Perspectives on new fertilizer formulations to increase nutrient use efficiency

Mike McLaughlin
CSIRO Sustainable Agriculture Flagship
University of Adelaide Fertiliser Technology Research Centre

THE UNIVERSITY OF ADELAIDE AUSTRALIA

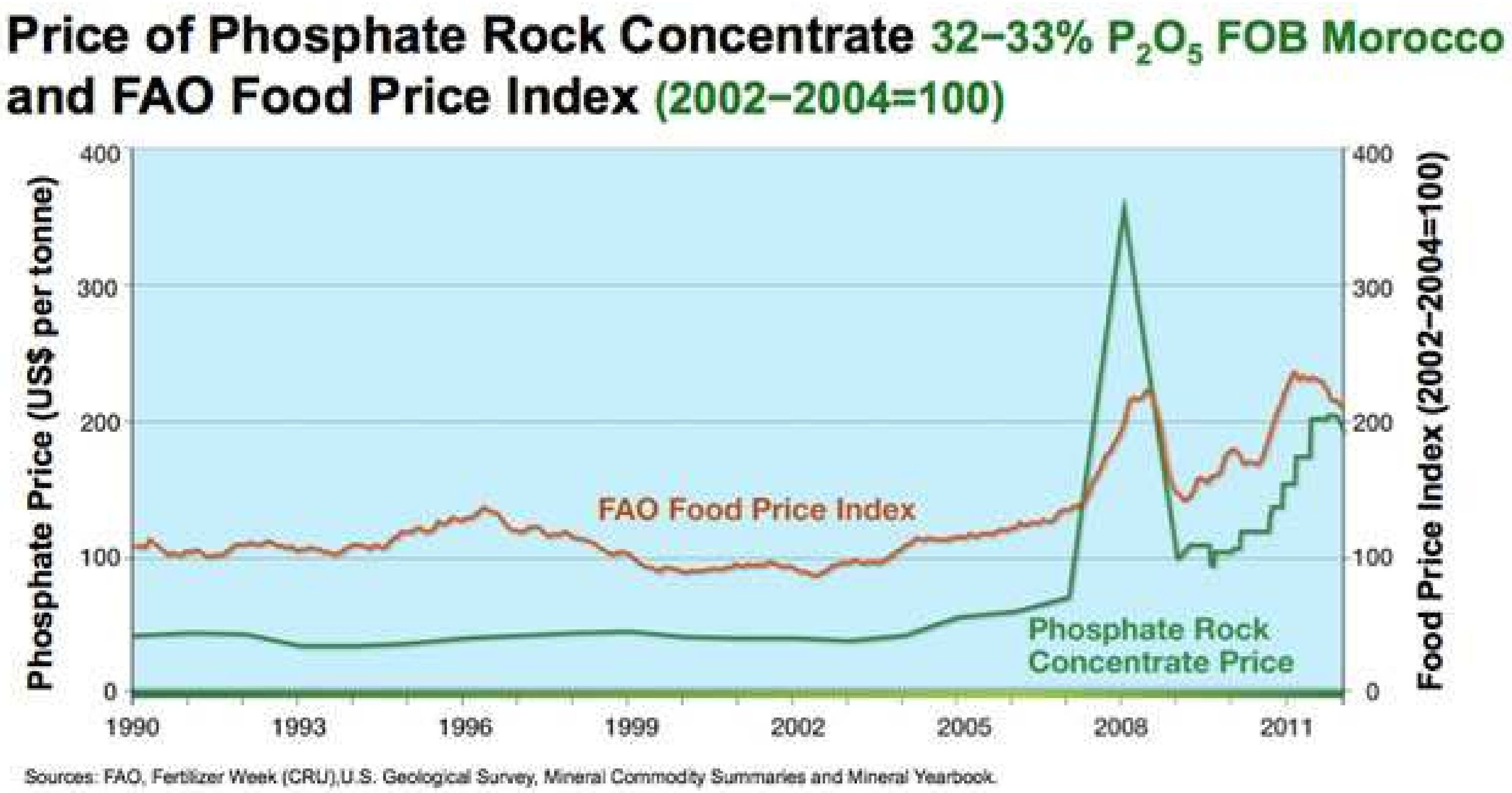
National Research FLAGSHIPS Sustainable Agriculture

CSIRO

Outline

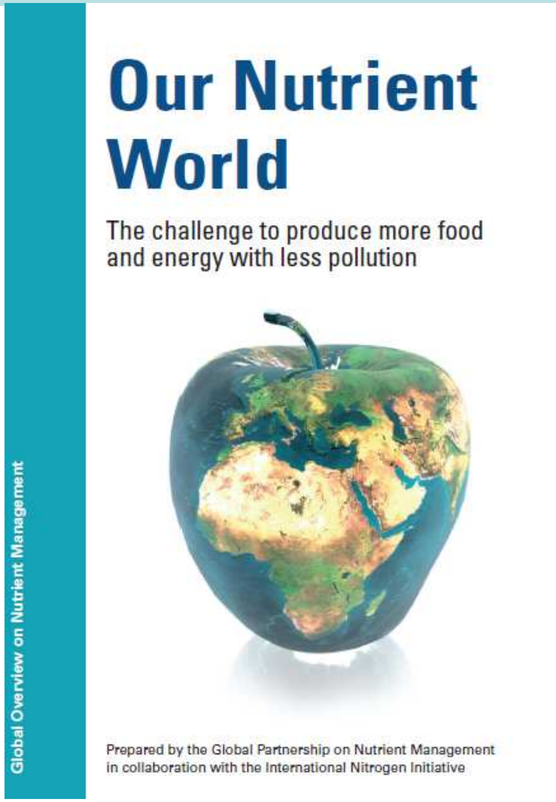
- Why nutrient efficiency is important
- Improving fertilizer efficiency
  - Nitrogen
  - Phosphorus
  - Potassium and sulfur
  - Trace elements
- Conclusions

Changes in global price for P



Global nutrient reserves

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



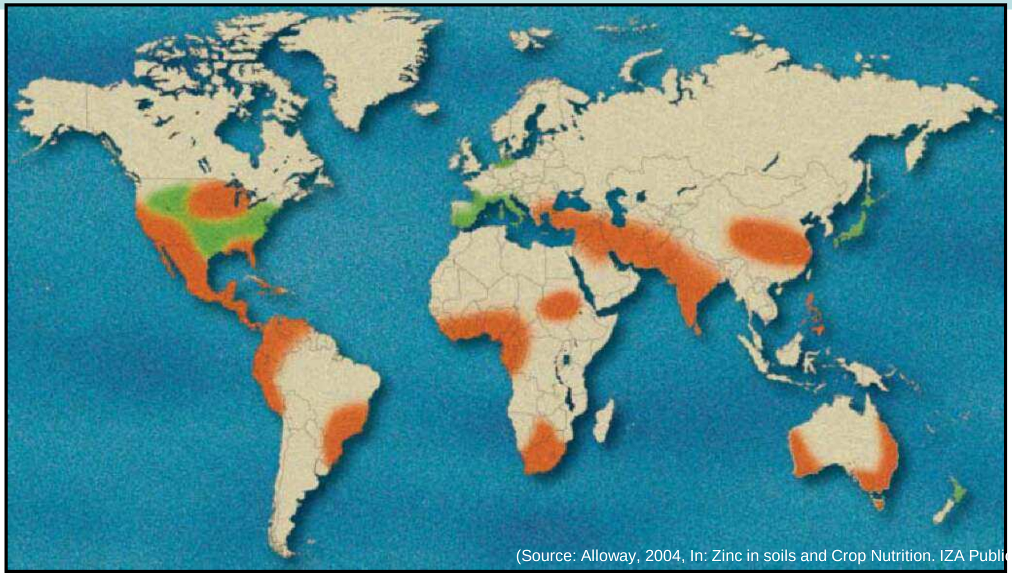
Sutton M.A. et al. (2013) Our Nutrient World: The challenge to produce more food and energy with less pollution, Global Overview of Nutrient Management, Centre for Ecology and Hydrology, Edinburgh on behalf of the Global Partnership on Nutrient Management and the International Nitrogen Initiative.

Global concerns regarding nutrient losses

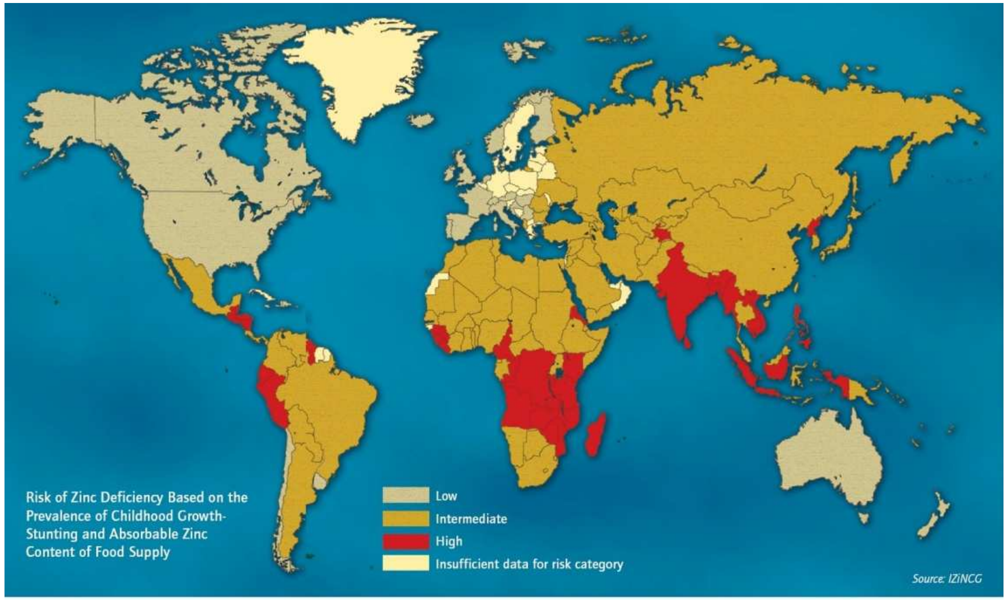
- Off-site movement of nutrients into waterways

- Emission of greenhouse gases to the atmosphere

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



Soil Zn deficiency



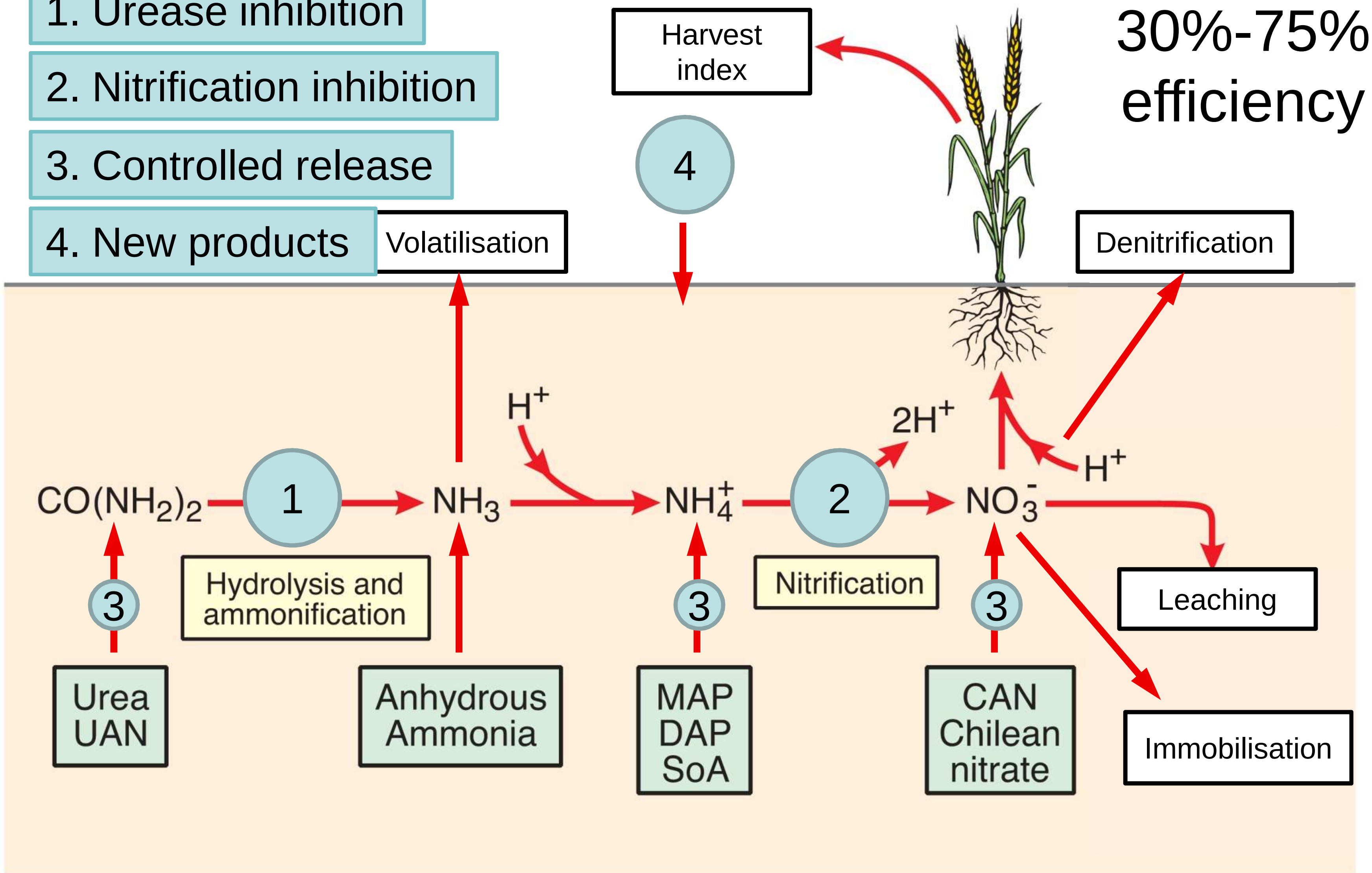
Human Zn deficiency

Nitrogen

Reactions important for
N fertilizer use efficiency

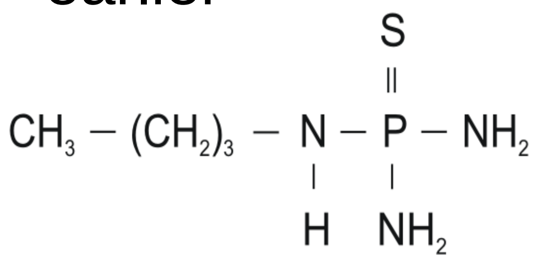
Reactions important for N fertilizer use efficiency

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

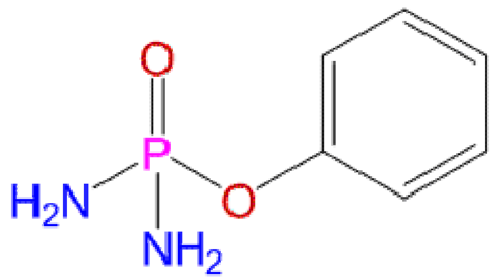


1 Urease inhibition

- 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



NBTPT(s)

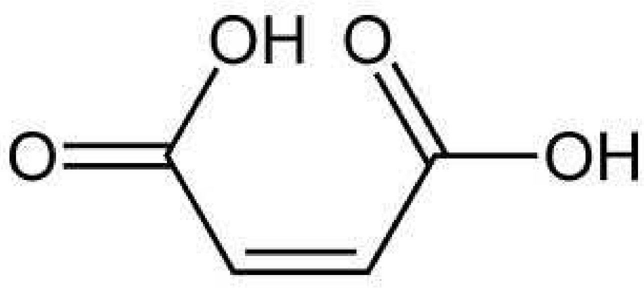


PPDA

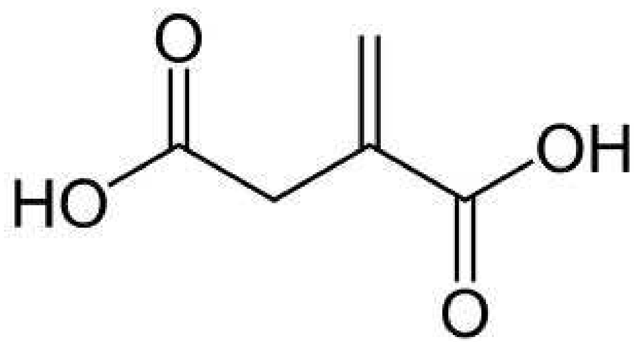
Source: Chien S.H., Prochnow L.I., Cantarella H. (2009) Recent developments of fertilizer production and use to improve nutrient use efficiency and minimize environmental impacts. Advances in Agronomy 102:267-322.

