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PROGRAMME

THEME: EFFICACY AND APPLICATION OF DIFFERENT FERTILIZERS AND LIME SOURCES

EFFICACY AND APPLICATION OF NITROGEN SOURCES

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ABSTRACT

The fertilizer industry has a responsibility to prescribe scientifically sound and safe application practises for different products that it intends to sell. Crop producers on the other hand could use prescriptions for the use of products and efficacy differences between products to optimize profits, but also to minimize possible risks.

The objectives of this paper were to review and demonstrate crop requirements and yield responses with respect to nitrogen (N) sources under different environmental conditions and practises. Conversion processes of N fertilizers in the soil, differences in potential toxicities, leaching and volatilization losses were used to explain differences in efficacy between N sources. Conditions favourable and unfavourable for recommendation of various N sources were identified. Specific preferences for N sources were indicated. Efficacy differences between N sources were quantified. Conclusions included indications and contra-indications for the use of nitrification inhibitors and urease inhibitors.

INTRODUCTION

The fertilizer industry annually sells about 400 000 ton of nitrogen (N) to end users in South Africa (Grant, 2011). N sources that form part of these sales mainly include granular products such as limestone ammonium nitrate (LAN/CAN), urea, ammonium sulphate, mono-ammonium phosphate (MAP), di-ammonium phosphate (DAP), potassium nitrate (KNO_3), calcium nitrate ($Ca(NO_3)_2$ and liquid products such as ammonium nitrate (AN) and urea ammonium nitrate (UAN). Anhydrous ammonia (NH_3) is to a limited extent also administered directly to soils as a gas. These products form the basis of many different granular and liquid plant mixtures or blends to be used in different stages of crop production. Apart from the fact that the fertilizer industry has a responsibility to advise on the optimization of N application rates, it also has a responsibility to prescribe specific applications and contra applications of different N sources. Responsible marketing in this manner should certainly improve the efficacy of N utilization to consumers but should also further the use thereof. Efficacy comparisons between N sources under field conditions together with cost comparisons should be invaluable to consumers in their quest to optimize profits above costs.

The objectives of this paper were to review and demonstrate the following with respect to N sources:

1. Crop requirements in terms of nitrate-N: ammonium-N ratios.
2. Conversion processes of applied N in the soil.
3. Toxicity.
4. Leaching
5. Volatilization
6. Yield responses.
7. Indications and contra indications for recommendations.
8. Conclusion

NITRATE-N : AMMONIUM-N CROP REQUIREMENT

Many research studies have shown that most crops require combinations of nitrate and ammonium rather than any of the two sources on its own (Hageman, 1984; Adriaanse, 1991). Yara International demonstrated that a 1:1 ratio result in much better maize vegetative growth than a 0:1 ratio in hydroponics (Figure 1). According to Adriaanse (1985), the optimum nitrate: ammonium ratio is closer to 3:1 when maize grain yield was determined in hydroponics (Figure 2). Similarly Adriaanse (1991), and Adriaanse and Human (1991) showed the optimum nitrate-N: ammonium-N ratio to be close to 3:1 for broadcast fertilizers under high rainfall conditions (Figure 3).

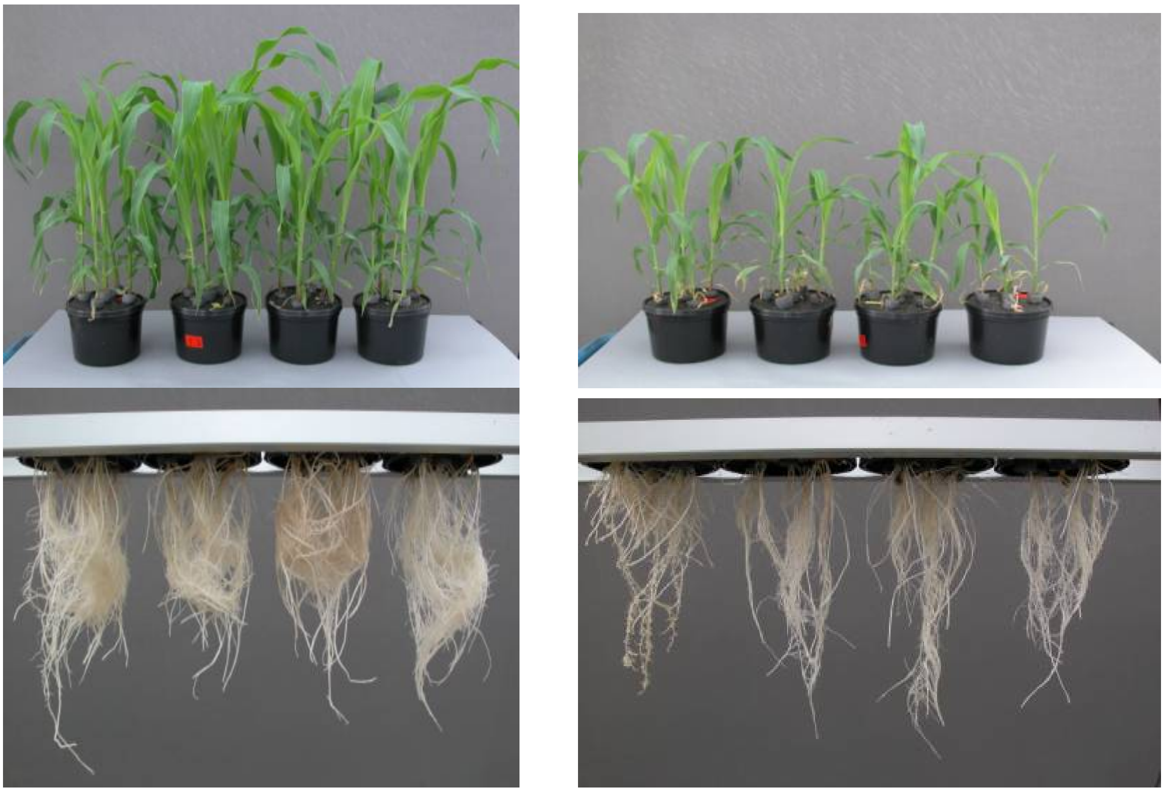

Figure 1. Maize grown in hydroponics with ammonium nitrate (left) and with ammonium sulphate + ammonium chloride (right) (Yara International).

