Perspectives on new fertilizer formulations to increase nutrient use efficiency

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Why nutrient efficiency is important

Improving fertilizer efficiency

- Nitrogen
- Phosphorus
- Potassium and sulfur
- Trace elements

Conclusions
Changes in global price for P

Price of Phosphate Rock Concentrate 32–33% P₂O₅ FOB Morocco and FAO Food Price Index (2002–2004=100)

Global nutrient reserves

- Reserves of N unlimited
- Reserves of P ~ 350-400 years
- Reserves of K ~ 300 years
- Reserves of Zn ~ 20 years

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
Geographic distribution of Zn-deficient soils and Zn deficiency in humans

Soil Zn deficiency

Human Zn deficiency
Reactions important for N fertilizer use efficiency
Reactions important for N fertilizer use efficiency

1. Urease inhibition
2. Nitrification inhibition
3. Controlled release
4. New products

30%-75% efficiency
Urease inhibition

- Reduce conversion of urea to ammonium
- An old technology – mainly phosphoramides used commercially but many chemicals can inhibit urease
- The most common chemical used is $N$-(n-butyl)-thiophosphoric triamide (NBPT) (Agrotain) but phenyl phosphorodiamidate (PPDA) also used earlier

Carboxylic acids also suggested to minimise urease activity

The most widely promoted commercial product is a polymer "Nutrisphere-N" containing maleic acid and itaconic acid

However the efficacy of these acids have been recently questioned (Goos et al. 2013)

Maleic acid

Itaconic acid
1. Urease inhibition

Fig. 2. Effect of inhibitor concentration on urea remaining after 2-h incubation with jackbean urease at pH 7. Initial urea concentration was 50 mg L⁻¹. NBPT, N-(n-butyl) thiophosphoric triamide; NSN-1, NSN-2, two sources of maleic-itaconic polymer.

# Nitrification inhibitors

<table>
<thead>
<tr>
<th>Common name</th>
<th>Chemical</th>
<th>Brand name</th>
<th>Inhibition</th>
<th>$\text{N}_2\text{O}$ reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrapyrin</td>
<td>2-chloro-6-trichloromethyl pyridine</td>
<td>N-Serve</td>
<td>82% by day 14</td>
<td>60-93%</td>
</tr>
<tr>
<td>DCD</td>
<td>Dicyandiamide</td>
<td>Guardian</td>
<td>53% by day 14</td>
<td>50-92%</td>
</tr>
<tr>
<td>DMPP</td>
<td>3,4-dimethyl pyrazole phosphate</td>
<td>ENTEC</td>
<td>4 weeks +</td>
<td>51%</td>
</tr>
<tr>
<td>ATS</td>
<td>Ammonium thiosulfate</td>
<td>THIO-SUL</td>
<td>Some</td>
<td>?</td>
</tr>
</tbody>
</table>

Source: IPNI
## Nitrification inhibitors – effect on yield

### Table 1  Response of maize to urea or UAN treated with the urease inhibitor NBPT in the USA

<table>
<thead>
<tr>
<th>N source</th>
<th>Number of field trials</th>
<th>Grain yield (t ha(^{-1}))</th>
<th>Yield increase due to NBPTPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea</td>
<td>316</td>
<td>8.02 7.13 0.89</td>
<td></td>
</tr>
<tr>
<td>UAN</td>
<td>119</td>
<td>8.21 7.62 0.56</td>
<td></td>
</tr>
</tbody>
</table>

Nitrification inhibitors – environmental use to control nitrate leaching in New Zealand
Nitrification inhibitors – consumer concerns

Fonterra moves to reassure customers

By Abby Gillies
7:33 PM Sunday Jan 27, 2013

Traces of a toxic agricultural substance detected in some Fonterra milk powders has international dairy customers asking for answers.

Testing of 100 samples from products last September revealed low levels of dicyandiamide (DCD) residues in 10 samples of whole milk powder, skim milk powder and buttermilk powder made with milk from the North and South islands.

The finding has caused concern among international customers of dairy giant Fonterra.