1 Urease inhibition

- 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

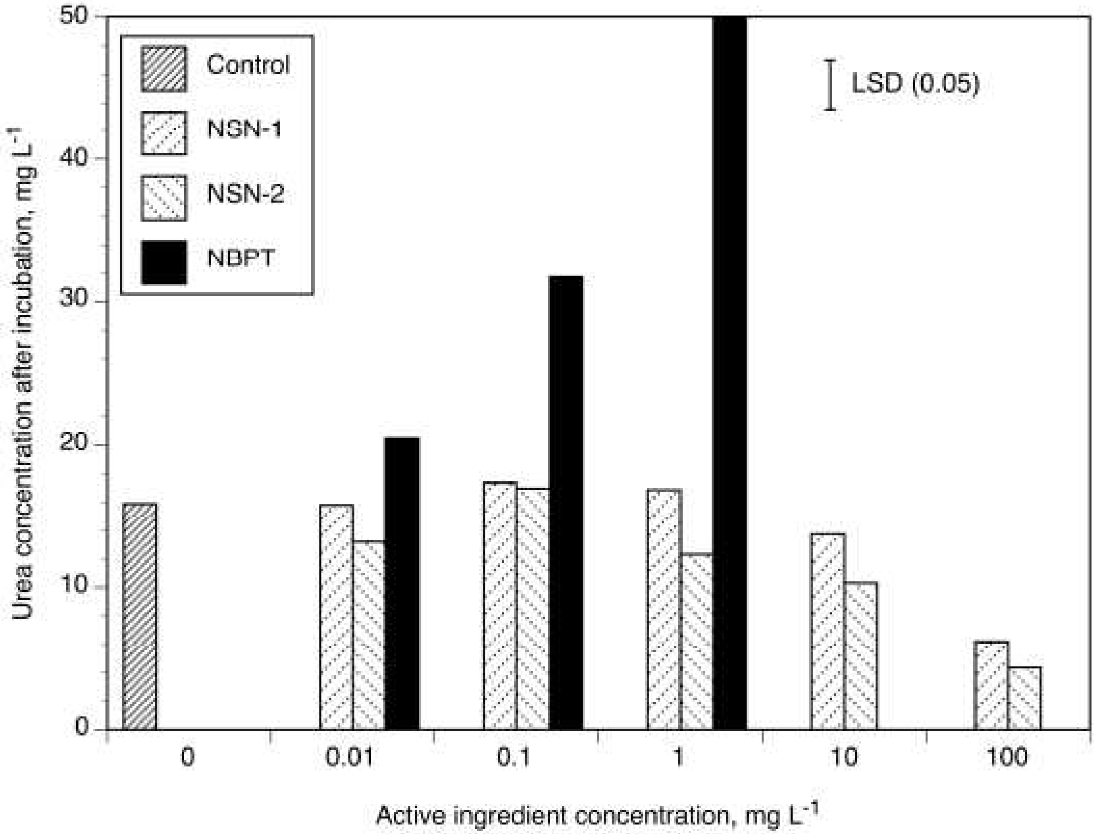


Fig. 2. Effect of inhibitor concentration on urea remaining after 2-h incubation with jackbean urease at pH 7. Initial urea concentration was 50 mg L^{-1}. NBPT, *N*-(*n*-butyl) thiophosphoric triamide; NSN-1, NSN-2, two sources of maleic-itaconic polymer.

Jay Goos R. (2013) A comparison of a maleic-itaconic polymer and N-(n-butyl) thiophosphoric triamide as urease inhibitors. Soil Sci. Soc. Am. J. 77:1418-1423.

2

Nitrification inhibitors

Common name	Chemical	Brand name	Inhibition	N_2O reduction
Nitrapyrin	2-chloro-6-trichloromethyl pyridine	N-Serve	82% by day 14	60-93%
DCD	Dicyandiamide	Guardian	53% by day 14	50-92%
DMPP	3,4-dimethyl pyrazole phosphate	ENTEC	4 weeks +	51%
ATS	Ammonium thiosulfate	THIO-SUL	Some	?

Source: IPNI

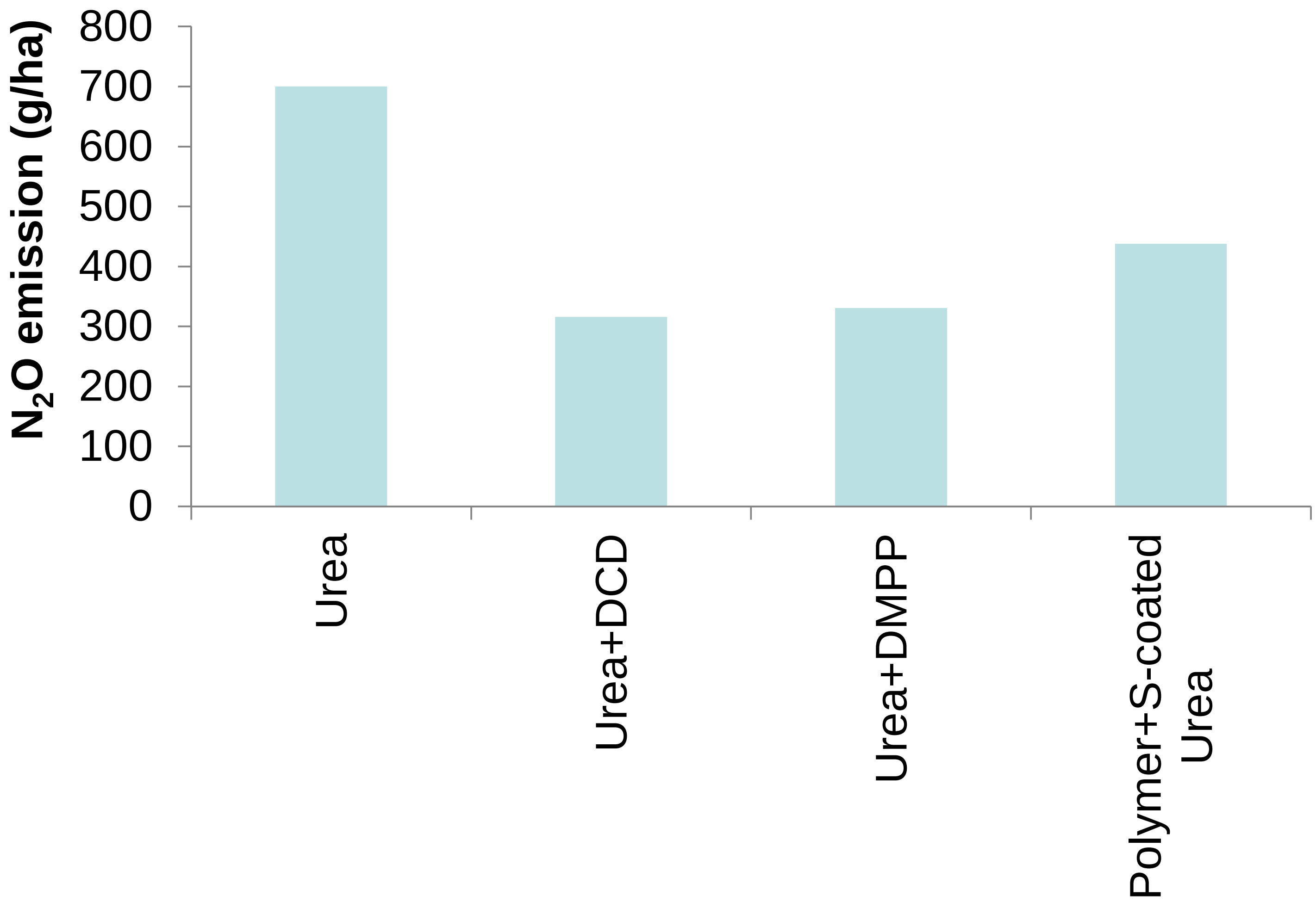
2 Nitrification inhibitors – effect on yield

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

		Grain yield ($t\ ha^{-1}$)		
N source	Number of field trials	With NBTPT	Without NBTPT	Yield increase due to NBTPT
Urea	316	8.02	7.13	0.89
UAN	119	8.21	7.62	0.56

Source: Chien S.H., Prochnow L.I., Cantarella H. (2009) Recent developments of fertilizer production and use to improve nutrient use efficiency and minimize environmental impacts. Advances in Agronomy 102:267-322.

2 Nitrification inhibitors



V.P. Vargas, H. Cantarella, J.R. Soares, J.B. Carmo, S. Del Grosso, A.A. Martins, and C.A. Andrade. 2013. Nitrification inhibitor decreases N_2O emission from soils amended with fertilizer N and sugarcane trash. **The Third International Conference on Slow- and Controlled-Release and Stabilized Fertilizers IFA & New Ag International 12-13 March 2013, Rio de Janeiro, Brazil**

2

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

2

Nitrification inhibitors – consumer concerns

The New Zealand Herald

Search keywords...

National | World | Business | Sport | Technology | Entertainment | Life & Style

National — Next Article: Man critical after dive

Fonterra moves to reassure customers

By Abby Gillies

7:33 PM Sunday Jan 27, 2013

☆ Save f 19 8 in 0 g+ 0 p 0

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

Photo / File

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.

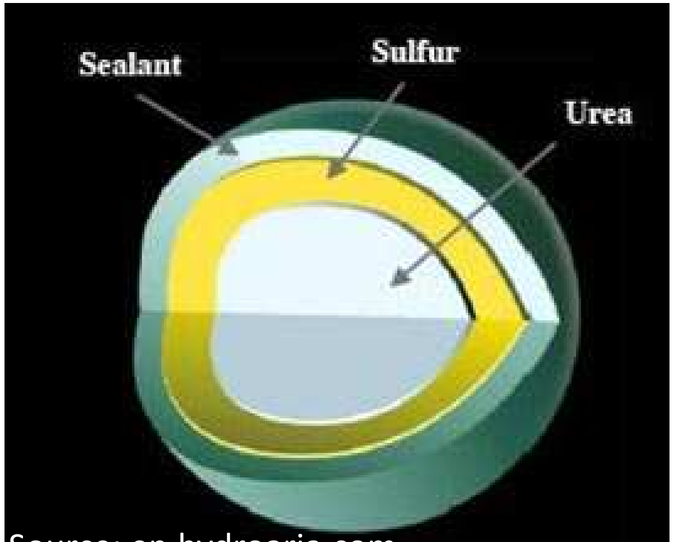
Greens hit out at milk contamination

- Fertiliser aid dropped after milk tests
- Fran O'Sullivan: Battle plan lacking for dairy trade risk
- Theo Spierings: Testing for DCD

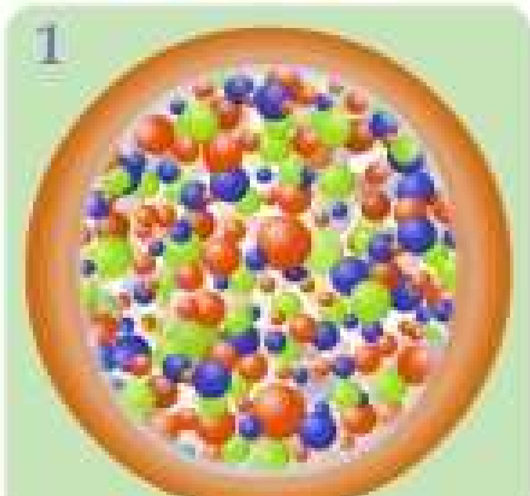
Related Tags

3 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

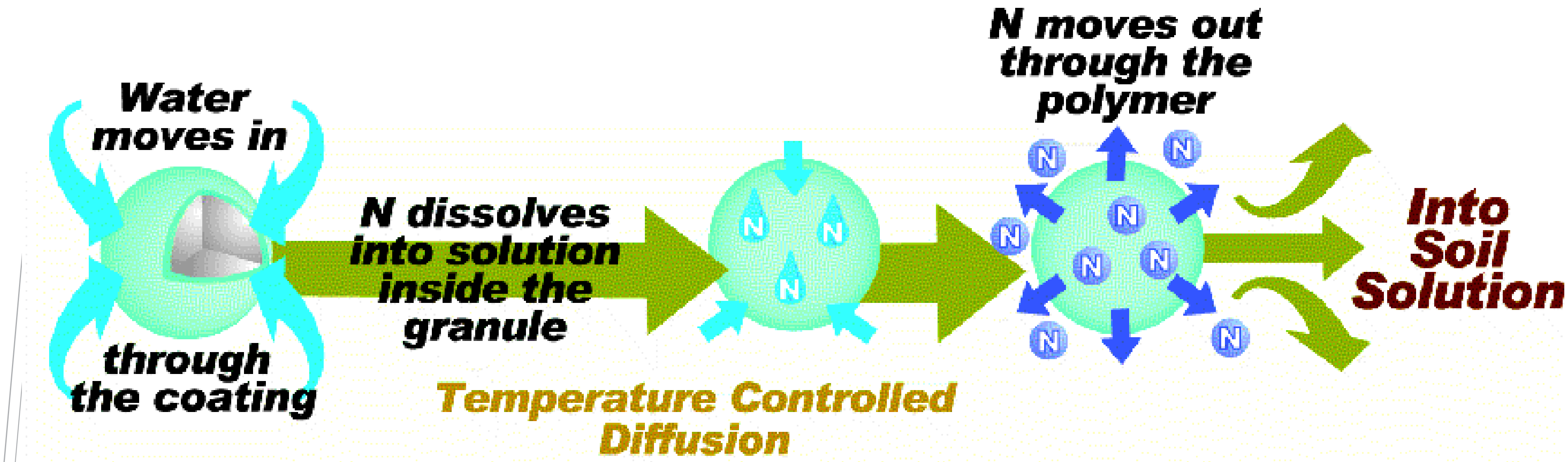


Source: en.hydroaria.com



Source: www.haifa-group.com

3 Controlled release N

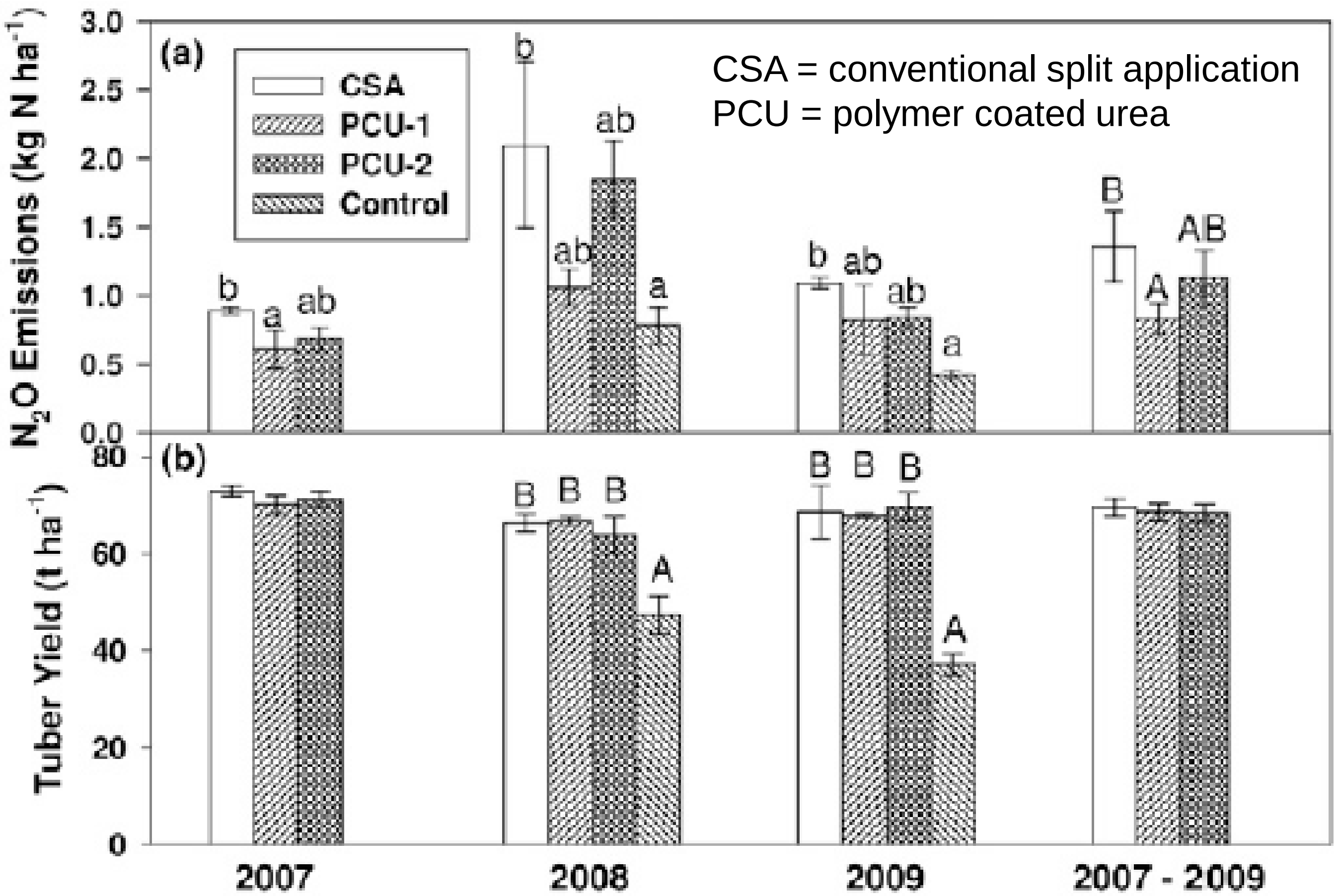


Major factors affecting release

- coating thickness
- temperature
- moisture

Source: IPNI

Controlled release N



Hyatt C.R., Venterea R.T., Rosen C.J., McNearney M., Wilson M.L., Dolan M.S. (2010) Polymer-coated urea maintains potato yields and reduces nitrous oxide emissions in a Minnesota loamy sand. Soil Science Society of America Journal 74:419-428.`

