New fertilizer technologies and their agronomic efficiency

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CSIRO Agricultural Productivity Flagship
Outline

- Why nutrient efficiency is important
- Improving fertilizer efficiency
  - Phosphorus
  - Boron
  - Zinc
- Measuring agronomic efficiency
- Conclusions
Nutrient efficiency = farmer viability/profitability
Global concerns regarding nutrient losses

- Off-site movement of nutrients into waterways

- Emission of greenhouse gases to the atmosphere

Source: www.csiro.au
Source: www.daff.gov.au
Human health issues

Soil Zn deficiency

Human Zn deficiency
Reactions important for P fertilizer use efficiency
Reactions of added fertilizer

Summary – P reactions in soils

- Both strong adsorption and precipitation reactions (often termed “fixation”) reduce P fertilizer efficiency, the latter more likely around fertiliser granules or fluid fertilizer injection points.
- “Fixation” not irreversible but kinetics of resupply from strongly sorbed P, or P precipitates, may be limiting to crop growth.
- More effective fertilizer P formulations will be most beneficial in soils receiving P fertilizer for the first time, in soils with high capacities to sorb P or precipitate P.
Developing effective fertilizers
Measuring fertilizer P behaviour/effectiveness

- Simple solubility in water/citrate or citric acid
- Measuring kinetics of nutrient release
- Measuring P released from fertilized soil by various reagents singly or in combination (e.g. Hedley fractionation)
- Measuring release and actual diffusion in soils
- Measuring ability to increase isotopically exchangeable P in soil
- Measuring plant P uptake using isotopic tracing or isotopic dilution
- Measuring agronomic effectiveness in pot trials
- Measuring agronomic effectiveness in the field
Quick method to screen fertilizer P and measure actual release/diffusion in soils

**Principle**

- Soil incubated with fertiliser for given time
  
- Fe oxide (Feox)-containing agar/paper (as a sink for P) put in contact with the soil

- Malachite-green reagent to colour P captured by Feox
Quick method to screen fertilizer P release/diffusion

∅ 5.5 cm

0.01 0.1 1 10 mg P/L
Quick method to screen fertilizer P release/diffusion

Excellent correlation with laboratory chemical analysis of P diffusion
Quick method to screen fertilizer P release/diffusion

Phosphorus Diffusion from Fertilizer: Visualization, Chemical Measurements, and Modeling

*Soil Science Society of America Journal* **78(3)**, 832-842.
How can we improve P fertilizer use efficiency?
The fate of added P in soil

- **Soil soln**
  - Fertilizer P
  - Plant P
  - Microbial P
  - Inorganic P
  - Organic P

**Inefficiency terms**
1. Erosion
2. Leaching/runoff
3. Strong sorption or ppt
4. Occlusion in OM
Controlled release P to reduce P leaching/runoff losses

- Leaching of P only a serious loss in very sandy soils
- P runoff may be more serious in some systems
- “Reverted” P compounds can be used e.g. neutralising SSP with lime
- Produce low-cost partially soluble P fertilizers e.g. partially acidulated rock phosphate (PAPR)
- Polymer coated formulations can reduce P losses - principle same as for N fertilizers – slow release from granule
Evaluating controlled release products

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<th>2h</th>
<th>4h</th>
<th>8h</th>
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Increasing polymer coating thickness
Controlled release P to reduce P leaching/runoff losses

Soluble P fertilizer

Slow release P
The fate of added P in soil

Inefficiency terms
1. Erosion
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Fertilizer P

Soil soln

Plant P

Microbial P

Inorganic P

Organic P
Reducing strong P adsorption or precipitation reactions

- Modify soil pH around fertiliser granule
- Disrupt adsorption or precipitation reactions
Reducing strong P adsorption or precipitation reactions

- In calcareous soils P use efficiency is low due to precipitation reactions around the granule

Microphotograph of P fertilizer granule incubated for 4 wks in a calcareous soil
High efficiency of fluid P in calcareous soils

Agronomic trials demonstrated that fluid forms of P and TE fertilisers were more effective than granular products in highly calcareous soils.