In Taiwan, health officials are investigating whether any of the tainted products reached their shores.
Controlled release N

- Sulfur-coated urea
- Polymer/resin/polyolefin coated formulations e.g. Policote, Osmocote, Multicote, Meister, ESN, etc.
- Slow release N forms e.g. urea-formaldehyde
- Principle is to slowly release N from the granule

Source: en.hydroaria.com
Source: www.haifa-group.com
Controlled release N

Major factors affecting release

- coating thickness
- temperature
- moisture

Source: IPNI
4 New formulations

- Combine urea and ammonium sulfate to reduce volatilisation losses
- Fuse ammonium nitrate and ammonium sulfate to produce less hazardous fertilizer with 26% N and 15% S (recent Honeywell patent)
- Add iron sulfate salts to ammonium nitrate to reduced hazardous nature of fertilizer
Phosphorus

Reactions important for P fertilizer use efficiency
The fate of added P in soil

Inefficiency terms
1. Erosion
2. Leaching/runoff
3. Strong sorption or ppt
4. Occlusion in OM

5%-40% efficiency Initially
100% eventually
Typical P sorption curve

$P_{adsorbed} \text{ (mmol/kg)}$

Equilibrium P concentration (mg/L)
P responses over time

Crop Yield (t/ha)

P applied (kg/ha)

Soil soln

Inorganic P

Organic P
Highly P sorbing soils require the greatest P accumulation to reach “equilibrium”

Source: De Sousa, 2011
High P fixation
(i modifier)

Source: HarvestChoice, 2010
Typical P precipitation curve

P adsorbed (mmol kg\(^{-1}\))

Equilibrium concentration (mg dm\(^{-3}\))
Calcareous soils have different issues

P precipitation may be more important
Reactions of added P

- Precipitation of P compounds around granules is a key process

Microphotograph of P fertilizer granule incubated for 4 wks in a calcareous soil

Concrete like outer shell, soil + precipitates
Low efficiency of granular P in calcareous soils

Summary – P reactions in soils

- Both adsorption and precipitation reactions reduce P fertilizer efficiency, the latter more likely around fertiliser granules or fluid injection points.
- “Fixation” not irreversible but kinetics of resupply from 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, and will decline (in most soils) as cumulative P fertiliser additions increase.
Improving P fertilizer efficiency in soil

Inefficiency terms
1. Erosion
2. Leaching/runoff
3. Strong sorption or ppt
4. Occlusion in OM

Soil soln

Fertilizer P

Plant P

Microbial P

Inorganic P

Organic P
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 with surface-applied P on steep slopes
- “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
Controlled release P to reduce P leaching/runoff losses
Reducing strong adsorption or precipitation reactions

- Modify soil pH around fertiliser granule
- Disrupt adsorption or precipitation reactions
Increasing P efficiency - modifying pH with S⁰

\[ S⁰ \rightarrow SO_4^{2-} + 2H^+ \]

Increasing P efficiency - modifying pH with SoA

Co-granulating ammonium sulfate (SoA) and elemental S with MAP can aid acidification and reduce Ca²⁺ activities releasing P

1. $\text{NH}_4^+ \rightarrow \text{NO}_3^- + 2\text{H}^+$

2. $\text{SO}_4^{2-} + \text{CaHPO}_4\cdot\text{H}_2\text{O} \rightarrow \text{CaSO}_4 + \text{HPO}_4^{2-}$

Both Mosaic (Microessentials) and Shell (Thiogro) have patented technologies in this area.
Increasing P efficiency - modifying pH with SoA

Soil pH vs. SoA in fertilizer (% S) for:
- Flaxley: $R^2 = 0.87$
- Peake: $R^2 = 0.96$
- Auburn: $R^2 = 0.91$
- Murray: $R^2 = 0.83$

Soil pH values:
- Flaxley: 7.4, 7.6, 7.8
- Peake: 4.8, 5.2, 5.6
- Auburn: 8, 8.2, 8.4
- Murray: 8.0, 8.1, 8.2