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

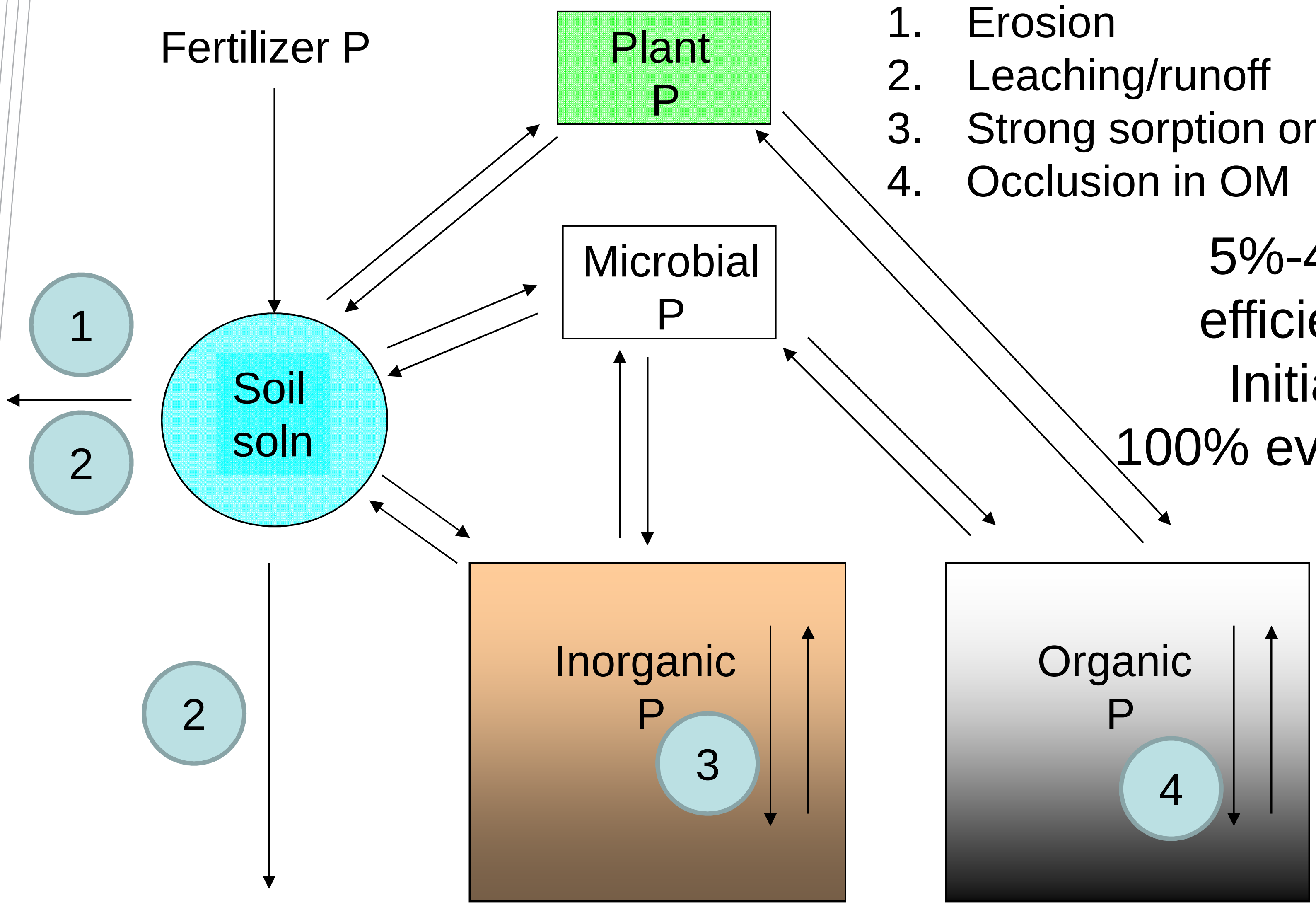
Reactions important for
P fertilizer use efficiency

The fate of added P in soil

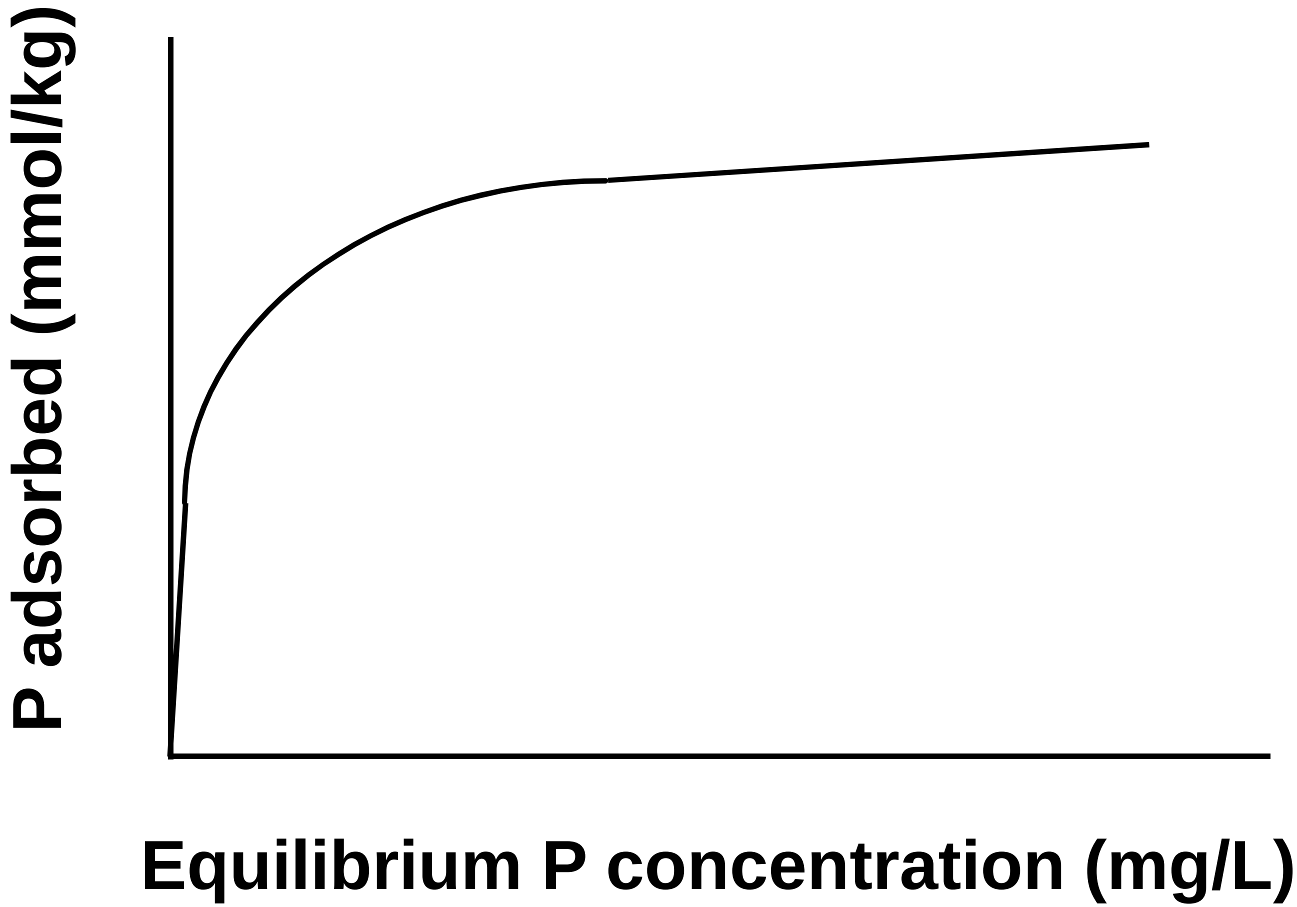
Inefficiency terms

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

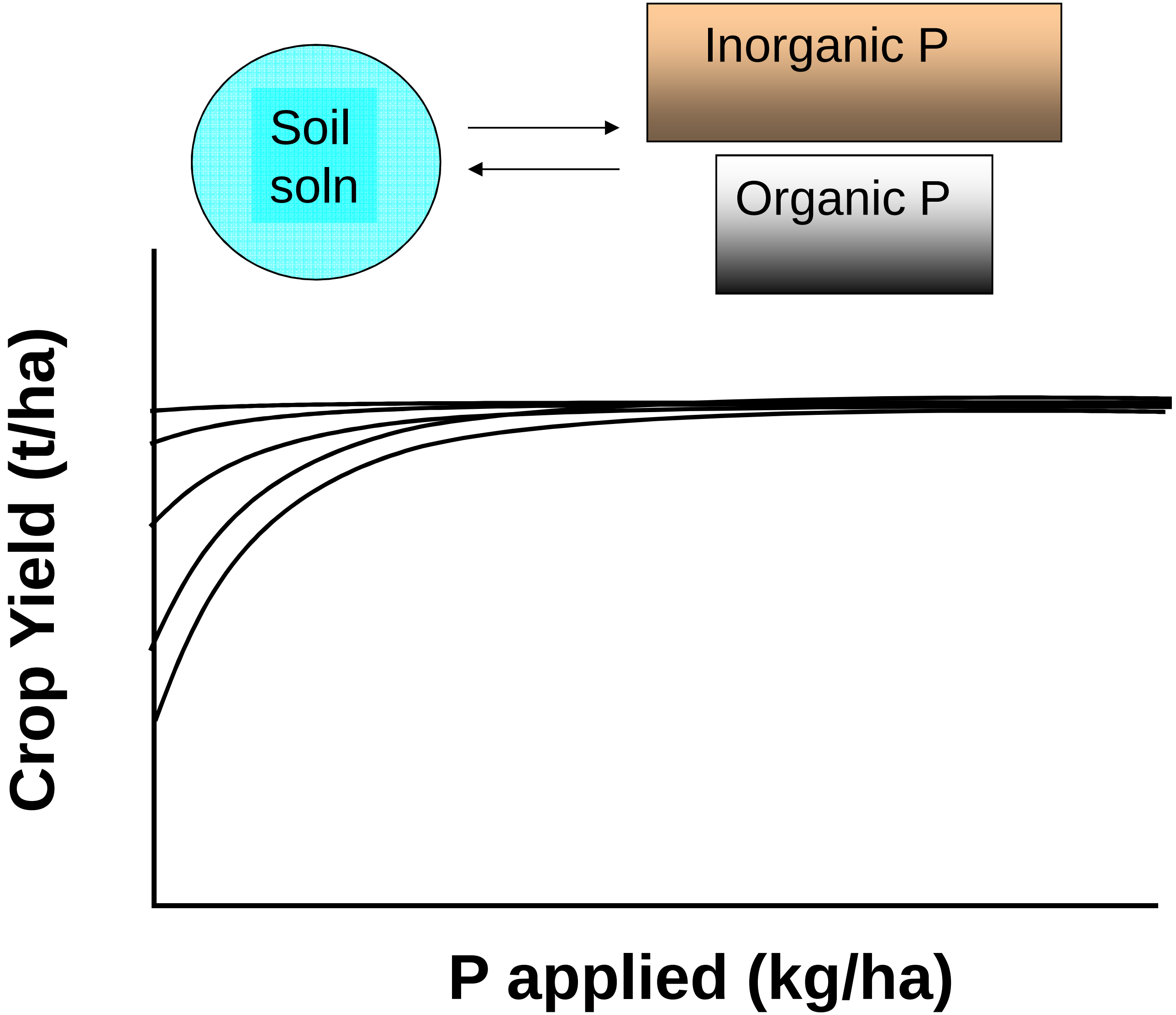
5%-40% efficiency Initially
100% eventually



Typical P sorption curve

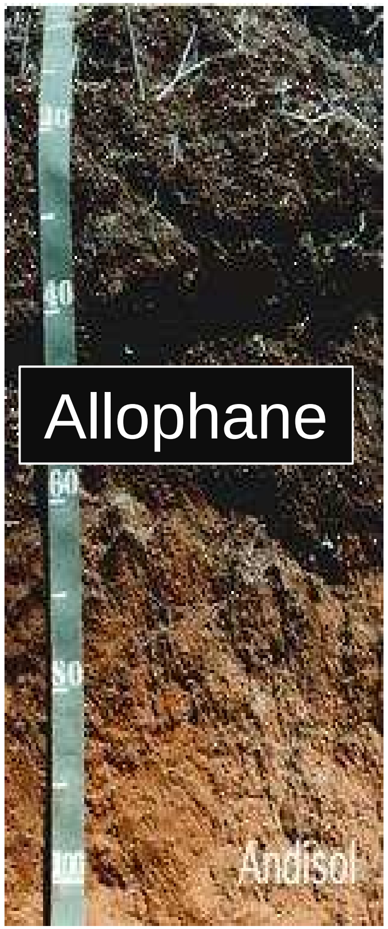


P responses over time



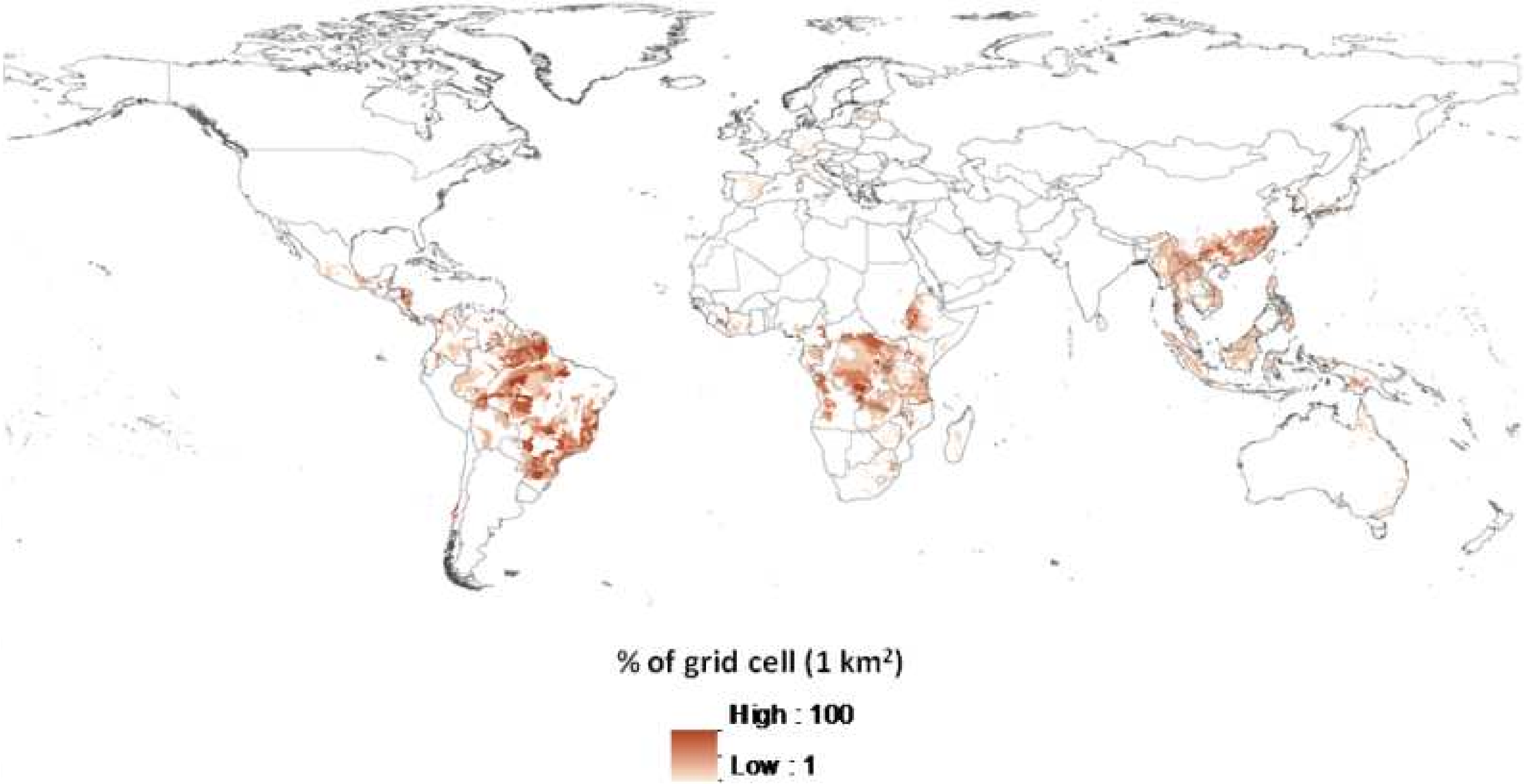
Highly P sorbing soils require the greatest P accumulation to reach “equilibrium”