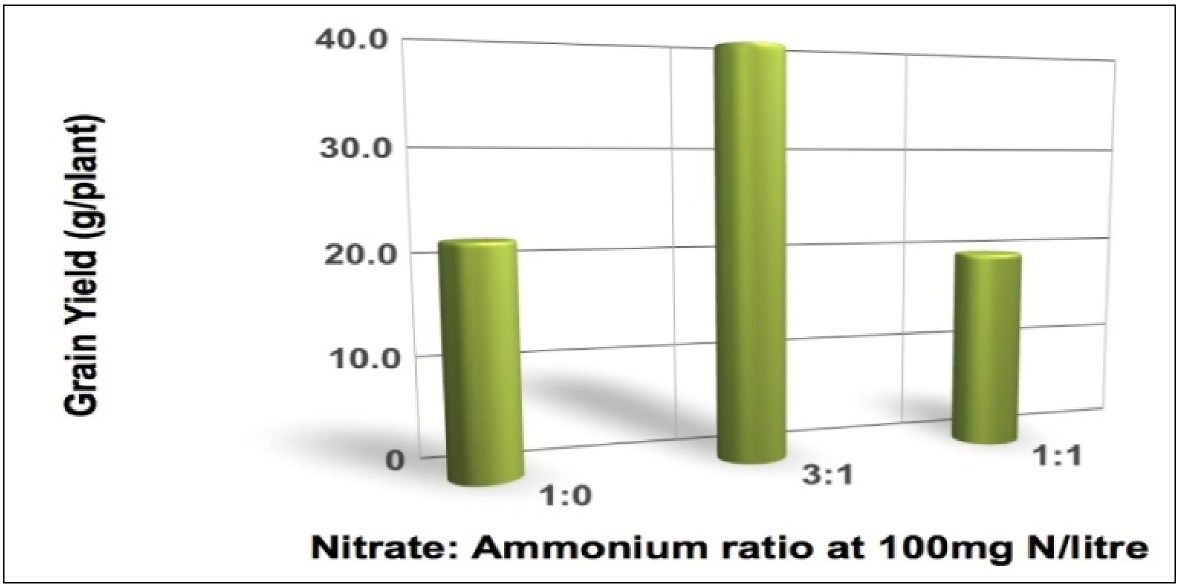

Figure 2. Effect of different nitrate-N: ammonium-N ratios on maize grain yield averaged over ten inbred lines, grown in hydroponics at 100 mg N/litre. LSD Tukey (0.05) = 9.39 g/plant (Adriaanse, 1985).

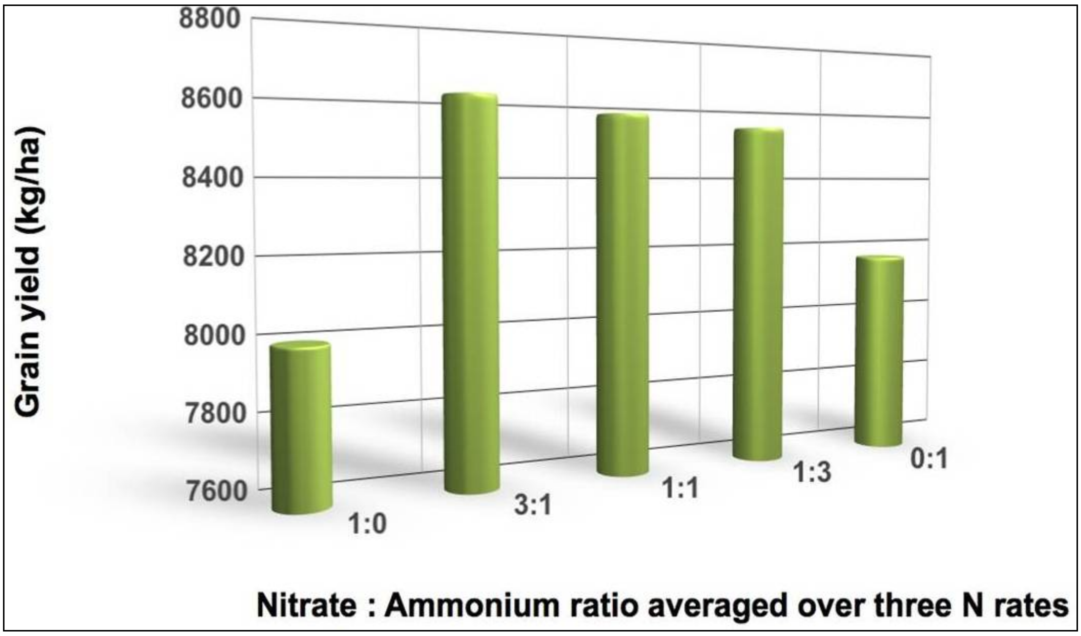

Figure 3. Effect of different nitrate-N: ammonium-N ratios on maize grain yield broadcast and soil incorporated 50% before and 50% after planting in a high rainfall area near Dundee RSA. LSD (0.05) = 586 kg/ha (Adriaanse, 1991; Adriaanse and Human 1991).

According to a case study conducted by Sasol Nitro impaired growth and a pale green colour in winter wheat was the result of 81% ammonium-N in the soil. Where there was no impairment of growth the ammonium-N was 35% (Figure 4). Under these conditions 100 kg ammonium sulphate was broadcast before planting and 100 kg MAP band placed at planting i.e. all N applied as ammonium. Environmental conditions resulted in the inhibition of the nitrification process.

Figure 4. Effect of only ammonium-N applications that was not effectively nitrified. Green patches of wheat: inorganic N in soil = 63 kg/ha of which ammonium-N = 35%. Pale patches of wheat: inorganic N in soil = 123 kg/ha of which ammonium-N = 81% (Sasol Nitro case study).

CONVERSION PROCESSES OF FERTILIZERS IN THE SOIL

Conversion processes in soils that some fertilizers undergo, after application, before crop uptake will be effective, are summarised in Figure 5. LAN is already in a 50/50 nitrate-N: ammonium ratio and some ammonium-N should quickly be nitrified resulting in a near optimum ratio of 75/25. The nitrification process is a two-step biological process for which two bacteria is responsible (Figure 5). All urea will first have to be hydrolysed through an enzymatic reaction (Figure 5) after which the ammonium-N resulting from this will be converted to nitrate-N through the process of nitrification. The formation of ammonium-N through hydrolysis of urea and directly from other fertilizers is not dependant on the availability of oxygen while the nitrification process is very much dependant on aerobic conditions. Other environmental conditions such as temperature, soil pH and organic material will also affect the reaction tempo of both processes.