Increasing P efficiency - modifying pH with SoA
Increasing P efficiency - modifying pH with SoA

- Soluble P (mg/kg)
  - Auburn: $R^2 = 0.67$
  - Flaxley: $R^2 = 0.73$
  - Murray: $R^2 = 0.74$
  - Peake: $R^2 = 0.74$

- Sulfate in fertilizer (%)
Increasing P efficiency – complex the “complexants”

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

- Polymers/chelates added at low rates (<1%) – complex cations in the vicinity of the fertiliser granule to reduce activities of \( \text{Al}^{3+}/\text{Ca}^{2+}/\text{Fe}^{3+} \) and liberate P
Increasing P efficiency – mode of action of chelates

- RCOO\(^-\) ion competes with \(\text{H}_2\text{PO}_4^{2-}\) for sorption sites

- RCOO\(^-\) ion complexes \(\text{Ca}^{2+}\) and reduces \(\text{Ca}^{2+}\) activity in soil solution, which encourages dissolution of easily soluble Ca-phosphates (or Al/Fe)

\[
\text{(RCOO)}_2\text{Ca} + \text{H}_2\text{PO}_4^{2-} \rightarrow \text{Ca}^{2+} + \text{RCOO}^- + \text{H}_2\text{PO}_4^{2-}
\]
Can complexation of Al, Ca or Fe improve P fertilizer efficiency?

Coatings tested on MAP:  
- NTA
- Tiron
- Citrate
- Citric acid
- Sulfate of ammonia
- Avail (commercial)
- Pmax (commercial)

Coated at 1%

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

Petri dish experiment - methods

- Oxisol and Calcareous soil (Inceptisol) used
- Treatments: Control (no P), 10 treatments with MAP granule in centre of dish (=control, 7 coatings on MAP, TopPhos and SSP)
- P visualization using a new technique at 1, 7 and 50 days
- P solubility, E values (isotopically exchangeable P) and total concentrations (for 3 concentric circles of soil) at day 50

Results – little effect on P diffusion

Oxisol - $pH_{Ca}$ 5.3

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

Calcareous soil - pH_{Ca} 7.7

**Results – little effect on P diffusion**

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

Results – no effect on P availability to plants

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

Why do the coatings have no effect? A quick calculation:

Can the ligand complex a substantial amount of Al, Ca or Fe?
- 135 mmol exchangeable Ca/kg in the Calcareous soil
- Diffusion zone: 1 cm radius or 6 g of soil $\Rightarrow$ 1 mmol Ca
- 0.3 mg product, complexation capacity of circa 2 mmol/g
  $\Rightarrow$ 0.0006 mmol complexing groups

NO

Can they block a significant amount of sorption sites?
- Sorption in both soils saturated near 30 mmol P/kg
- Diffusion zone: 1 cm radius (~6 g soil) $\Rightarrow$ 0.18 mmol sites
- 0.0006 mmol complexing groups

NO

Complexation unlikely to aid P effectiveness
What other strategies could be used to improve P formulations?

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

Reactions important for K fertilizer use efficiency
Potassium

- Potassium does not have significant loss mechanisms from soil as does N, and does not have extensive and strong reaction with soil components that reduce plant availability as does P.
- Hence, effectiveness of most K fertilizers is good and there is no strong driver for new formulation development.
- Some slow-release products have been developed for leaching environments.
- Efficiency generally 60-100%, with leaching the major loss mechanism.
Reactions important for S fertilizer use efficiency
Sulfur – fertilizer inefficiency processes

Product removal

10%-100% efficiency

Fertilizer/gypsum addition

Crop uptake

Immobilization in OM

Leaching
Controlled/slow-release S

- In environments where sulfate leaching is problematic, the cheapest and easiest way to supply slow-release S is via elemental S ($S^0$).
- Oxidation of $S^0$ is too slow to provide S for crop nutrition at early growth stages so generally some $SO_4$ is needed in the fertilizer.
- Many combined $SO_4/S^0$ products have been produced over the years on base products such as SSP.
- Less common are $SO_4/S^0$ formulations with TSP and MAP/DAP.
S⁰/SO₄-enhanced MAP

e.g. Microessentials, Thiogro

- Mixture of sulfate and elemental S throughout granule
- Increase S content without compromising P content
- Provides N, P and both fast and slow release S
- Soil pH decrease around granule can increase P solubility in neutral/alkaline soils
**S⁰/SO₄²⁻-enhanced products**