High efficiency of fluid P in calcareous soils

Granular P+TE  Fluid P+TE
Reactions of added granular P

Efficiency of fluid and granular P in calcareous soils

- Granular fertilisers act like a “sponge” soaking up Ca from soil solution and causing the P to revert to less soluble minerals in the granule

- Fluid P does not have the same reaction
Disrupting adsorption/precipitation – complex the “complexants”

- Common ion – adding excess sulfate (Olatuyi et al. 2010) to reduce Ca$^{2+}$ activities and stimulate P release or minimise precipitation (c.f. Olsen/Colwell reagent, HCO$_3^-$ ion)

- Polymers/chelates – complex cations in the vicinity of the fertiliser granule to reduce activities of Al$^{3+}$/Ca$^{2+}$/Fe$^{3+}$ and liberate P
Increasing P efficiency – mode of action of chelates

- $\text{RCOO}^- \text{ ion competes with } H_2PO_4^{2-} \text{ for sorption sites}$

- $\text{RCOO}^- \text{ ion complexes } Ca^{2+} \text{ and reduces } Ca^{2+} \text{ activity in soil solution, which encourages dissolution of easily soluble } Ca\text{-phosphates}$

$\text{RCOO}^- + Ca^{2+} \rightarrow (\text{RCOO})_2Ca + H_2PO_4^{2-}$
Can complexation of Al, Ca or Fe improve P fertilizer efficiency?

Coatings tested on MAP: NTA
All coated at 1%
NTA
Tiron
Citrate
Citric acid
Sulfate of ammonia
Avail (commercial)
Pmax (commercial)

SSP and SSP coated with a humic-based organic chelate (“TopPhos”) also compared

Results – little effect on P diffusion (Oxisol)

- MAP treatments: diameter ~2.4 cm
- TopPhos and SSP: diameter ~ 1.3 cm

Results – little effect on P diffusion (Calcarosol)

- MAP treatments: diameter ~ 2.2 cm
- TopPhos and SSP: diameter ~ 1.1 cm

Can complexation of Al, Ca or Fe improve P fertilizer efficiency?

- At 1% coating rate on MAP granules, all metal-complexing compounds had no effect on P diffusion or P uptake by wheat in P-deficient soils.
- Even at very elevated coating rates (100%) of metal-complexing ligands (citrate and Avail) on MAP granules, the extent of P diffusion was not significantly changed.
- Plant yield/P uptake not affected in pot trials.
- Review of field trial data confirms these results (Chien et al. 2014).
What other strategies could be used to improve P formulations?

- Compounds which interfere with Ca-P bonding in neutral/calcareous soils
- Moieties which complex the orthophosphate ion and render it more diffusible through soil pores
- Nanomaterials which have special properties/coatings to retain P in an available form
Trace elements

Reactions important for B fertilizer use efficiency
Commonly used B fertilisers are water soluble

- B is an uncharged molecule at most soil pH values and has extremely low retention in soils
- The window between deficiency and toxicity for plants is narrow
- Hence problems with leaching and potential toxicity to seedlings
Trace elements - boron

- Need slow-release B fertilizer for high rainfall environments
- Ulexite and colemanite often used as slow-release B sources
Co-granulation of B with MAP

Improving B fertilizers

- Co-granulating slow-release B sources e.g. colemanite or ulexite with ammonium phosphates results in loss of slow-release characteristics

\[
\text{CaB}_3\text{O}_4(\text{OH})_3\cdot\text{H}_2\text{O} + 4 \text{H}_2\text{O} \leftrightarrow 3\text{B(OH)}_4^- + \text{Ca}^{2+} + \text{H}^+
\]

\[
\text{NaCaB}_5\text{O}_6(\text{OH})_6\cdot5\text{H}_2\text{O} + 3 \text{H}^+ \leftrightarrow 5 \text{H}_3\text{BO}_3 + \text{Ca}^{2+} + \text{Na}^+ + 2\text{H}_2\text{O}
\]

\[
\text{Ca}^{2+} + \text{H}_2\text{PO}_4^- + 2\text{H}_2\text{O} \leftrightarrow \text{CaHPO}_4\cdot2\text{H}_2\text{O} + \text{H}^+
\]

Boron phosphate is an ideal source of slow-release B for inclusion in ammoniated phosphates as dissolution is retarded by the presence of P.

\[
\text{BPO}_4 + 3\text{H}_2\text{O} \leftrightarrow \text{H}_3\text{BO}_3 + \text{H}_3\text{PO}_4
\]

Improving B fertilizers

- Release from co-granulated BPO$_4$ synthesized at different temperatures was slow and continuing.