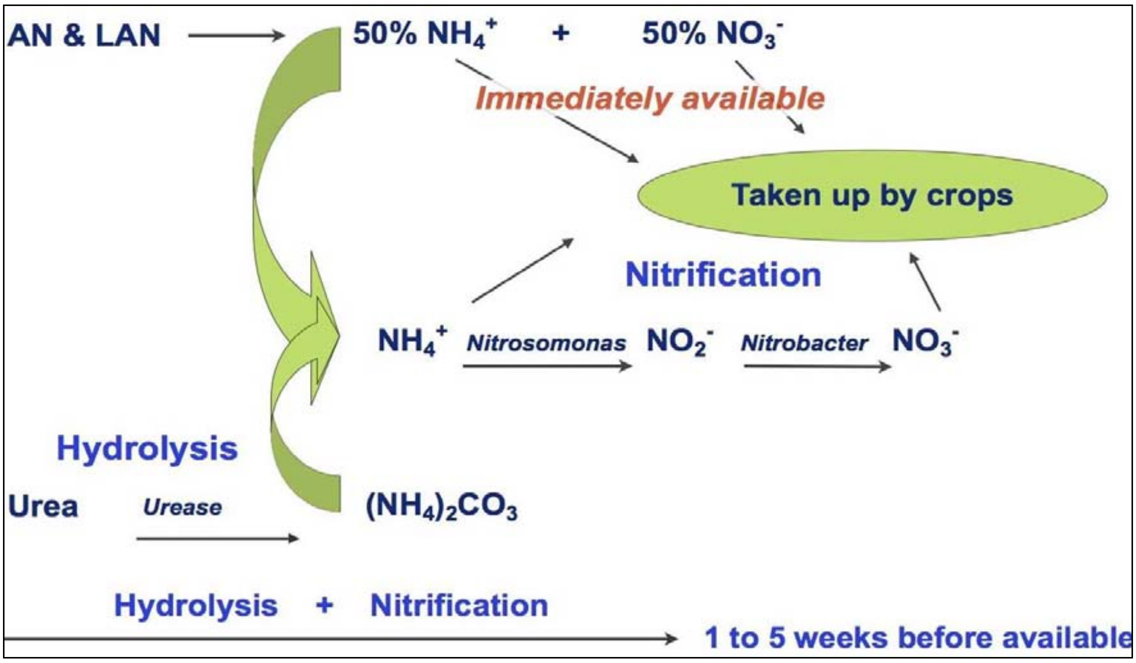

Figure 5. Conversion processes of fertilizers in the soils. The ammonium-N derived from ammonium sulphate, MAP, DAP and NH_3 will also be subjected to nitrification. The nitrate-N derived from potassium nitrate and calcium nitrate will be readily available for crop uptake.

TOXICITIES

Ammonia (NH_3) as a gas is toxic to plants (Hoeft *et*. *al*., 2000) but when ammonia dissolves in soil water to form ammonium (NH_4^+), high concentrations of ammonium, could also be toxic to plants, as was already indicated (Figure 1,2,3 and 4).

Ammonia toxicity may also result from urea and DAP applications. When urea dissolves in soil water the surrounding pH will be about 9.0 and with DAP about 8.1 (Hauck, 1984). At high pH of above 8 the formation of ammonia is very likely to occur (Hauck, 1984).

Urea toxicity symptoms resulting in scorching of wheat leaf tips is given in Figure 6. Urea toxicity symptoms resulting in mortality of maize seedlings is given in Figure 7 and quantified in terms of plants/ha in Figure 8.

Figure 6. Urea applications at 60 kg N/ha resulted in scorching of wheat leaf tips on the left while LAN applications at the same N rate showed no symptoms on the right (Yara International, 2007).

Figure 7. Urea applications resulted in seedling mortality on the left while LAN applications at the same N rate showed no symptoms on the right (Yara International, 2007).

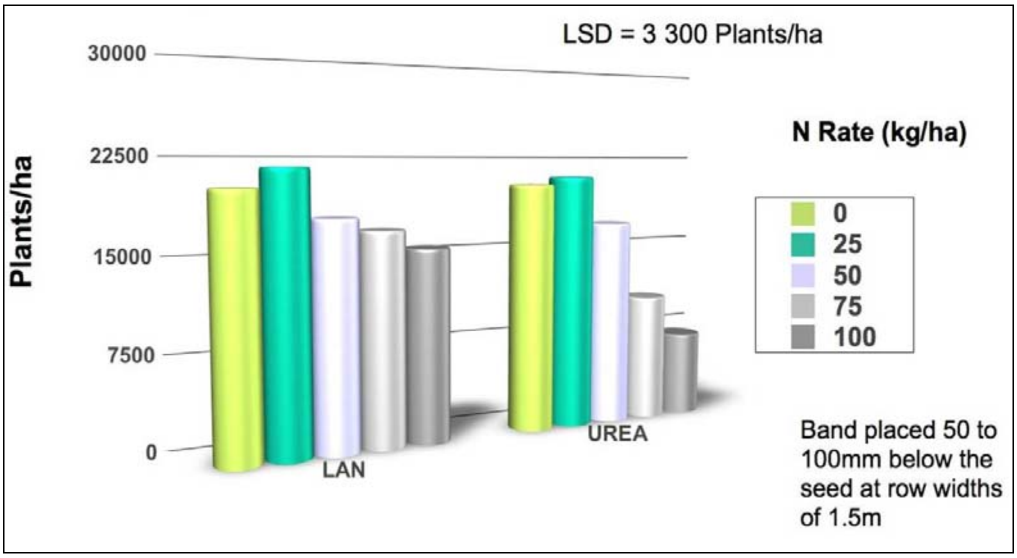

Figure 8. Urea and LAN mortality effects on maize seedlings when band placed directly below the seed. Viljoenskroon RSA (Adriaanse, 2012b).

Mortality effects on maize seedlings due to the band placement of fertilizer plant mixtures is often wrongly ascribed to genetically associated poor germination and vitality of seedlings. These effects may also wrongly be ascribed to poor environmental conditions affecting germination and seedling development. Many producers are therefore often unaware of these toxicity effects.

High concentrations of urea in close proximity of developing seedlings may also result in yield losses which may pass undetected due to a lack of visual symptoms. This is indicated for maize in Figure 9. Seasonal variation in yield is often between 4.5 and 6.5 ton/ha in this area while this variation was shown to occur due to the difference in efficacy between LAN and urea, band placed at planting, over three years (Figure 9).