**Microessentials**
- MES10
- MAP
  - 5% ES
  - 5% SO₄²⁻-S

**Shell Thiogro**
- Granulock
- DAP
  - 8% ES
  - 4% SO₄²⁻-S

**S⁰ prills**
- Tiger 90
  - 90% ES
S\textsuperscript{0}/SO\textsubscript{4\textendash}enhanced products

Soil saturated from bottom to top
At day 1: leached with 35 ml deionized water
Incubated at 25°C
Leached every two weeks for first two months, and then monthly
Ammonium sulfate used as “control”
$S^0/\text{SO}_4$-enhanced products

- (NH$_4$)$_2$SO$_4$
- Tiger90
- MES10
- Granulock S
Trace elements

Reactions important for B and Zn fertilizer use efficiency
Trace elements - boron

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

5%-80% efficiency
Improving B fertilizers

- Formulations containing small amounts of fast-release B and a reserve of slow-release B are needed
- Co-granulating slow-release B sources e.g. colemanite or ulexite with ammonium phosphates results in loss of slow-release characteristics

\[
\begin{align*}
\text{CaB}_3\text{O}_4(\text{OH})_3\cdot\text{H}_2\text{O} + 4 \text{H}_2\text{O} & \leftrightarrow 3\text{B(OH)}_4^- + \text{Ca}^{2+} + \text{H}^+ \\
\text{NaCaB}_5\text{O}_6(\text{OH})_6\cdot5\text{H}_2\text{O} + 3 \text{H}^+ & \leftrightarrow 5 \text{H}_3\text{BO}_3 + \text{Ca}^{2+} + \text{Na}^+ + 2\text{H}_2\text{O} \\
\text{Ca}^{2+} + \text{H}_2\text{PO}_4^- + 2\text{H}_2\text{O} & \leftrightarrow \text{CaHPO}_4\cdot2\text{H}_2\text{O} + \text{H}^+
\end{align*}
\]
Improving B fertilizers

- 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 rates of B from co-granulated MAP with borax, ulexite and colemanite were very rapid.
- Release from co-granulated BPO$_4$ synthesized at different temperatures was slow and continuing.

![Graph showing cumulative B released over time with different markers for co-granulated BPO$_4$ samples at different temperatures.]
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.
Trace elements - zinc

- Incompatibility of trace element cations (Cu, Mn, Zn) incorporated with phosphates – reduces solubility

\[
\begin{align*}
\text{Cu} + \text{PO}_4^3 & \rightarrow \text{Cu}_3(\text{PO}_4)_2 \\
\text{Mn} + \text{PO}_4^3 & \rightarrow \text{Mn}_3(\text{PO}_4)_2 \\
\text{Zn} + \text{PO}_4^3 & \rightarrow \text{Zn}_3(\text{PO}_4)_2
\end{align*}
\]

+ other mixed phosphate precipitates

- Trace element coatings do not escape this chemistry

\[
3\text{ZnO} + 2\text{H}_3\text{PO}_4 \iff \text{Zn}_3(\text{PO}_4)_2 + 3\text{H}_2\text{O}
\]

Efficiency < 1%

ZnO or ZnSO\textsubscript{4} incorporated or coated at granulation
For banded fertilizers, water solubility of Zn in granule is a key predictor of performance

Source: Prof. Ismail Cakmak, Sabanci University
Improved Zn fertilizers

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

Ammonium phosphate

\[\rightarrow\]

Barrier Coating

\[\rightarrow\]

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

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

Photo: Courtesy Prof. Ismail Cakmak, Sabancı University
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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www.adelaide.edu.au/fertiliser/