Rapid method to screen seedling toxicity of fertilisers

Images were taken 7 days after germination and analysed using GIMP 2.8

Percentages of vegetative areas quantified on transformed images

**Toxicity effects of B co-granulated with MAP**

<table>
<thead>
<tr>
<th></th>
<th>Borax</th>
<th>Ulexite</th>
<th>Colemanite</th>
<th>BPO$_4$-500</th>
<th>BPO$_4$-800</th>
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Effectivenss of co-granulated B sources

Trace elements

Reactions important for Zn fertilizer use efficiency
Trace elements - zinc

- Zinc reacts strongly with soil components, especially in alkaline/calcareous soils so that Zn deficiency can be severe in these soils.
- High organic matter of high Al/Fe oxides content can also lead to low Zn availability.
- Zinc needs to be supplied to soil with N/P fertilizer to give good distribution in soil.
- Many NP fertilizers are enriched with ZnSO$_4$ or ZnO.
Incompatibility of trace element cations (Cu, Mn, Zn) incorporated with phosphates – reduces solubility

\[
\text{Cu} + \text{PO}_4 \rightarrow \text{Cu}_3(\text{PO}_4)_2 \\
\text{Mn} + \text{PO}_4 \rightarrow \text{Mn}_3(\text{PO}_4)_2 \\
\text{Zn} + \text{PO}_4 \rightarrow \text{Zn}_3(\text{PO}_4)_2
\]

+ other mixed phosphate precipitates

Trace element coatings do not escape this chemistry

\[
3\text{ZnO} + 2\text{H}_3\text{PO}_4 \leftrightarrow \text{Zn}_3(\text{PO}_4)_2 + 3\text{H}_2\text{O}
\]
For banded fertilizers, water solubility of Zn in granule is a key predictor of performance.

Source: Prof. Ismail Cakmak, Sabanci University
For banded fertilizers, water solubility of Zn in granule is a key predictor of performance. 

\[ R^2 = 0.78 \]

Improved Zn fertilizers

Physical barriers to reduce phosphate precipitation of zinc and to increase water solubility

Ammonium phosphate

↓

Barrier Coating

↓

Trace element

“New” chelates to reduce ppt reactions

- **Rhamnolipid (RH)** – produced by bacteria, can diffuse easily across plant root membranes

- **Polyethylenimine (PEI)** – polymer with high Zn-complexing ability


Stacey SP, MJ McLaughlin and E Lombi. 2005. Australian Application No. 2006269807; PCT no. PCT/AU2006/000951; PCT OPI Date 18/1/2007 - Chelating agents for Micronutrient Fertilisers
“New” chelates to reduce ppt reactions

Photo: Courtesy Prof. Ismail Cakmak, Sabanci University

Rhamnolipid (mg/kg). All pots 2ppm Zn
Improved Zn fertilizers

MAP

MAP+Zn

Zn-PEI barrier coated products

Photo: Courtesy Prof. Ismail Cakmak, Sabanci University
Zinc uptake efficiency for NPK–Zn fertilizers

- K-Mag+PEI
- SOP+PEI
- ZnSO$_4$
- Amm.Sul+PEI
- Urea+PEI
- MAP-Zn

The graph shows a linear relationship with $R^2 = 0.92$. The x-axis represents Water Soluble Zn (%) and the y-axis represents Zn in wheat derived from fertilizer (%).
Summary

- The reasons for inefficiencies of our current fertilizers vary according to the nutrient of interest.
- For all nutrients, there are opportunities to improve fertilizer efficiency and part of this gain can be made by developing novel formulations to assist agronomic management.
- Gains are most likely to be achieved by improving our fundamental knowledge of the reactions occurring during fertilizer formulation, dissolution, interaction with soil, and transport across the root membrane or leaf surface.
- Beware false claims for effectiveness and design robust experiments to test mechanisms claimed!
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Further information

[Website](www.adelaide.edu.au/fertiliser/)