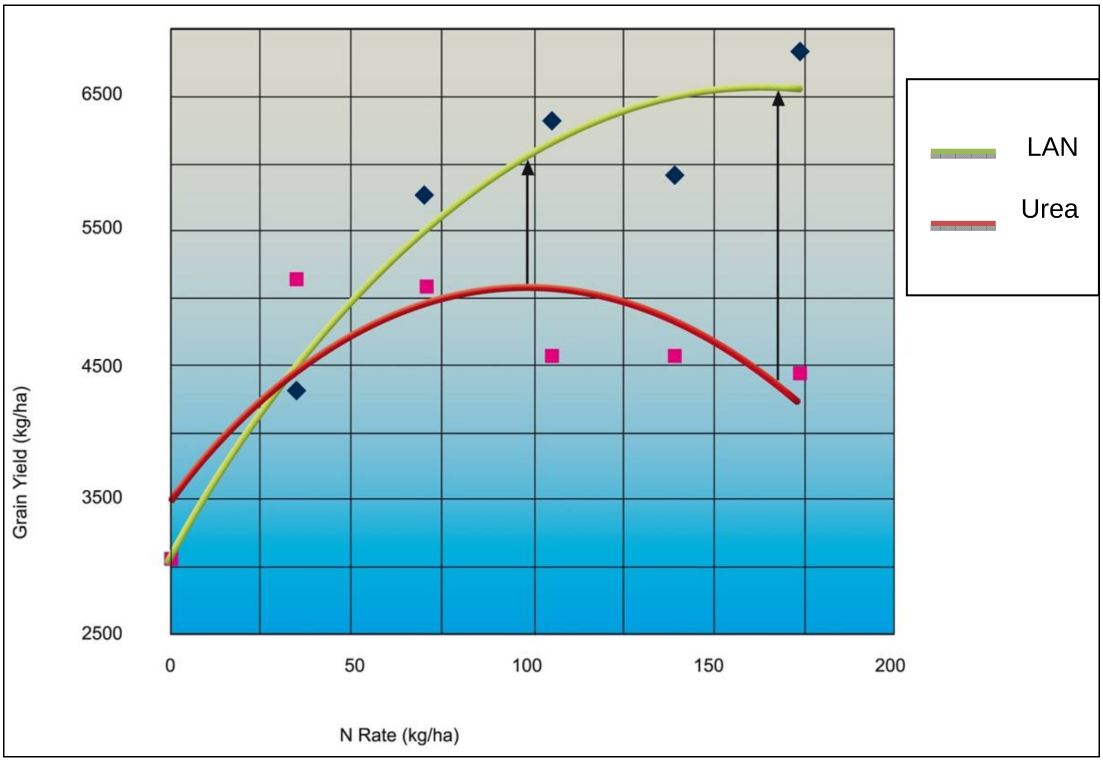

Figure 9. Relationship between N rates and maize grain yield, over three years, for LAN and urea, applied at planting. Treatments were applied 10 to 15 cm from the row at a depth of 10 cm. At planting 20 kg N/ha of each N rate, except the control was applied as LAN in the plant mixture (Adriaanse, 2012a).

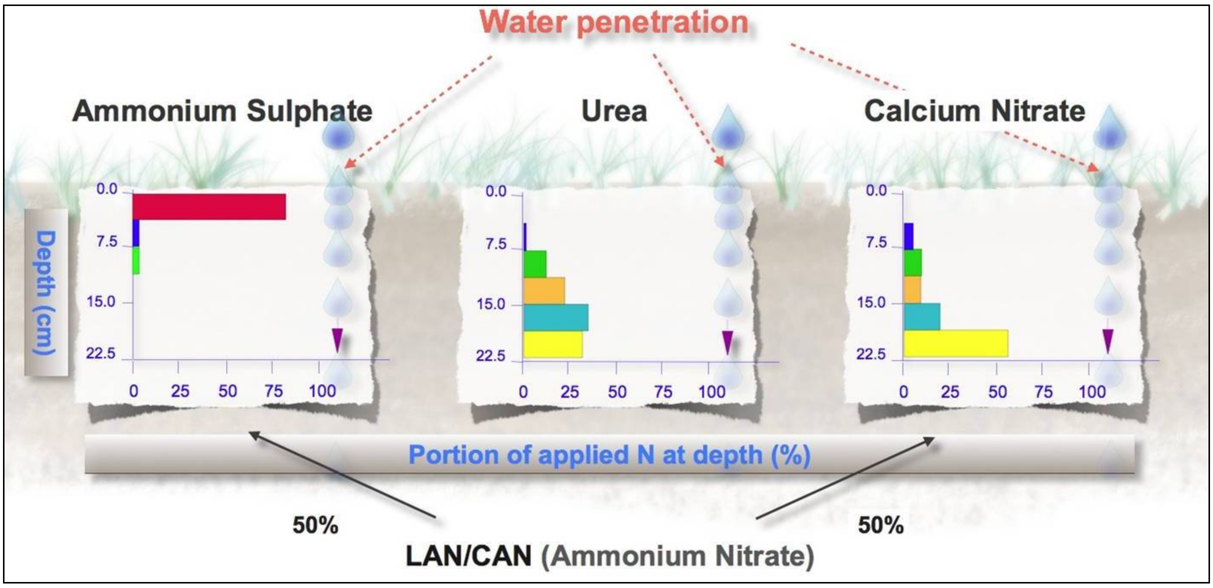

Figure 10. Leaching of different N sources in a clay soil. (Redrawn from Broadbent* et al*. 1958, Gardner and Roth, 1984).

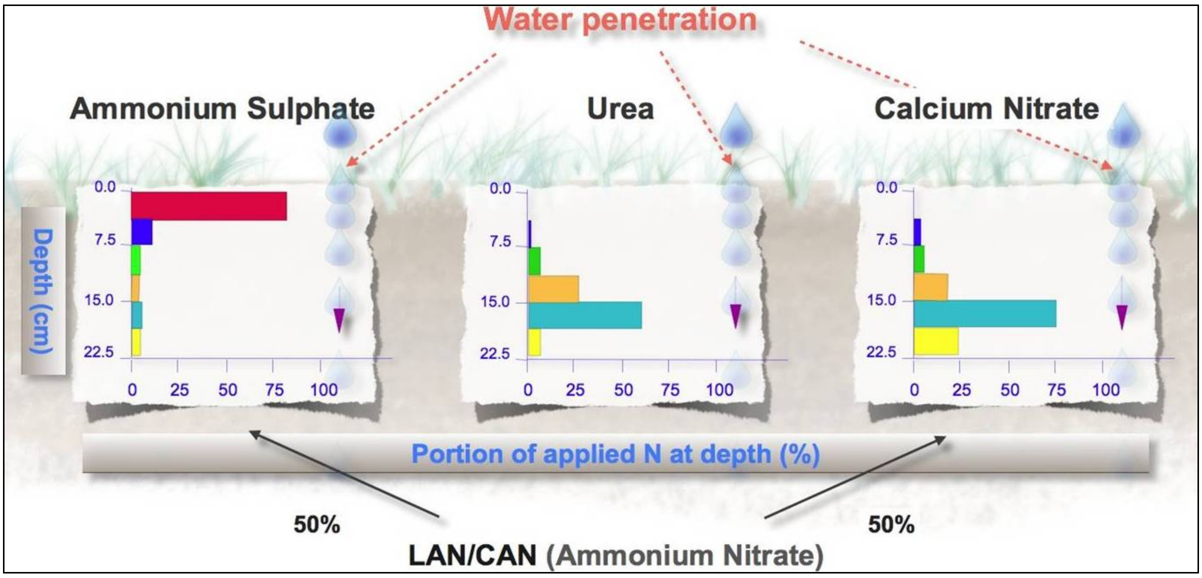

Figure 11. Leaching of different N sources in a sandy loam soil. (Redrawn from Broadbent* et al*. 1958, Gardner and Roth, 1984).

