, and plants to nanofertilizers.

The results from Chapter 6 that demonstrated the contribution of colloidal P to plant P uptake are intriguing. Further research is needed to understand the implications and relevance of colloidal P to plants in *in situ* soil solutions of Andisols. Management practices that enhance the release of colloids may be an appropriate complimentary management practice to P fertilization for strongly P-sorbing soils and this can be further investigated. For a sustainable management of P resources an integrated approach is needed that involves new fertilizer formulations as well as management practices to enhance the availability of soil P.

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