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

DANIELA FERNANDA MONTALVO GRIJALVA

School of Agriculture, Food and Wine

The University of Adelaide

December 2014

Table of contents

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 ($Ca_{10}(PO_4)_6(OH)_2$, 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.

I give consent to this copy of my thesis when deposited in the University Library, being made available for loan and photocopying, subject to the provisions of the Copyright Act 1968.

The author acknowledges that copyright of published works contained within this thesis (as named in "List of publications and presentations") resides with the copyright holder(s) of those works.

I also give permission for the digital version of my thesis to be made available on the web, via the University's digital research repository, the Library Search and also through web search engines, unless permission has been granted by the University to restrict access for a period of time.

Daniela Fernanda Montalvo Grijalva 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 Condron, 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.