Source: De Sousa, 2011



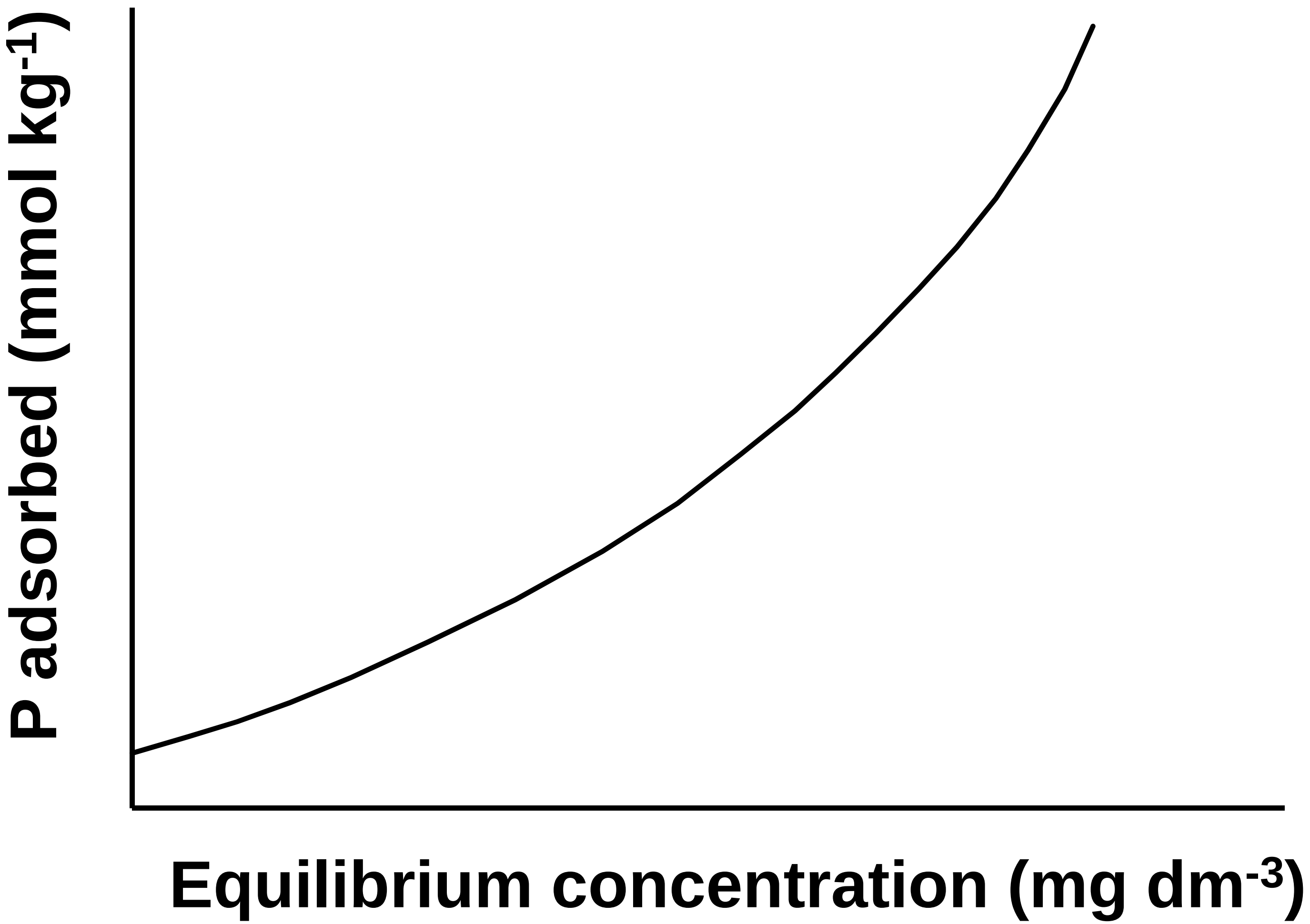
High P fixation

(i modifier)



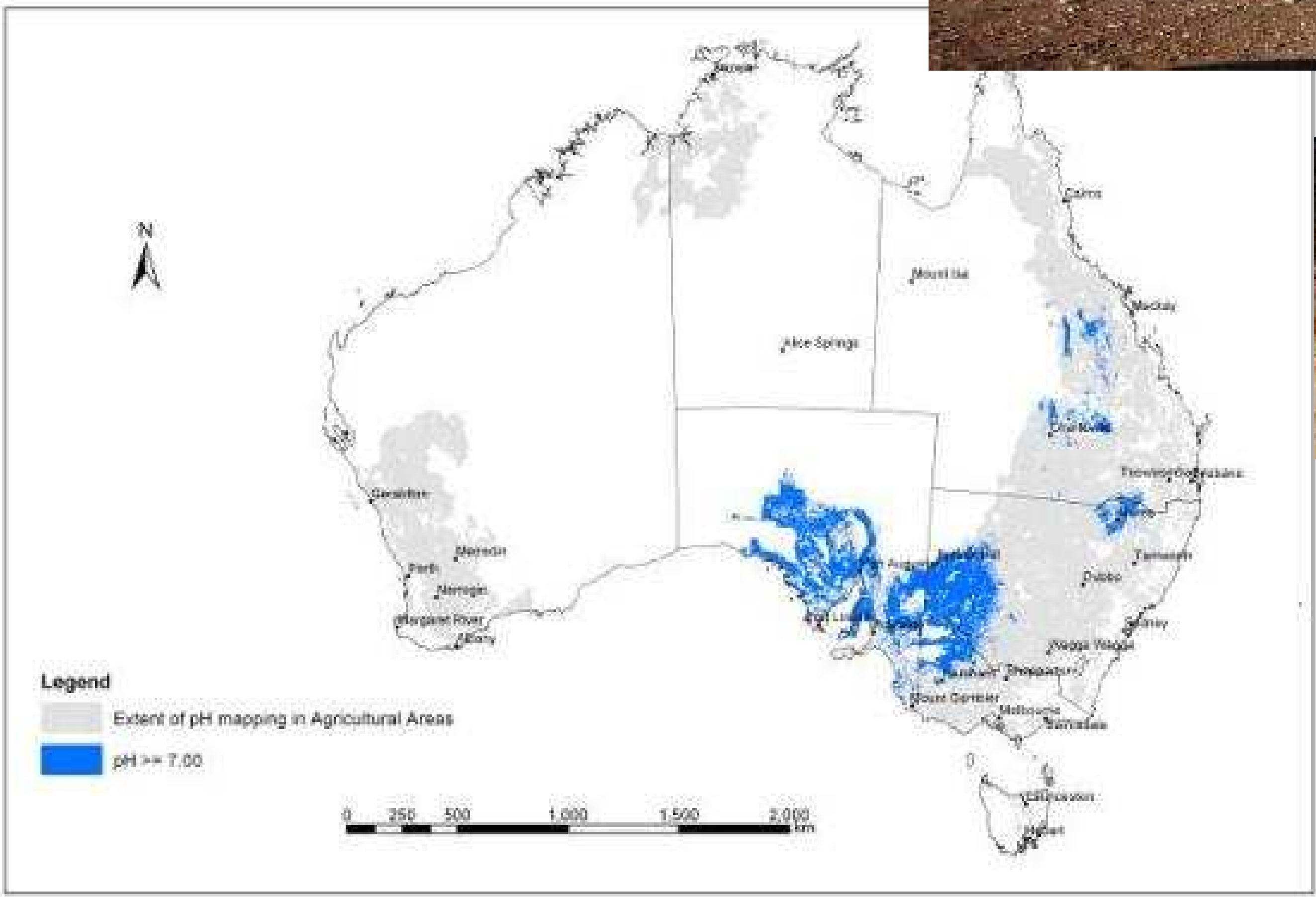
Source: HarvestChoice, 2010

Typical P precipitation curve



Calcareous soils have different issues

P precipitation may be more important

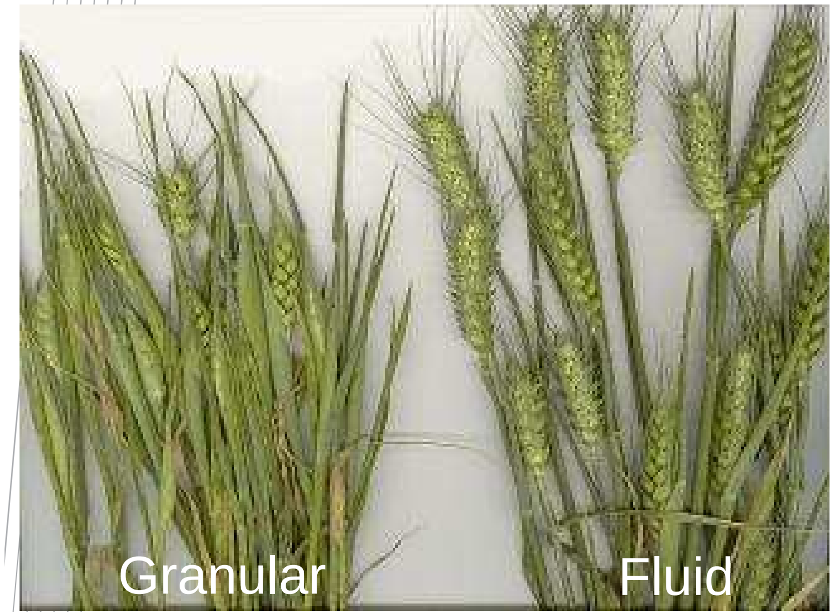


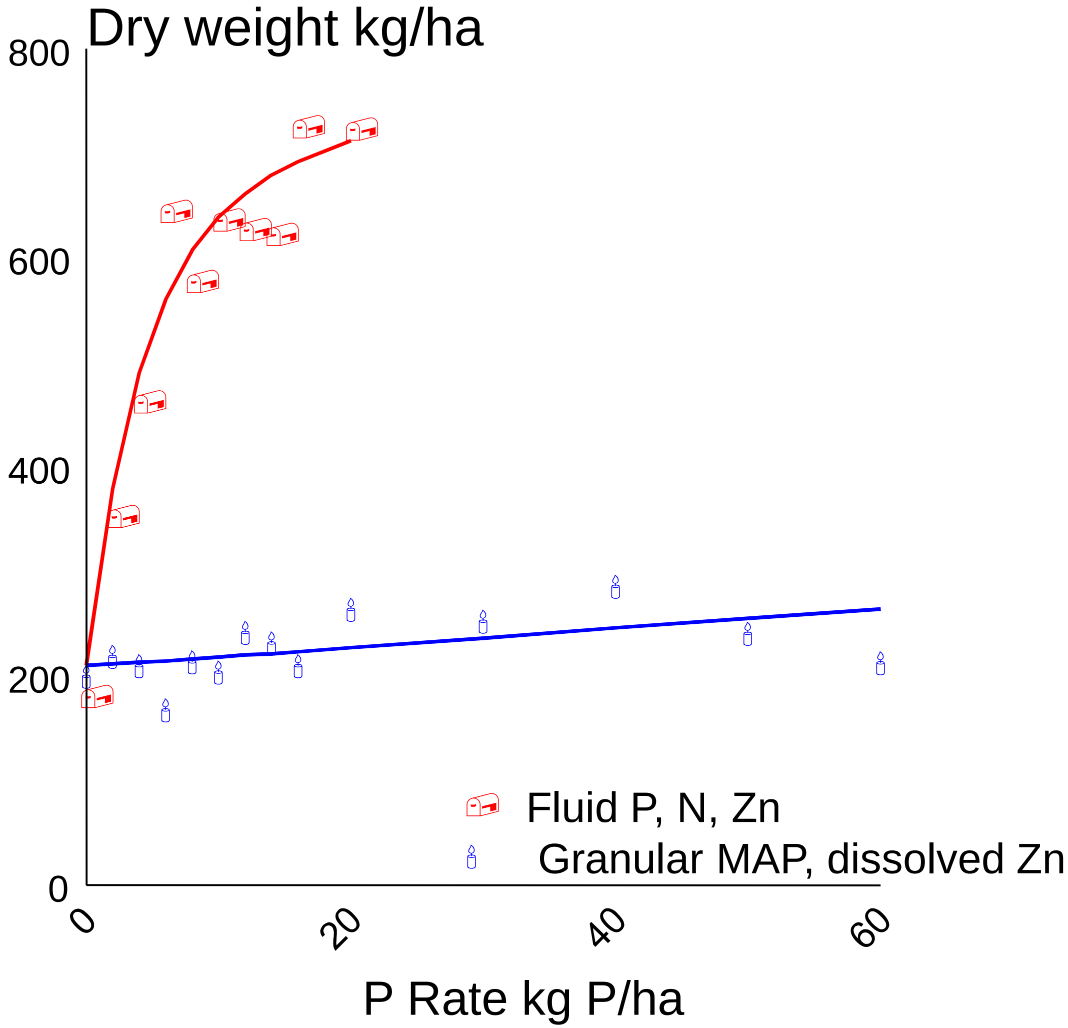
Reactions of added P

- Precipitation of P compounds around granules is a key process

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

Low efficiency of granular P in calcareous soils



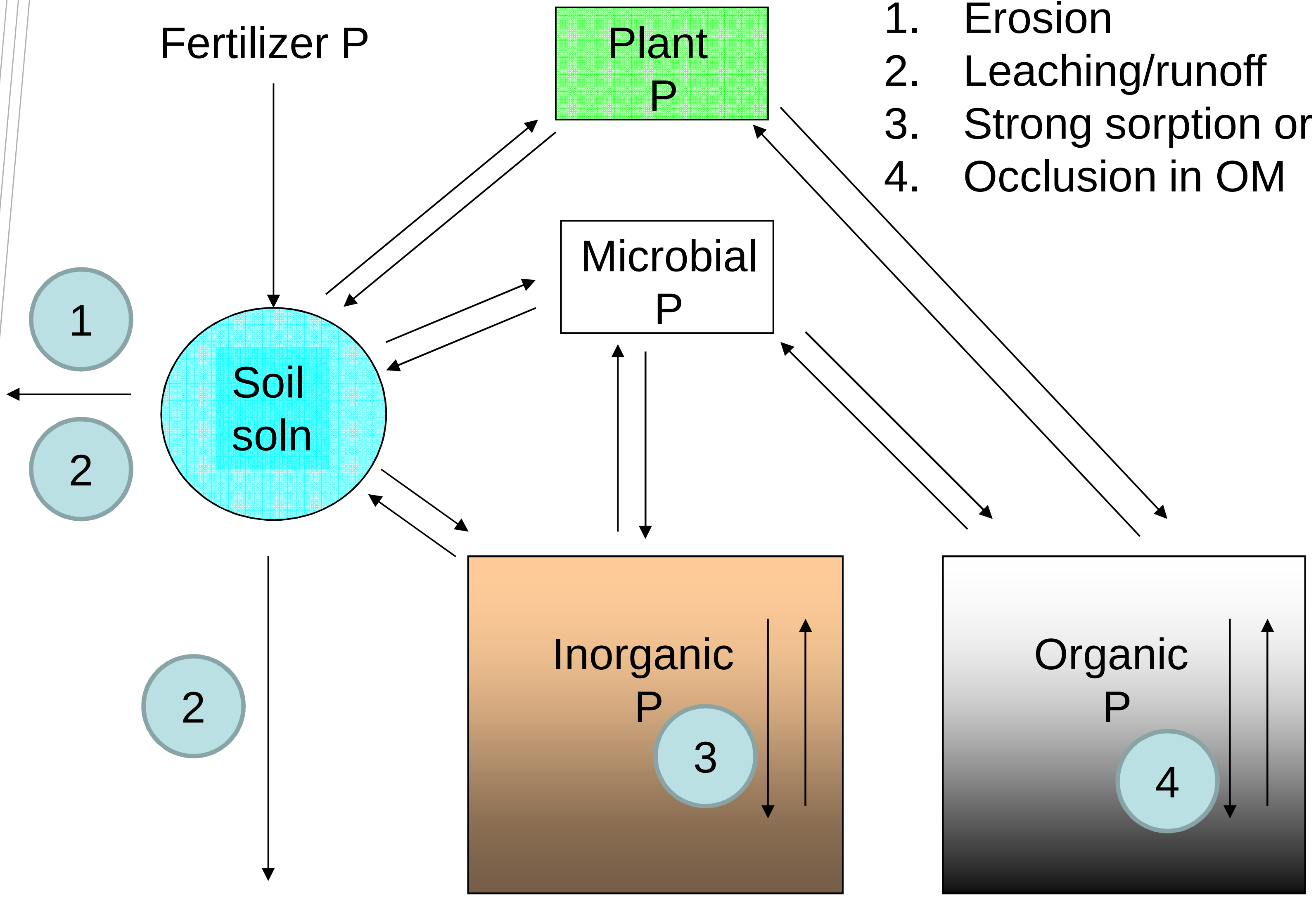


Holloway R.E., Bertrand I., Frischke A.J., Brace D.M., McLaughlin M.J., Sheppard W. (2001) Improving fertiliser efficiency on calcareous and alkaline soils with fluid sources of P, N and Zn. Plant and Soil 236:209-219.