Leaching of ammonium sulphate, urea and calcium nitrate is illustrated for a clay soil in Figure 10 and for a sandy loam soil in Figure 11. Ammonium leaching was insignificant in both soils while urea and nitrate leaching was substantial in both soils. More urea and more nitrate reached the level of water penetration in the sandy loam soil (Figure 11) compared to the clay soil (Figure10). Since LAN consists of 50% ammonium-N and 50% nitrate-N, half of the N in LAN can be expected to react like that of ammonium sulphate and the other half like that of calcium nitrate. Although clearly demonstrated that ammonium does not leach it should be emphasised that ammonium will also become leachable through the process of nitrification in the form of nitrate. The leach ability of LAN applied two weeks before planting and at planting on a well-drained soil is demonstrated in Figure 12.

Figure 12. Leaching of LAN applied at a rate of 63 kg N/ha two weeks before planting and at a rate of 40 kg N/ha in a plant mixture at planting. More than 100 mm rain fell shortly after planting on this well-drained sandy soil. (Sasol Nitro case study.)

VOLATILIZATION

An increase in the soil pH will increase NH_3 volatilization from all ammonium containing and forming N sources applied on the soil surface (Figure 13). Volatilization at high pH will be the most for urea, followed by DAP, ammonium sulphate, MAP and the least for LAN (Figure 13). Higher temperature significantly increases ammonia volatilization from surface applications of urea and UAN but volatilization from CAN (LAN in RSA terms) remains relatively low (Figure 14).

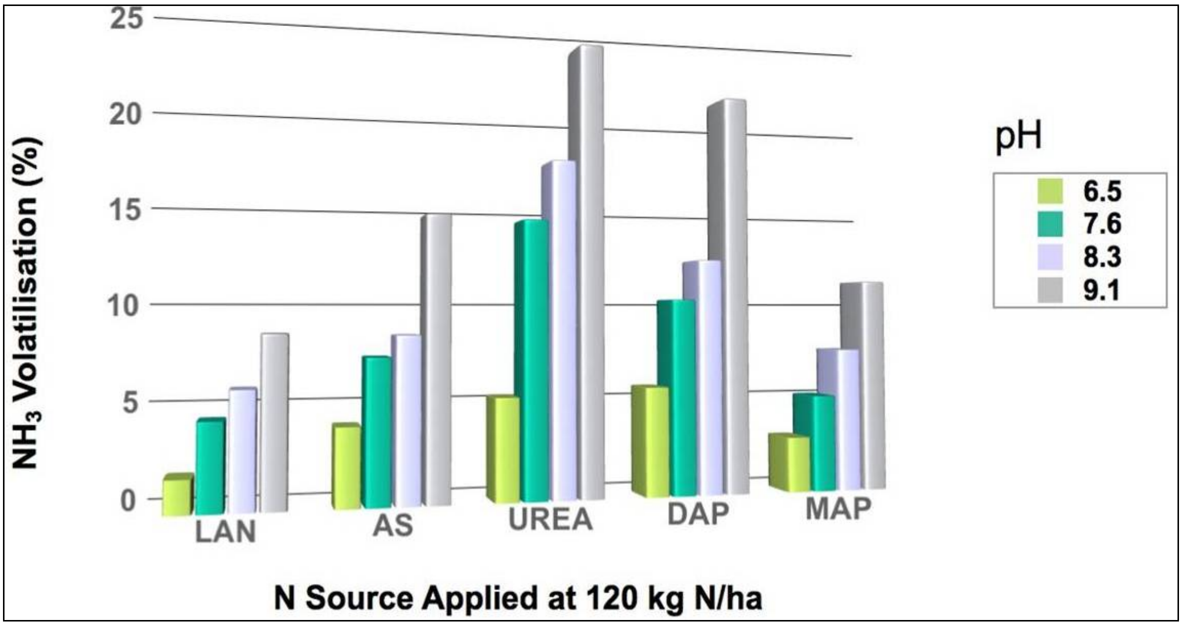

Figure 13. Effect of soil pH on ammonia volatilization from different N sources. Laboratory incubation study of surface applied N sources. (Redrawn from Du Preez and Burger, 1986).

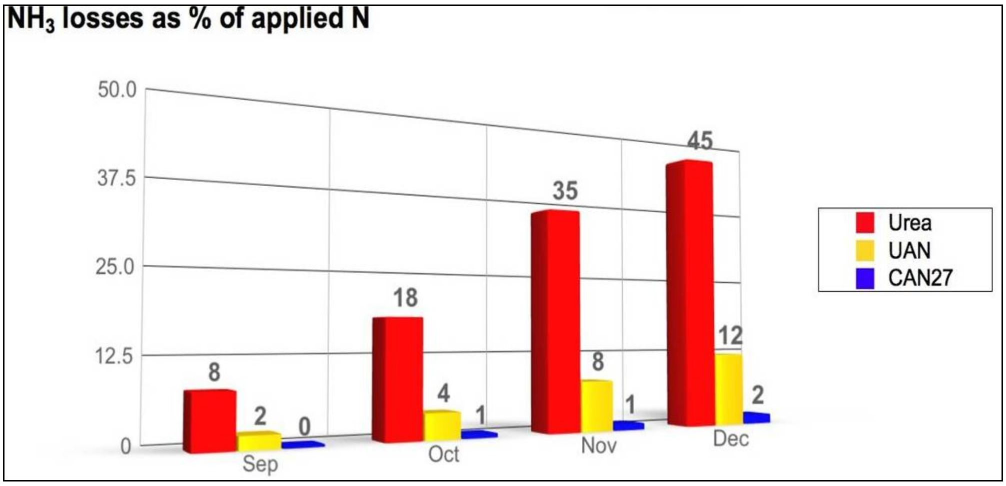

Figure 14. Seasonal effect of rising temperature on ammonia volatilization from surface applications of different N sources in Argentina (Fantanetto, 1995).

YIELD RESPONSES TO N SOURCES

Maize yield responses to urea and LAN, band placed before planting on a water table soil in South Africa are presented in Figure 15. No differences in yield responses between LAN and urea at low N rates are indicative of conversion processes that were completed, no differences in leaching losses and no differences in availability for uptake under these specific conditions. Above 110 kg N/ha yield for LAN was as much as 600 kg/ha or 7% higher than for urea. The reason for yield depression at high urea N rates was probably due to urea toxicity. Nitrification was probably inhibited when more than 90 kg urea N/ha was band placed before planting.