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

Controlled release P to reduce P leaching/ runoff losses

2

- 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

2

SSP

Slow release P

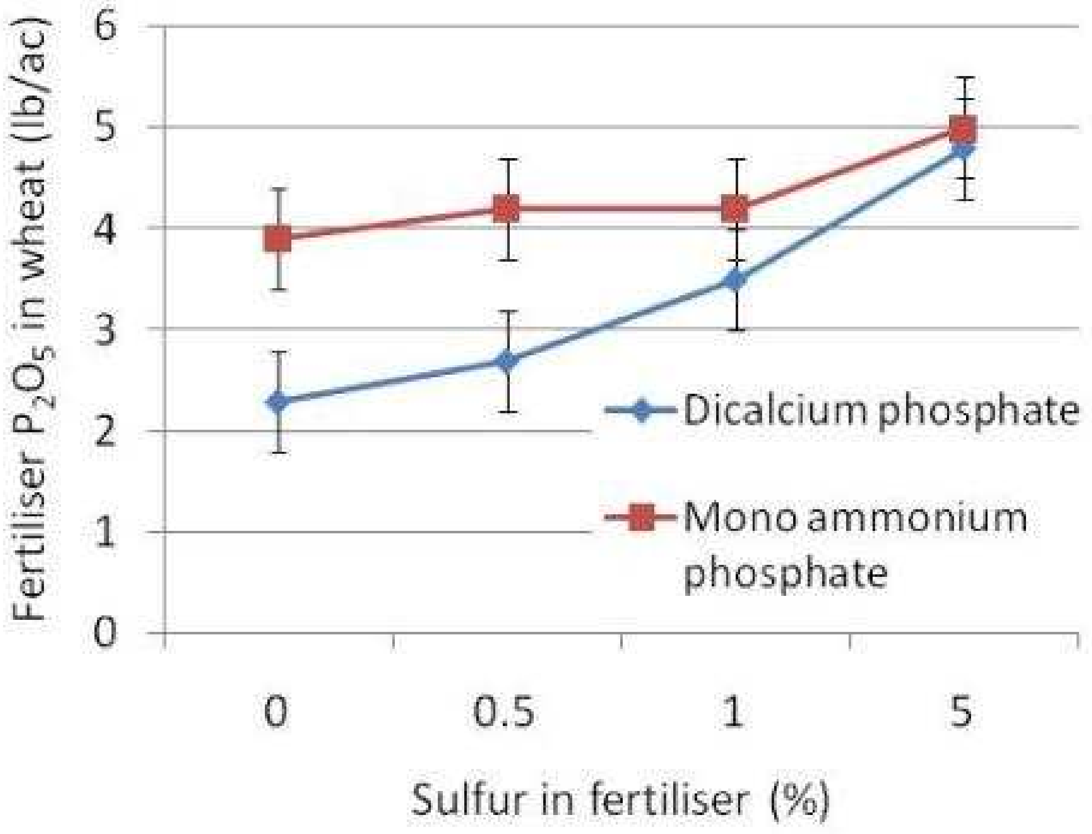
3

Reducing strong adsorption or precipitation reactions

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

3 Increasing P efficiency - modifying pH with S^0

$$S^0 \rightarrow SO_4^{2-} + 2H^+$$

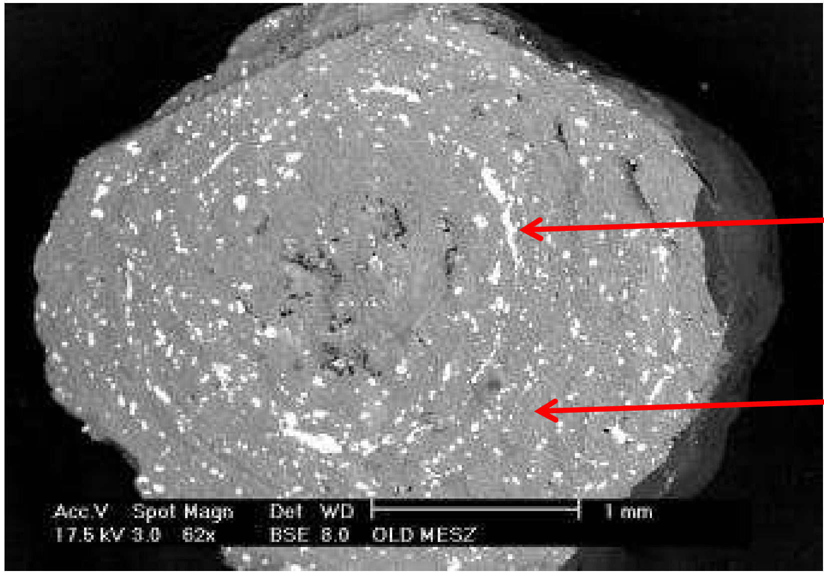


Source: Mitchell J., Dehm J.E., Dion H.G. (1952) The effect of small additions of elemental sulphur on the availability of phosphate fertilizers. Scientific Agriculture [Ottawa] 32:311-316.

3 Increasing P efficiency - modifying pH with SoA

Co-granulating ammonium sulfate (SoA) and elemental S with MAP can aid acidification and reduce Ca^{2+} activities releasing P

1. $NH_4^+ \rightarrow NO_3^- + 2H^+$
2. $SO_4^{2-} + CaHPO_4.H_2O \rightarrow CaSO_4 + HPO_4^-$

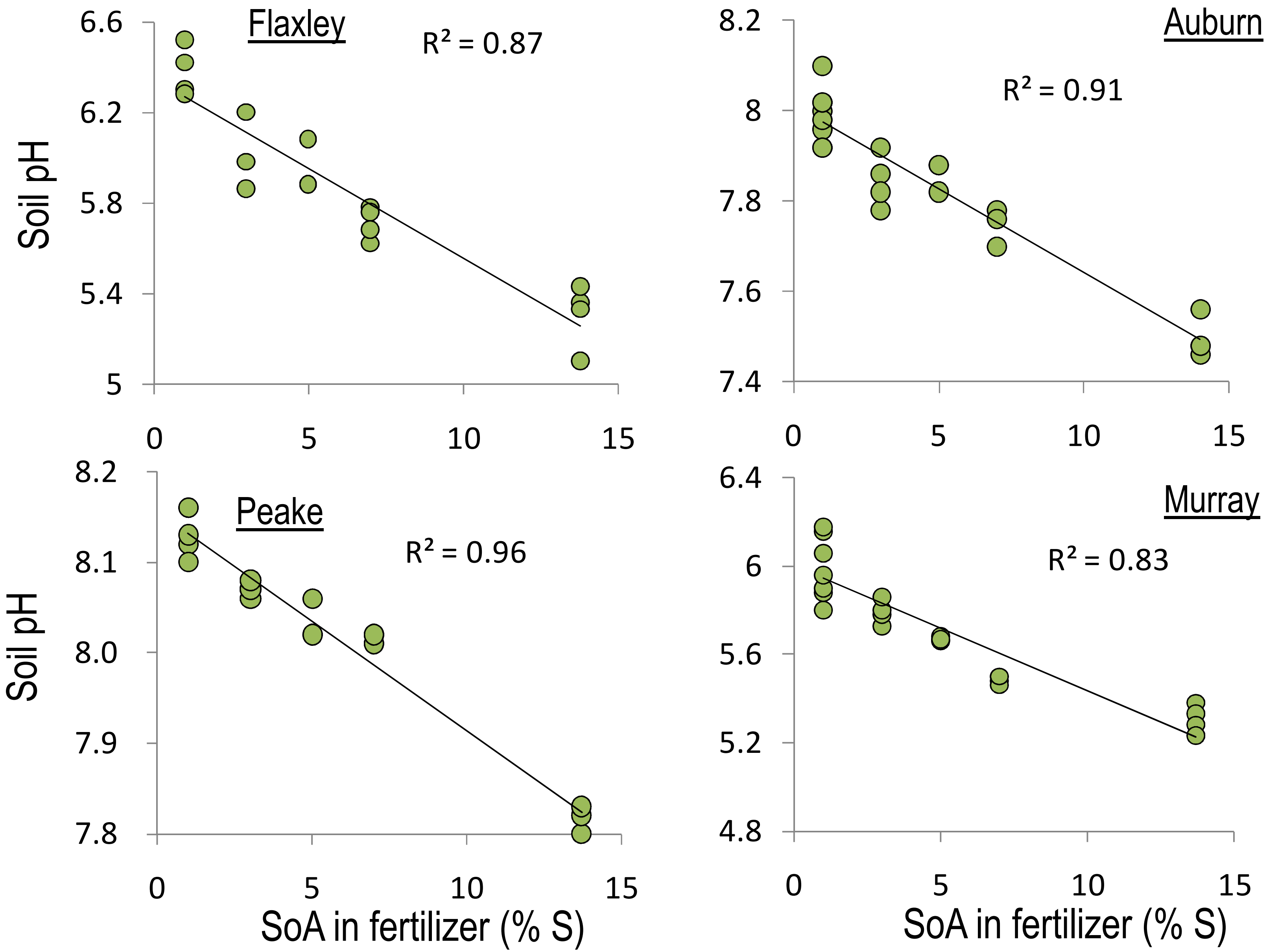


Elemental S

Ammonium sulfate

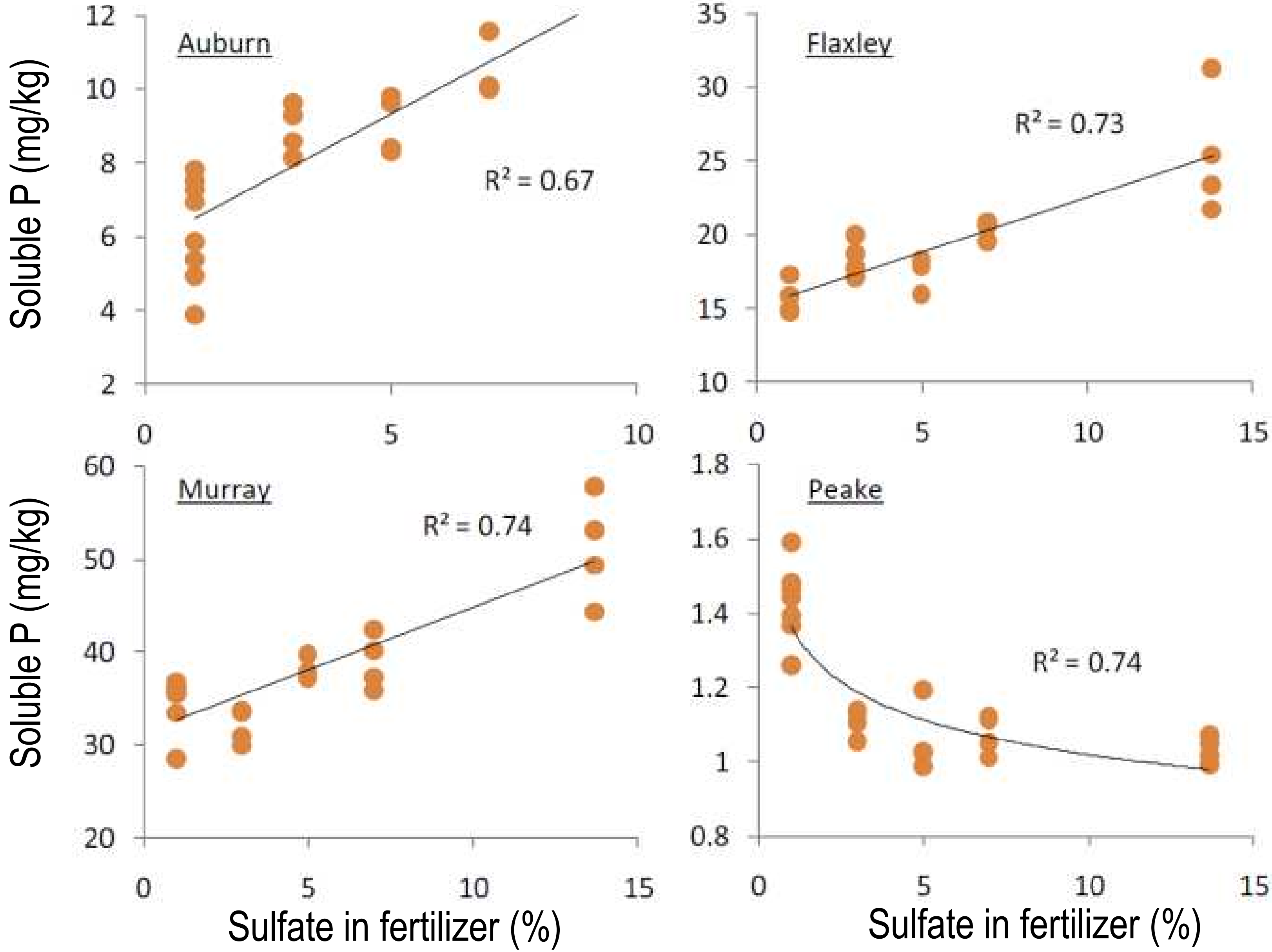
Both Mosaic (Microessentials) and Shell (Thiogro) have patented technologies in this area

3 Increasing P efficiency - modifying pH with SoA



Increasing P efficiency - modifying pH with SoA

3



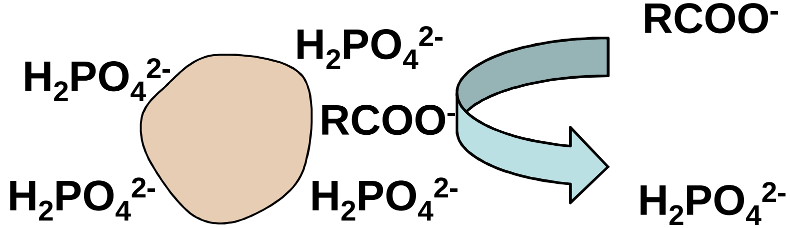
Increasing P efficiency – complex the "complexants"

- 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) 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 $Al^{3+}/Ca^{2+}/Fe^{3+}$ and liberate P

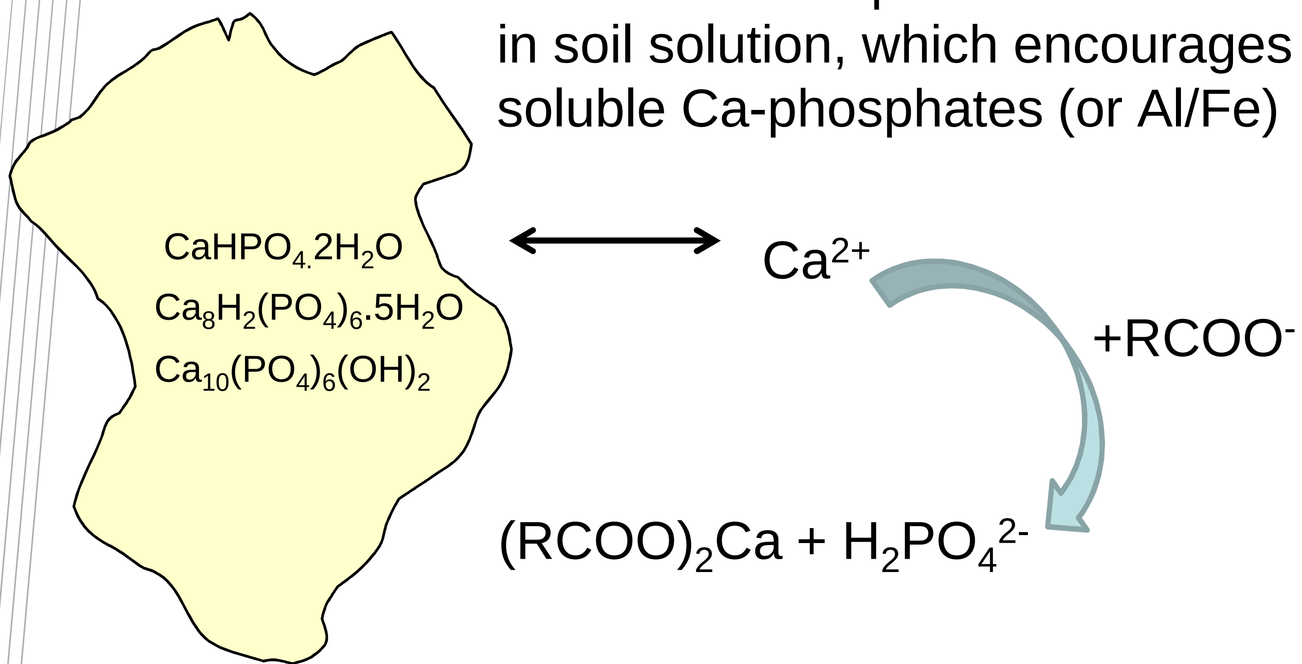
3

Increasing P efficiency – mode of action of chelates

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



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

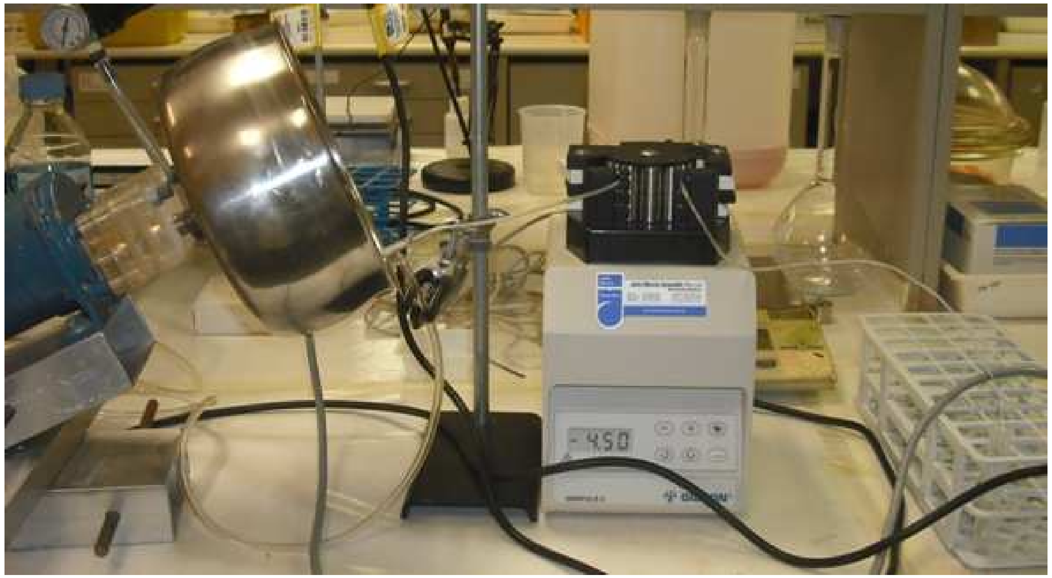


3 Can complexation of Al, Ca or Fe improve P fertilizer efficiency?

Coatings tested on MAP:

- NTA
- Tiron
- Citrate
- Citric acid
- Sulfate of ammonia
- Avail (commercial)
- Pmax (commercial)

Coated at 1%

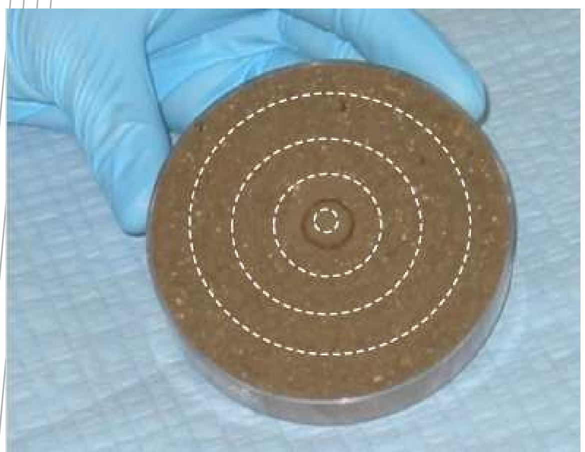


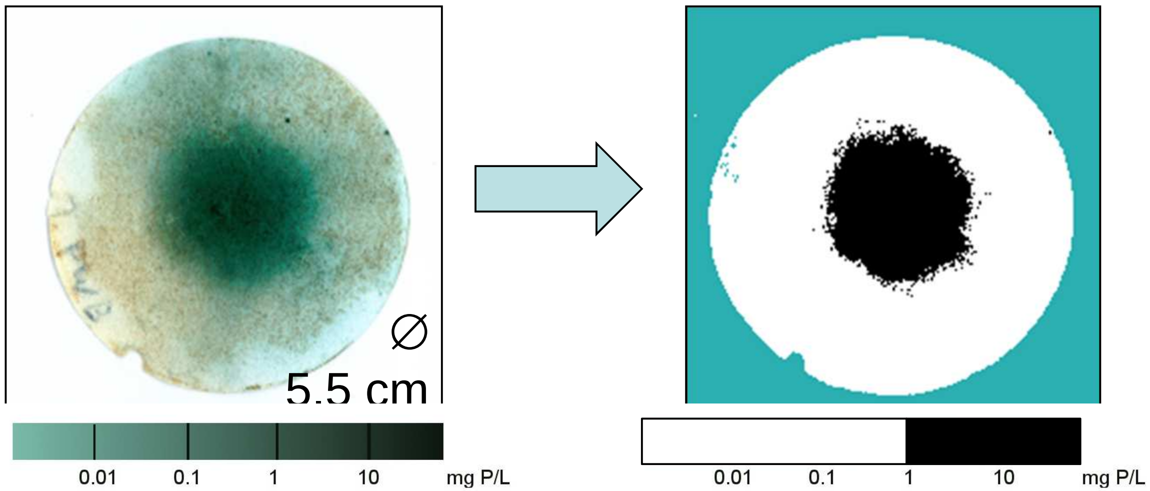
SSP and SSP coated with a humic-based organic chelate ("TopPhos") also compared

Degryse, F., Ajiboye, B., Armstrong, R.D.A. and McLaughlin M.J. (2013). Sequestration of phosphorus-binding cations by complexing compounds is not a viable mechanism to increase P efficiency. Soil Science Society of America Journal (in review).

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

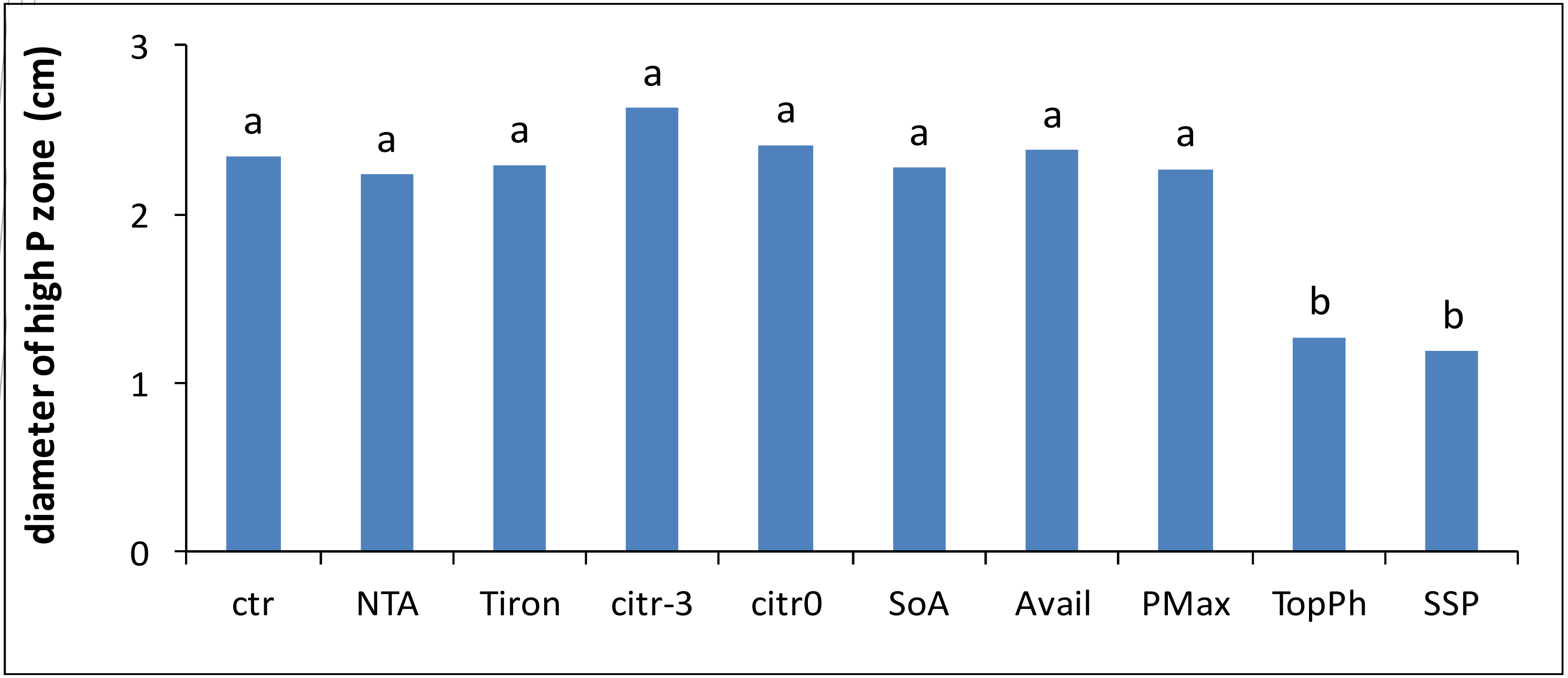




Degryse F., McLaughlin M.J. (2013) A method to visualize diffusion of phosphorus from fertilizer and comparison with chemical measurements and modeling results. Soil Science Society of America Journal (in review).

Results – little effect on P diffusion

Oxisol - pH_{Ca} 5.3

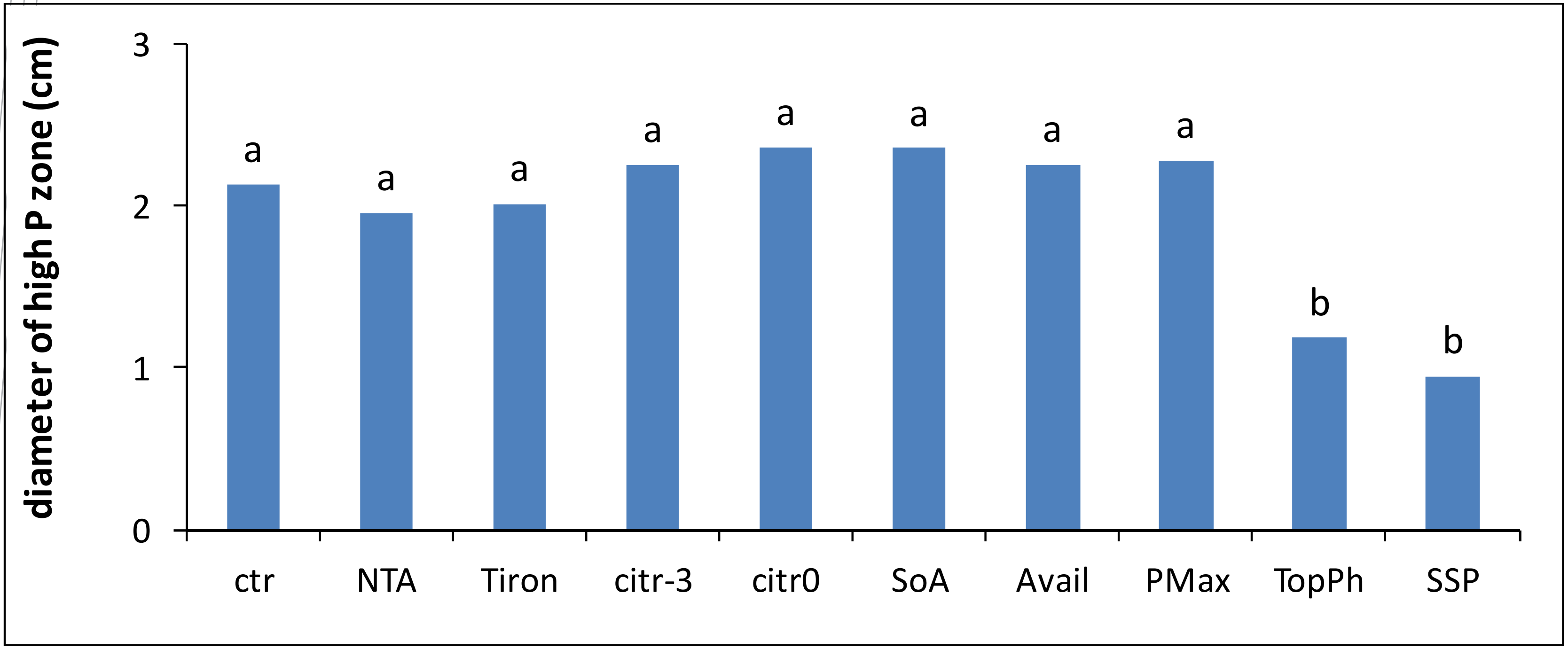


- MAP treatments: diameter ~2.4 cm
- TopPhos and SSP: diameter ~ 1.3 cm

Degryse, F., Ajiboye, B., Armstrong, R.D.A. and McLaughlin M.J. (2013). Sequestration of phosphorus-binding cations by complexing compounds is not a viable mechanism to increase P efficiency. Soil Science Society of America Journal (in review).

Results – little effect on P diffusion

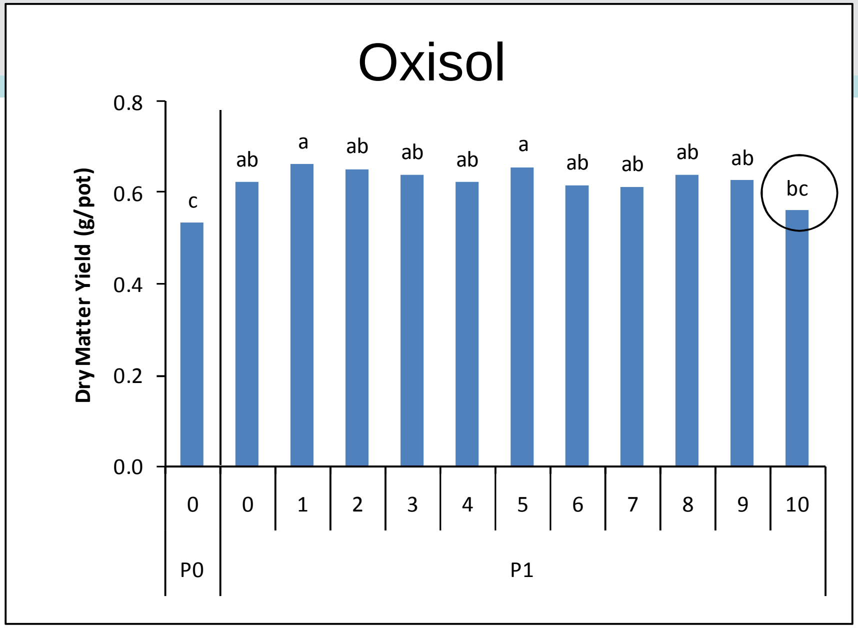
Calcareous soil - pH_{Ca} 7.7

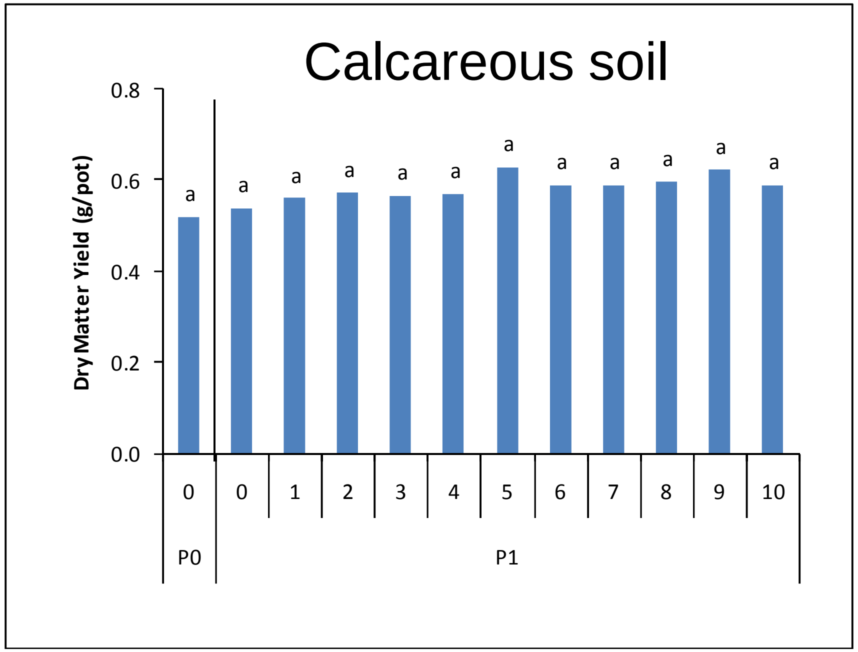


- MAP treatments: diameter ~2.2 cm
- TopPhos and SSP: diameter ~ 1.1 cm

Degryse, F., Ajiboye, B., Armstrong, R.D.A. and McLaughlin M.J. (2013). Sequestration of phosphorus-binding cations by complexing compounds is not a viable mechanism to increase P efficiency. Plant and Soil (in review).

Results – no effect on P availability to plants





0 none
1 NTA
2 Tiron
3 Citr-3
4 Citr-2
5 Citr0
6 (NH4)2SO4
7 Avail
8 PMax
9 TopPhos
10 SSP

Degryse, F., Ajiboye, B., Armstrong, R.D.A. and McLaughlin M.J. (2013). Sequestration of phosphorus-binding cations by complexing compounds is not a viable mechanism to increase P efficiency. Soil Science Society of America Journal (in review).