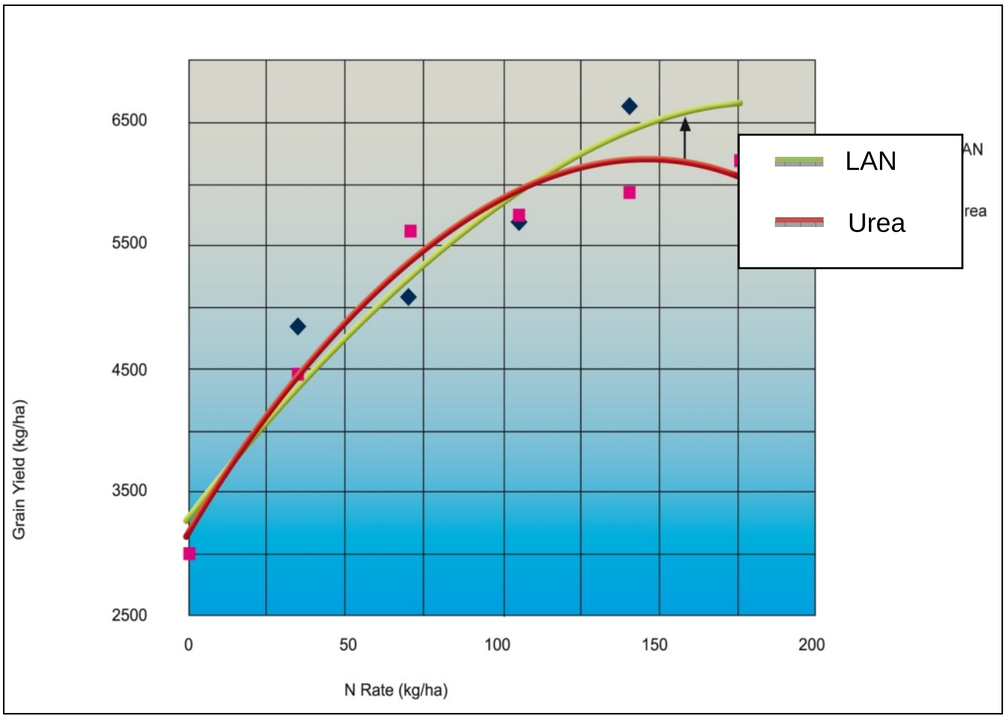

Figure 15. Relationship between N rates and maize grain yield, over three years, for LAN and urea, applied three weeks before planting. Treatments were applied 10 to 15 cm from the row at a depth of 10 cm. At planting 20 kg N/ha of each N rate, except the control was applied as LAN in the plant mixture (Adriaanse, 2012a).

Maize yield responses to urea and LAN, band placed after planting on a water table soil in South Africa are presented in Figure 16. These responses to LAN, was clearly more efficient than to urea. Grain yield at 100 kg N/ha was 350 kg/ha or 5.8% more with LAN than with urea. Viewed from another angle, 140 kg N/ha applied as urea resulted in the same yield as 100 kg N/ha applied as LAN. LAN was more efficient because the N in LAN was immediately available for uptake which on its own will result in less leaching. Furthermore, the ammonium-N from LAN will not leach much after band placement. The N in urea, in contrast to that of LAN, is not readily available for crop uptake while at the same time it is 100% subjected to leaching. Although nitrogen leaching will not be out of the profile on these soils, it can be expected that N leachate in deeper soil layers will be less available for uptake.

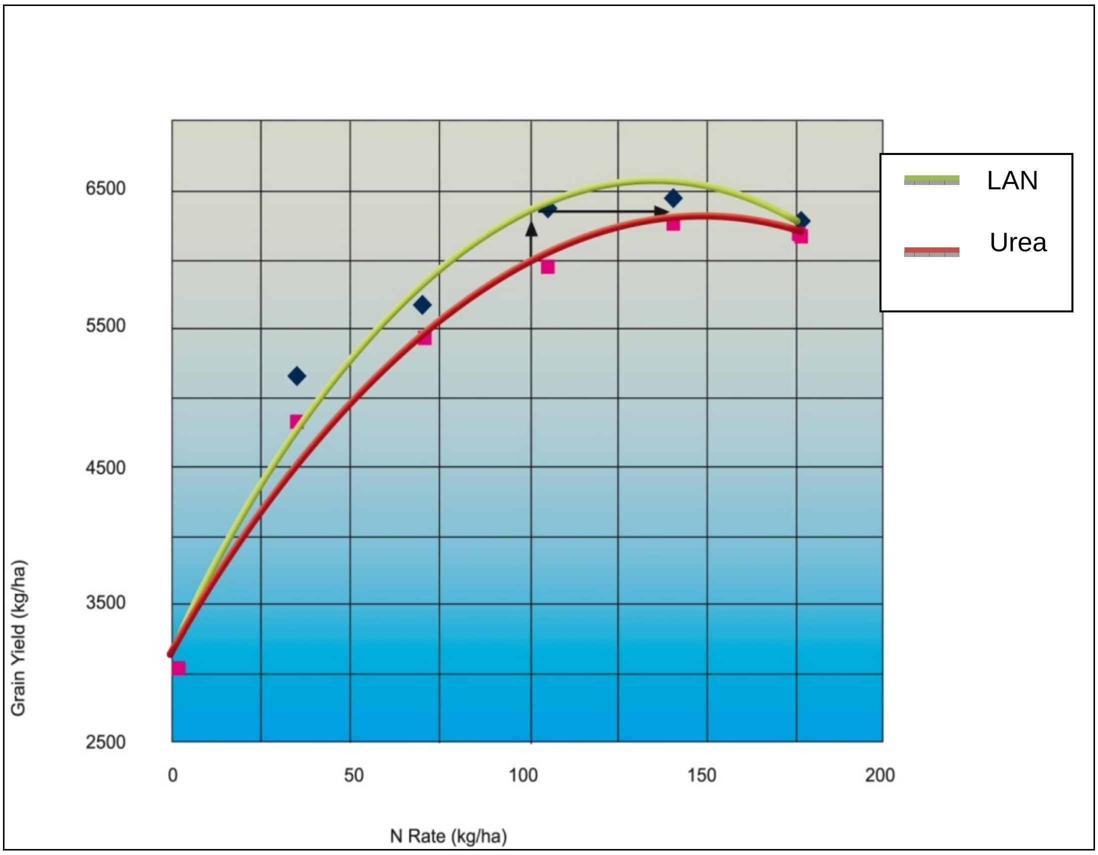

Figure 16. Relationship between N rates and maize grain yield, over three years, for LAN and urea, applied three weeks after planting. Treatments were applied 10 to 15 cm from the row at a depth of 10 cm. At planting 20 kg N/ha of each N rate, except the control was applied as LAN in the plant mixture (Adriaanse, 2012a).

Mangle and Hawkins (1995) demonstrated 14.5% higher maize yields for top dressed ammonium nitrate compared to urea over an eight year period in the USA (Figure 17). UAN yields were between the yields for these two N sources. The application of more ammonium nitrate probably resulted in a reduction in volatilization and leaching losses but also supplied nitrate and ammonium closer to the optimum ratio.

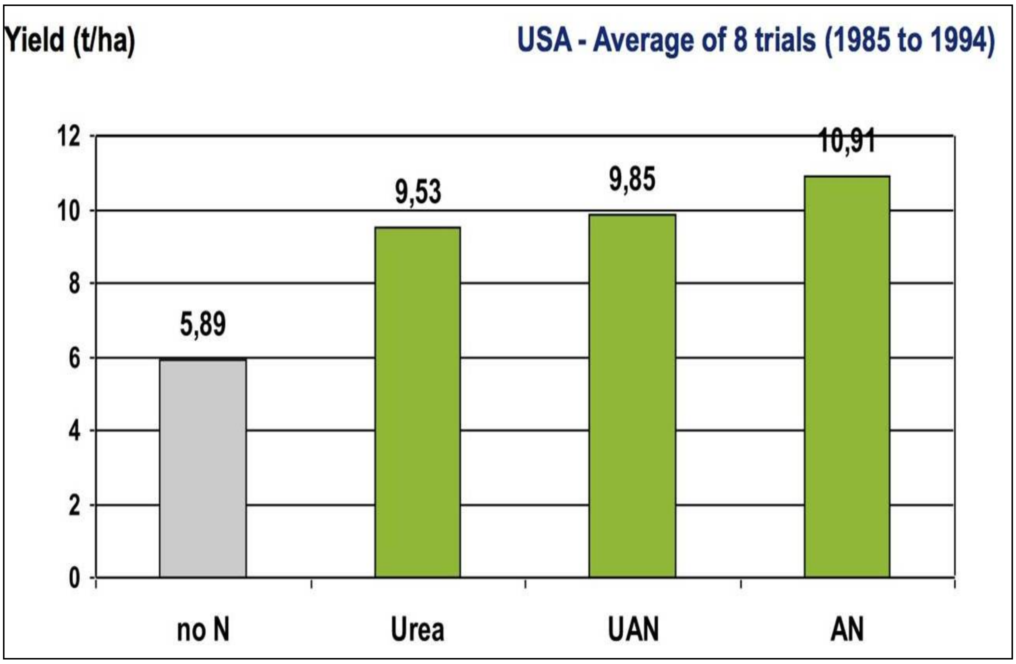

Figure 17. Average maize grain yield for different N sources at the same N rate over 8 years (Mangle and Hawkins, 1995).

Similarly it was demonstrated that more ammonium nitrate and by implication also more nitrate, resulted in higher wheat yields in the UK over a 15 year period (Figure 18). The same reasoning as in the previous (Mangle and Hawkins, 1995) applies. The fact that calcium nitrate (CN) resulted in higher yield than calcium ammonium nitrate (LAN in RSA terms) is an indication that there was at least some ammonium in the soil due to the mineralization of organic material. This would have resulted in a nitrate: ammonium ratio closer to the optimum when CN was applied.

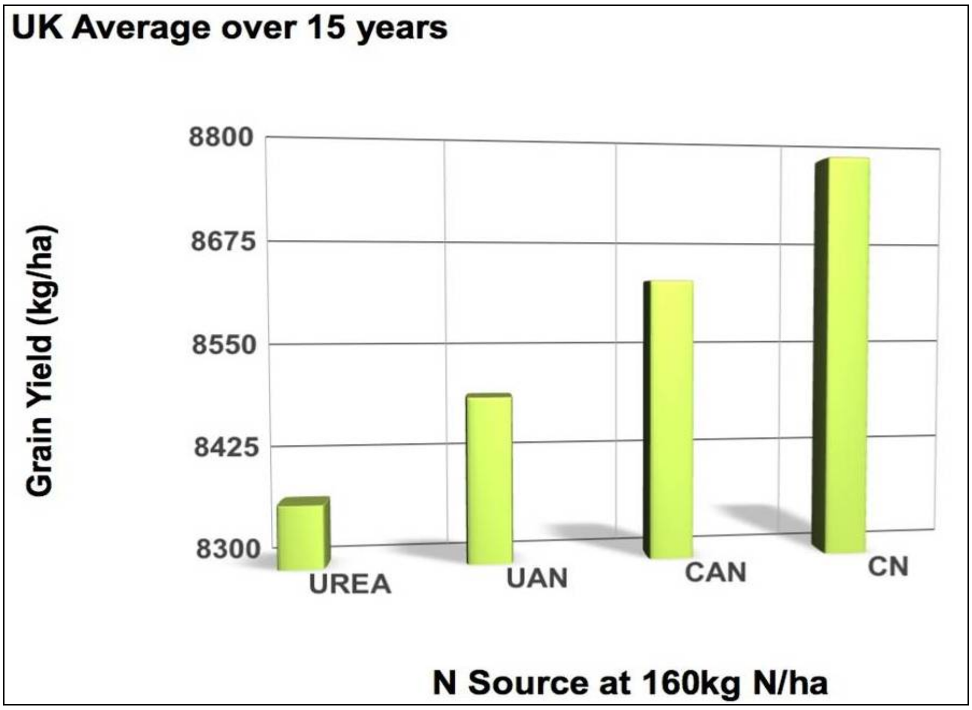

Figure18. Average maize grain yield for different N sources at the same N rate over 15 years (Levington Agriculture, 2009).

Greater efficacy of ammonium nitrate over urea for maize was also demonstrated in Spain at N rates of 180 kg N /ha (Figure 19). A substantial yield difference of 1.7 ton /ha or 13.4% was reported (Figure 19). Similar reasoning than in the previous applies.

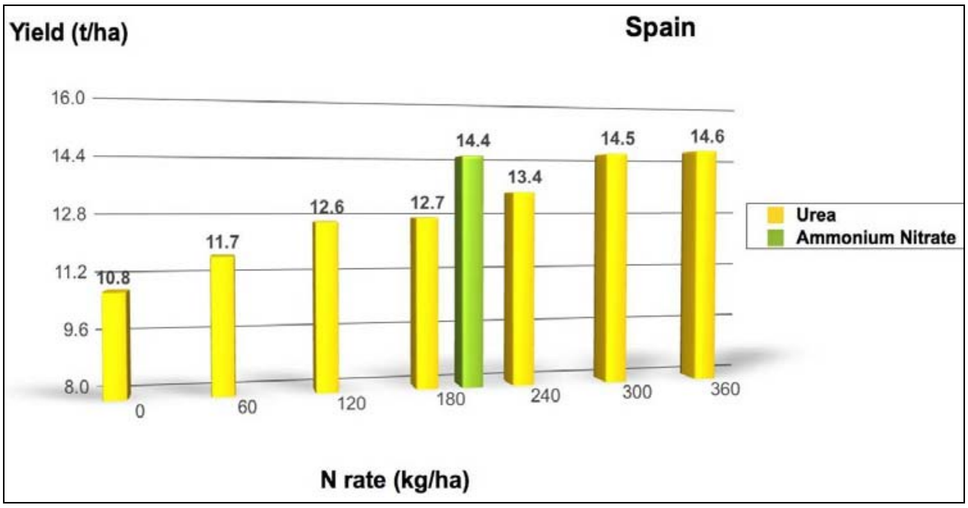

Figure19. Average maize grain yield foruUrea at different N rates compared to ammonium nitrate at 180 kg/ha (ITGC, 2004).