3

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

3

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 ⇒ **1 mmol Ca**
- 0.3 mg product, complexation capacity of circa 2 mmol/g
  ⇒ **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) ⇒ **0.18 mmol** sites
- **0.0006 mmol complexing groups**

NO

Complexation unlikely to aid P effectiveness

3

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

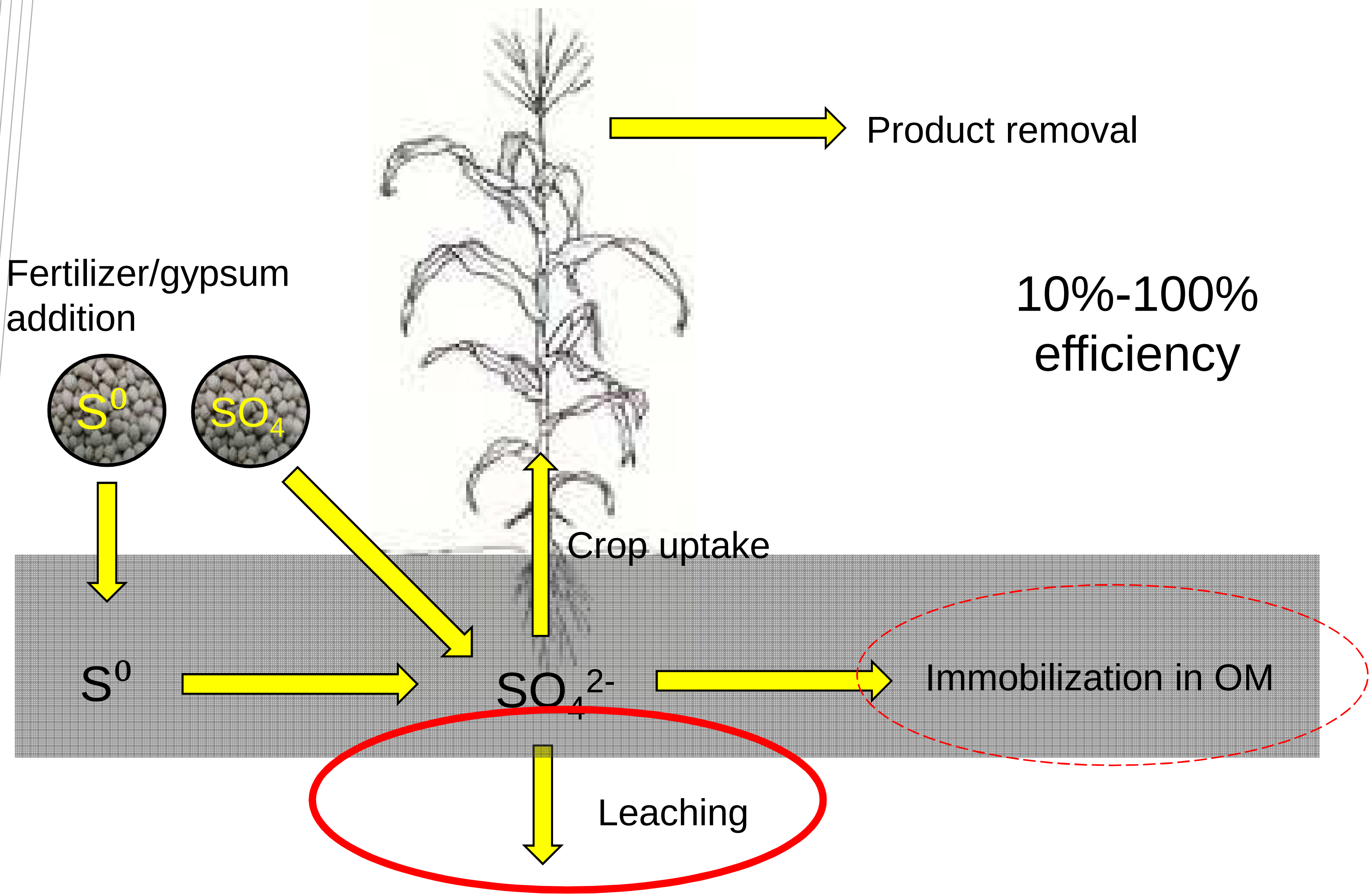
Potassium

- 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

Sulphur

Reactions important for
S fertilizer use efficiency

Sulfur – fertilizer inefficiency processes

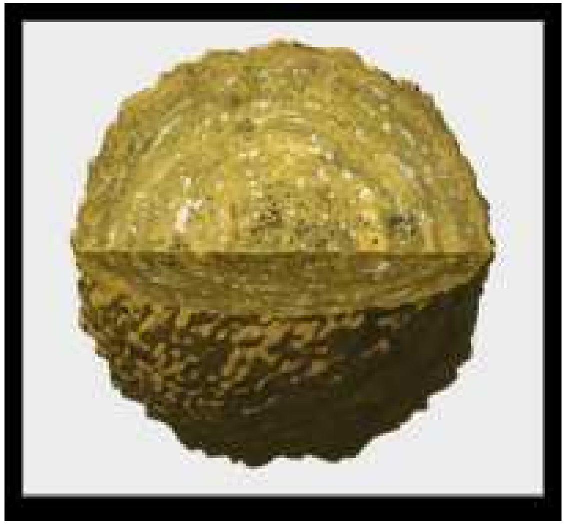


Controlled/slow-release S

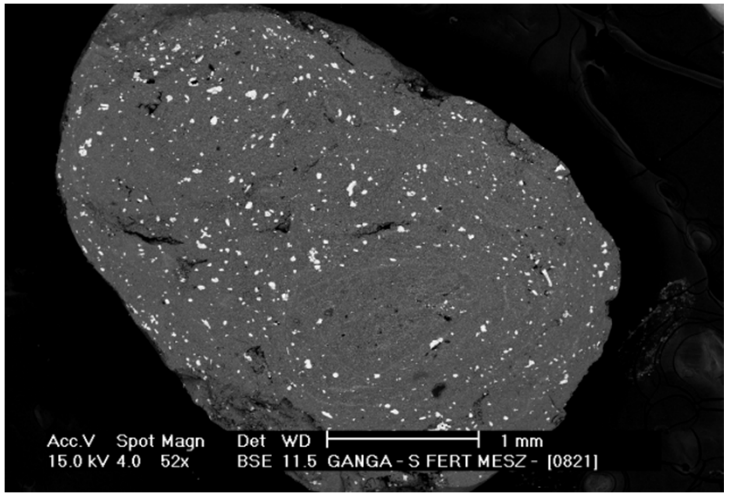
- In environments where sulfate leaching is problematic, the cheapest and easiest way to supply slow-release S is via elemental S (S^0)
- Oxidation of S^0 is too slow to provide S for crop nutrition at early growth stages so generally some SO_4 is needed in the fertilizer
- Many combined SO_4/S^0 products 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

S^0/SO_4-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



S^0/SO_4-enhanced products

Microessentials

MES10

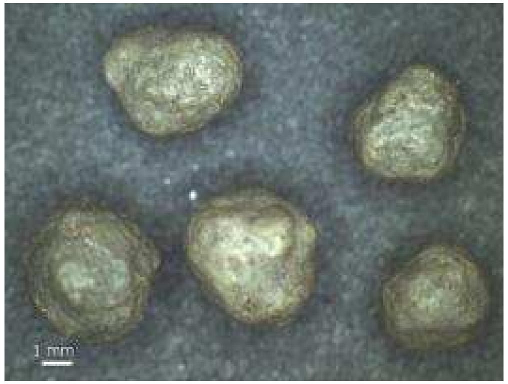
MAP

5% ES

5% SO_4-S

Shell Thiogro

Granulock



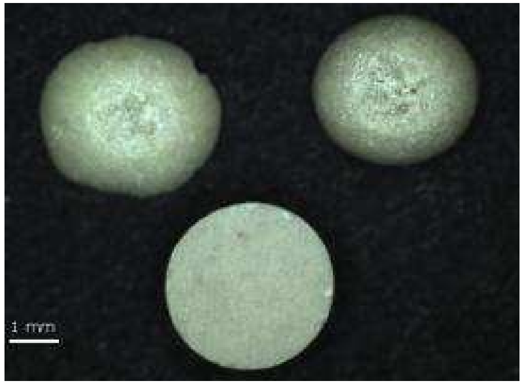
DAP

8% ES

4% SO_4-S

S^0 prills

Tiger 90



90%ES

S^0/SO_4-enhanced products

Soil saturated from bottom to top

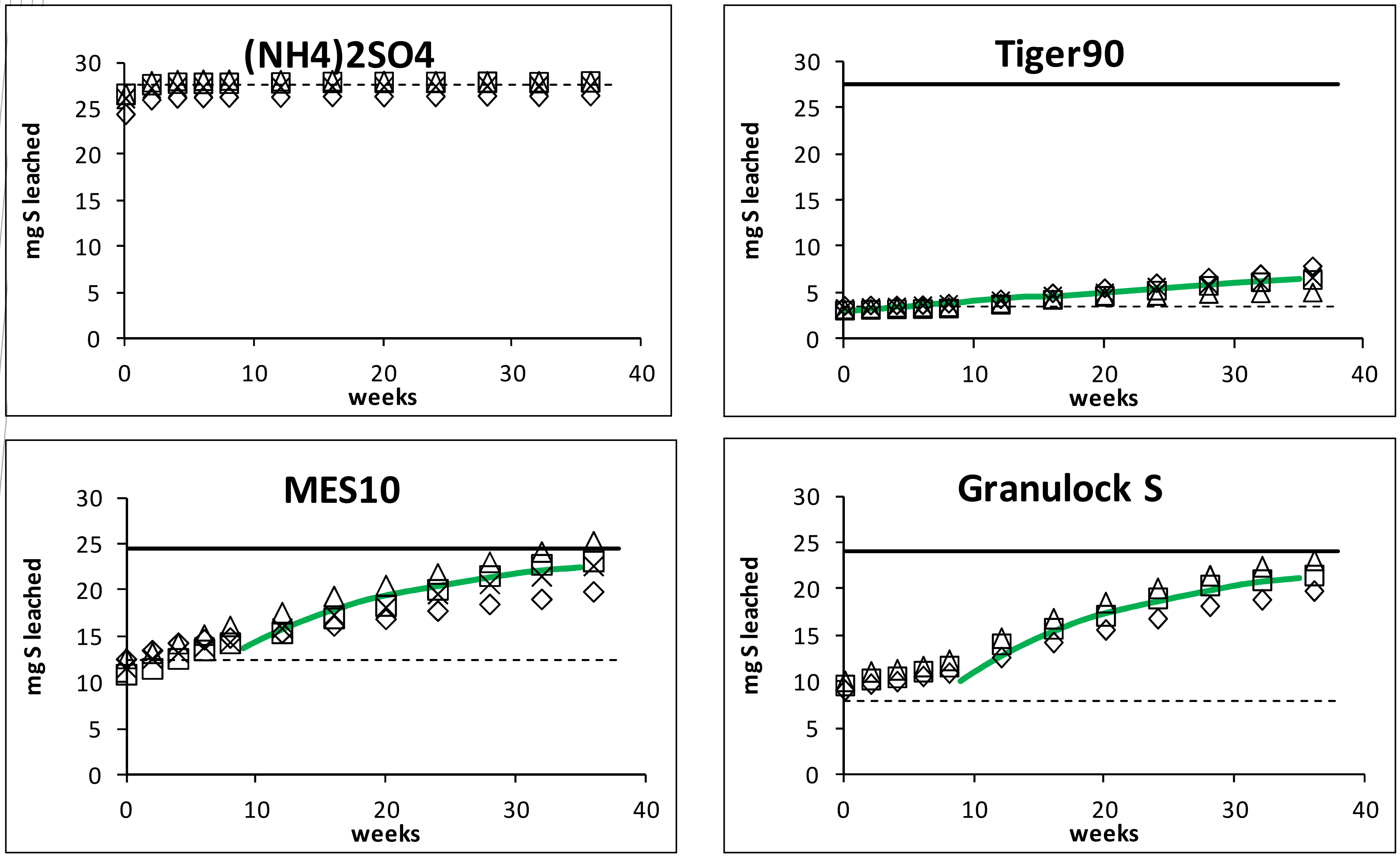
At day 1: leached with 35 ml deionized water

Incubated at 25°C

Leached every two weeks for first two months, and then monthly

Ammonium sulfate used as “control”

S^0/SO_4-enhanced products



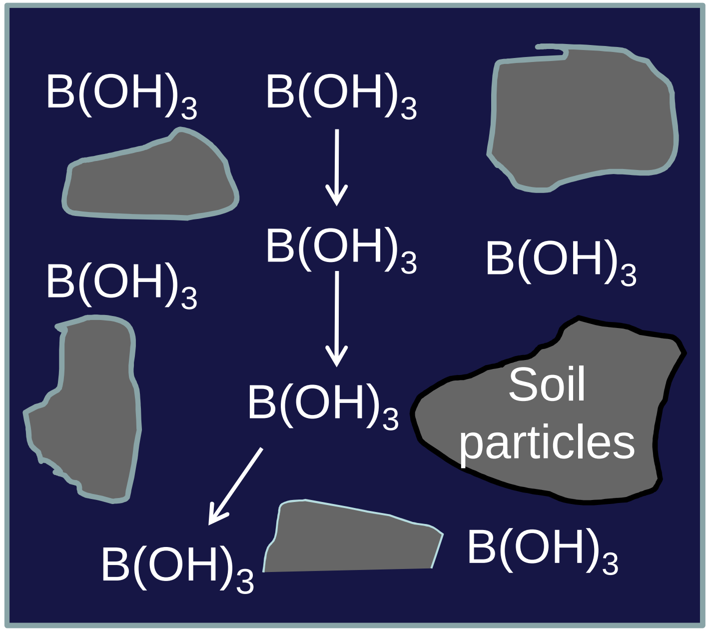
Trace elements

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

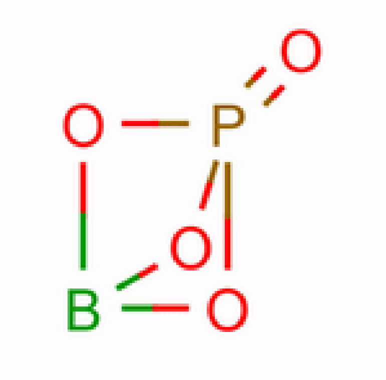
$$CaB_3O_4(OH)_3.H_2O + 4\ H_2O \leftrightarrow 3B(OH)_4^- + Ca^{2+} + H^+$$

$$NaCaB_5O_6(OH)_6.5H_2O + 3\ H^+ \leftrightarrow 5\ H_3BO_3 + Ca^{2+} + Na^+ + 2H_2O$$

$$Ca^{2+} + H_2PO_4^- + 2H_2O \leftrightarrow CaHPO_4.2H_2O + H^+$$

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

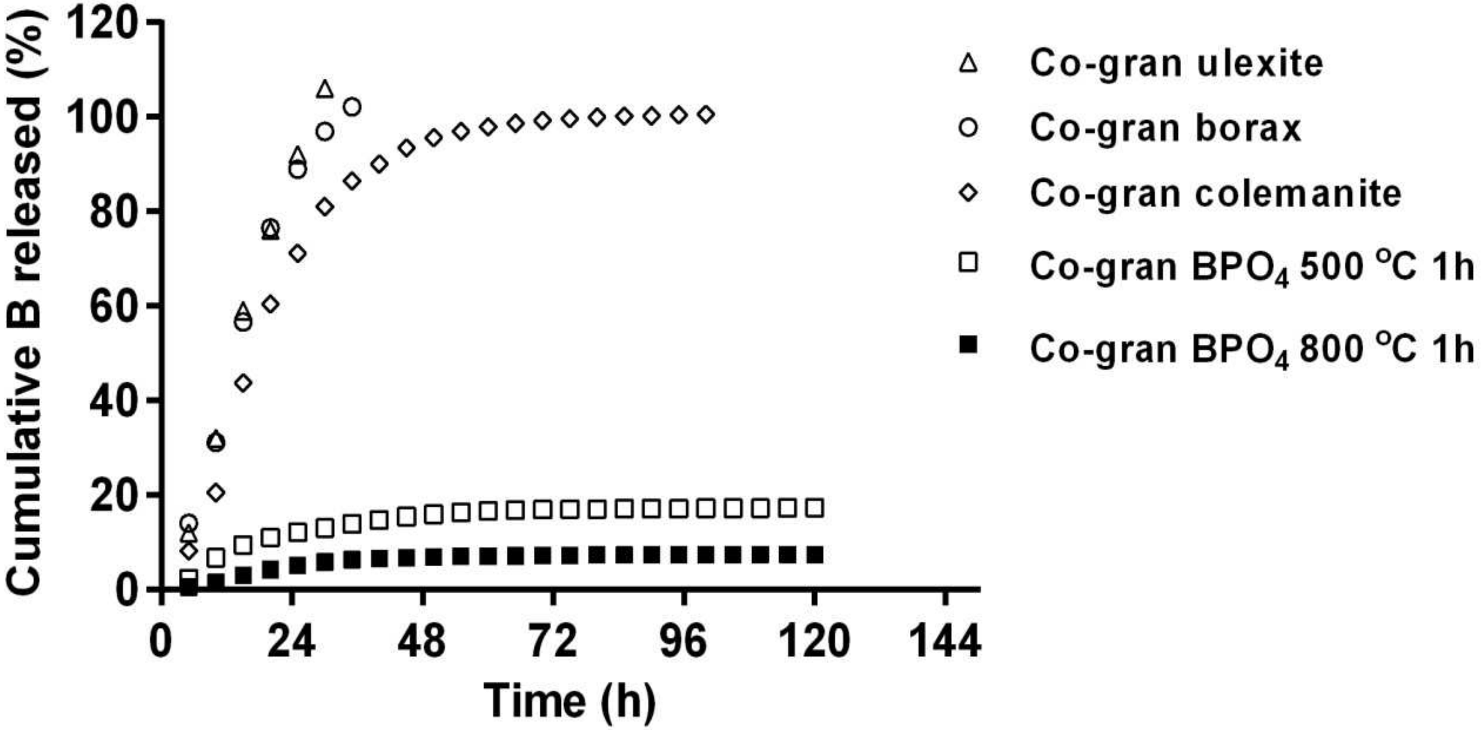


BPO_4

$$BPO_4 + 3H_2O \leftrightarrow H_3BO_3 + H_3PO_4$$

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



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

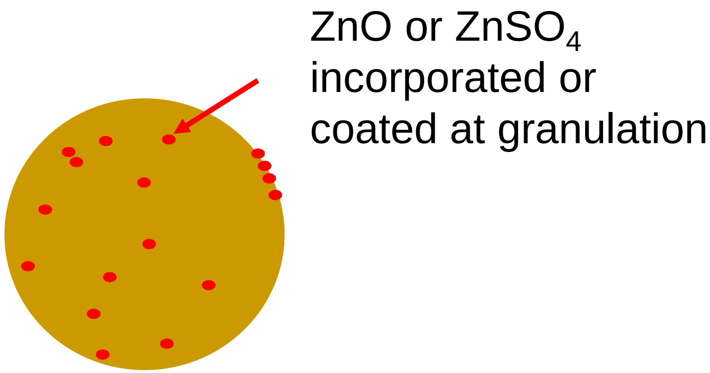
Trace elements - zinc

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

$Cu + PO_4 \rightarrow Cu_3(PO_4)_2$

$Mn + PO_4 \rightarrow Mn_3(PO_4)_2$

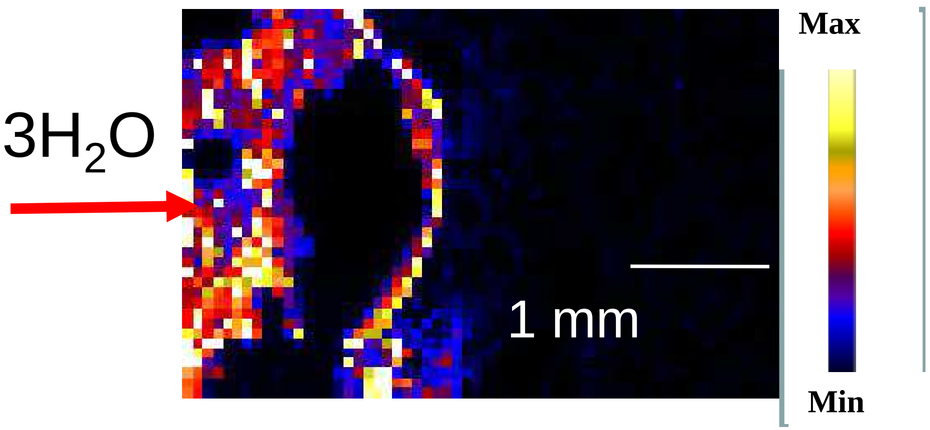
$Zn + PO_4 \rightarrow Zn_3(PO_4)_2$



+ other mixed phosphate precipitates

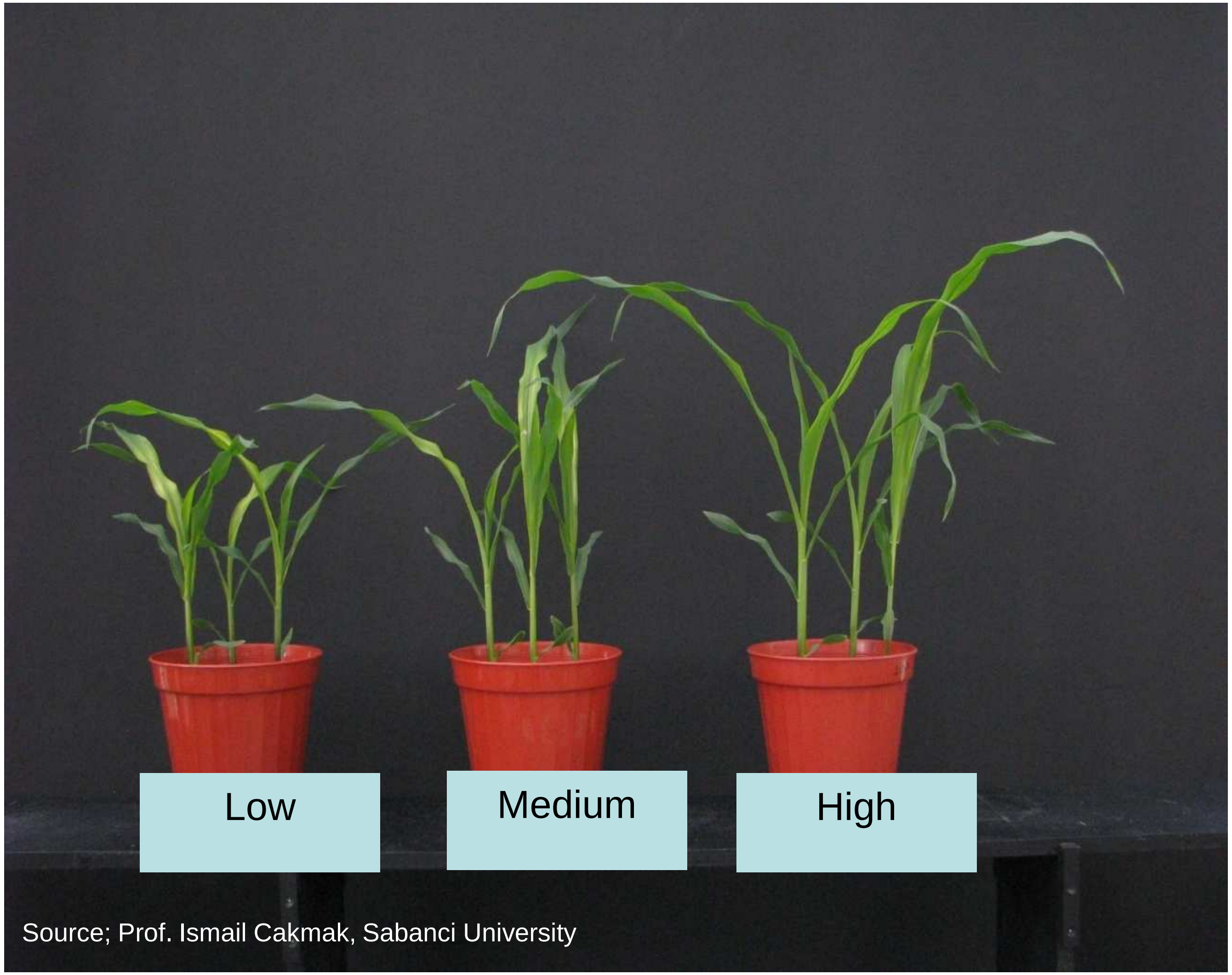
- Trace element coatings do not escape this chemistry

$$3ZnO + 2H_3PO_4 \Leftrightarrow Zn_3(PO_4)_2 + 3H_2O$$



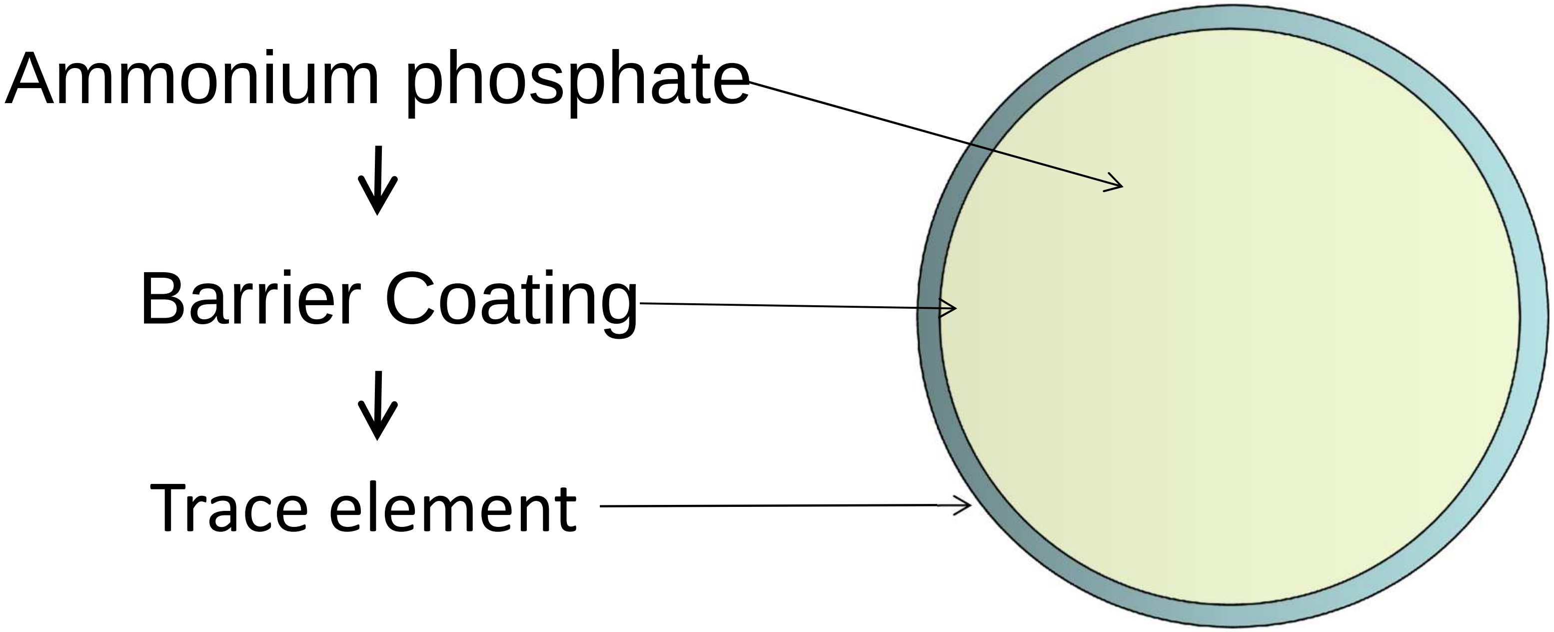
Efficiency < 1%

For banded fertilizers, water solubility of Zn in granule is a key predictor of performance



Improved Zn fertilizers

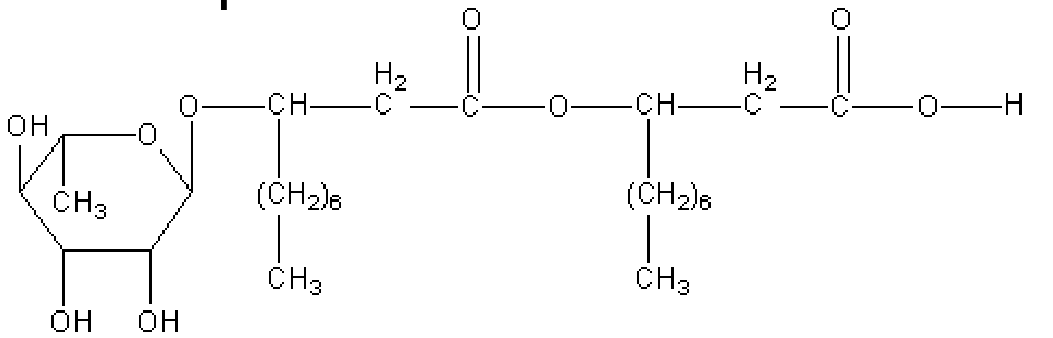
Physical barriers to reduce phosphate precipitation of zinc and to increase water solubility



Peacock A, Stacey SP and McLaughlin MJ. 2010. United States Patent and Trademark Office Application No 61/309,894. Fertilizer Composition Containing Micronutrients and Methods of Making Same.

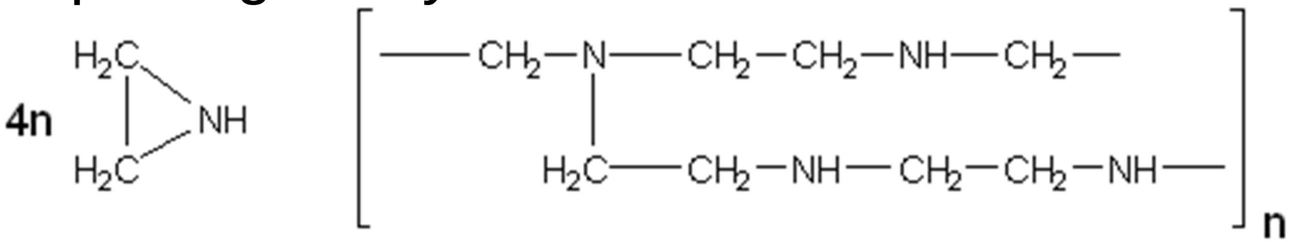
"New" chelates to reduce ppt reactions

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



Stacey SP, MJ McLaughlin and E Lombi. 2005. Australian Application No. 2006225072; PCT No. PCT/AU2006/000334; PCT OPI Date 21/9/2006 - Sequestering agent for Micronutrient Fertilisers.

- Polyethyleninime (PEI) – polymer with high Zn-complexing ability



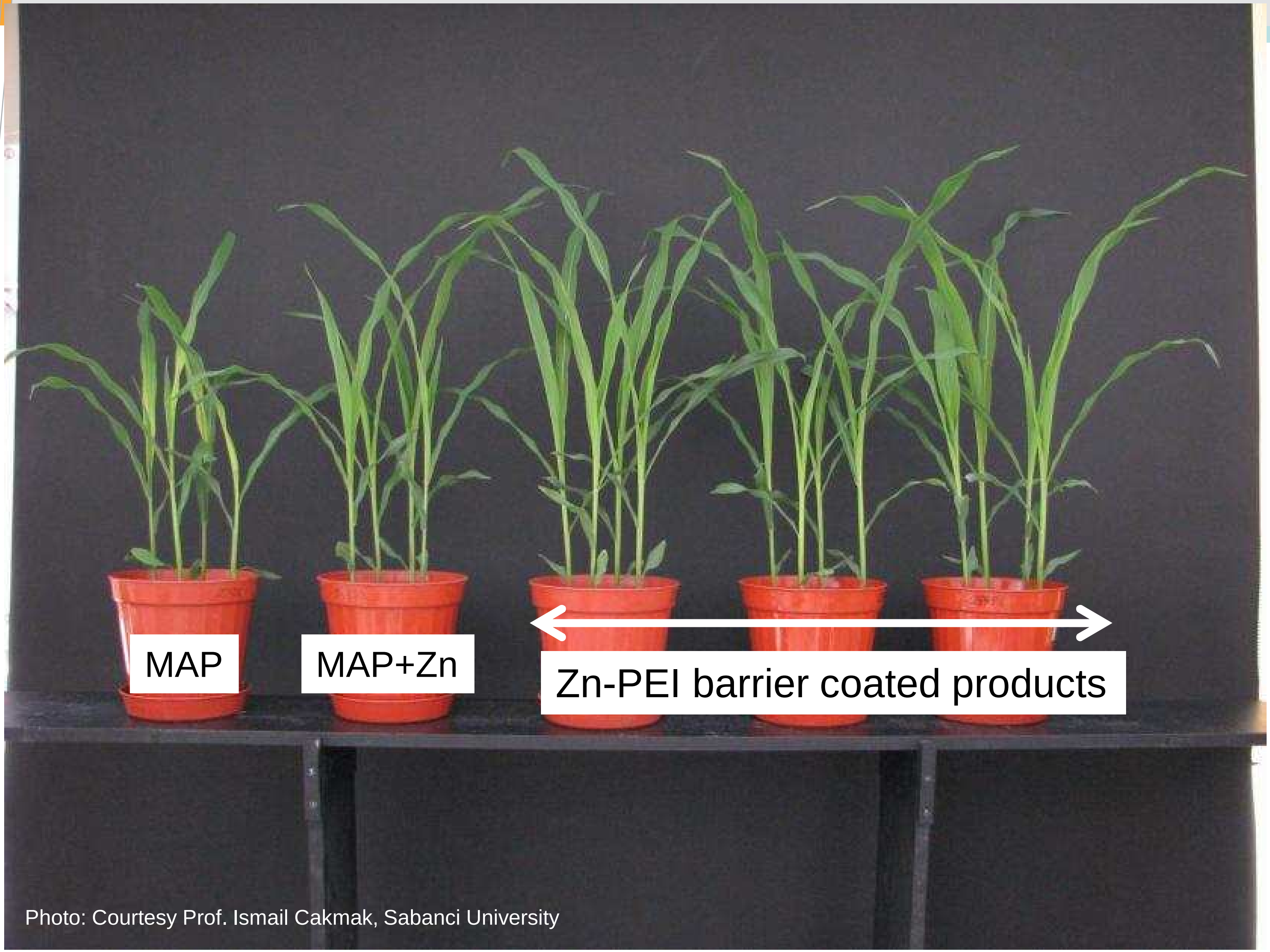
Stacey SP, MJ McLaughlin and E Lombi. 2005. Australian Application No. 2006269807; PCT no. PCT/AU2006/000951; PCT OPI Date 18/1/2007 - Chelating agents for Micronutrient Fertilisers

“New” chelates to reduce ppt reactions

0 0.75 2 4 6

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

Improved Zn fertilizers



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!

Acknowledgements

Fien Degryse
Rosalyn Baird
Rodrigo Coqui Dasilva
Margaret Abat
Cuicui Zhao
Daniela Montalvo
Bogumila Tomczak
Colin Rivers
Deepika Setia
Ashleigh Broadbent
Roger Armstrong
Caroline Johnston
Sam Stacey
Sola Ajiboye

Acknowledgements

Mosaic

GRDC
Grains Research & Development Corporation

AUSTRALIAN SYNCHROTRON RESEARCH PROGRAM

IPNI
INTERNATIONAL PLANT NUTRITION INSTITUTE

mla
MEAT & LIVESTOCK AUSTRALIA

State Government Victoria

Further information

www.adelaide.edu.au/fertiliser/