Greater efficacy of ammonium nitrate over urea for maize was demonstrated at several N rates over 11 localities in France (Figure 20). These responses were very much similar to those reported in Figure 16 for one locality in South Africa over three years although yields and N rates were much higher. At N rates of 180 kg N/ha the yield difference was 600 kg/ha (Figure 20). Alternatively 30 kg N/ha more urea was required compared to ammonium nitrate for the same yield of 11.5 ton/ha (Figure 20). The difference in yield for ammonium nitrate and urea at 180 kg N/ha did however vary a lot between localities (Figure 21). At one out of nine localities the yield for urea was 300 kg/ha more than with ammonium nitrate (Figure 21). This exceptional result can possibly be explained by very specific conditions. Urea was possibly washed into the soil very effectively but not leached out of the root zone and therefore volatilization from urea was limited. Ammonium nitrate consists of 50% ammonium-N which will not wash into the soil but which might be subjected to volatilization especially under alkaline conditions. During dry periods most nitrogen will be absorb from the wetter deeper soil layers and not from the dryer topsoil were most of the ammonium–N will remain.

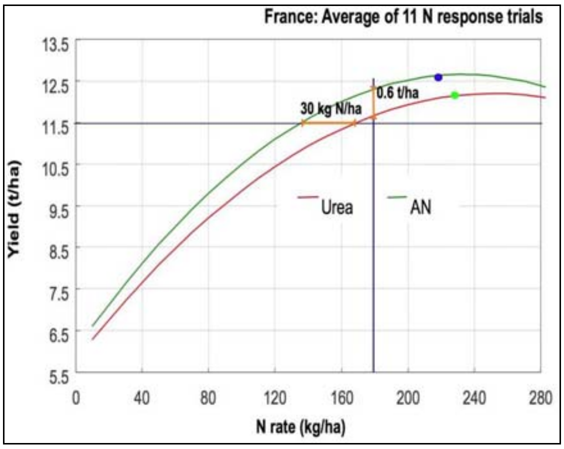

Figure 20. A comparison of yield responses to N rates between urea and ammonium nitrate over 11 localities. (Avails, 1998.)

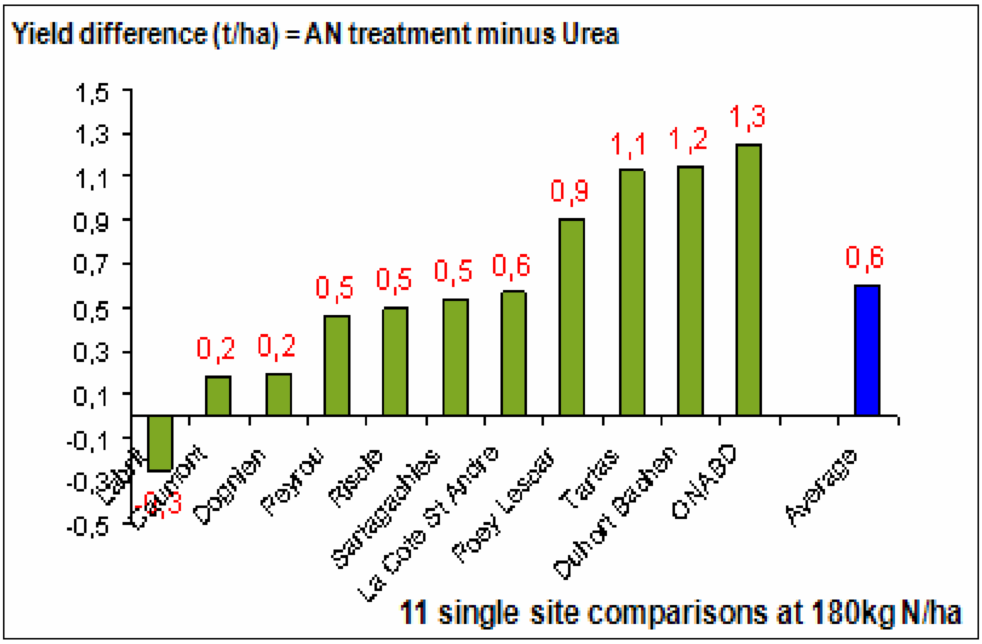

Figure 21. Difference in maize yield between urea and ammonium nitrate at 180 kg N/ha for 11 localities. (Avails, 1998.)

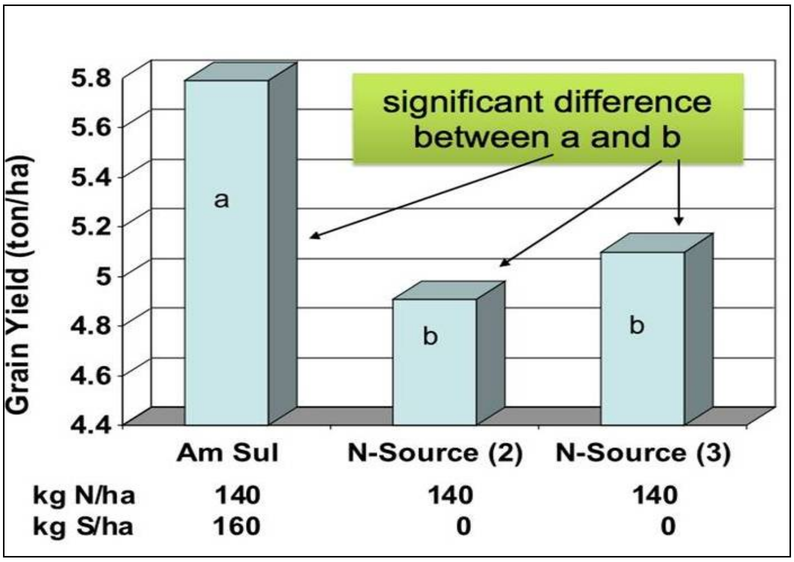

Figure 22. Greater effect of ammonium sulphate on wheat grain yield compared to LAN and urea (95% probability difference from b). N-Sources spread and ploughed in. Hutton soil form, Mangano soil series with a clay content of 9.3% to a depth of 750 mm and a pH (H_2O) = 6.4. (Redrawn from Snyman, P. J.* et al.*, 1985, and published in Adriaanse, 2011.)

The application of ammonium sulphate as the main source of N before planting could result in higher grain yields compared to other N-sources under specific conditions (Figure 22).

Possible reasons for higher yields obtained with ammonium sulphate compared to other N-Sources as in Figure 22 are:

1. Less leaching compared to other N-Sources (probably the main reason for higher yield in this study).
2. Response to S due to S-deficiency in the soil.

3. A greater acidifying effect of ammonium sulphate can enhance the uptake of other plant nutrients under strongly alkaline conditions.
4. The application of excess S can displace excess Sodium (Na), which is detrimental to most crops.

INDICATIONS AND CONTRA-INDICATIONS

After consideration of expected soil and crop responses under various possible scenarios indications for the use of N sources were summarised in Table 1 and contra-indications in Table 2. All possible scenarios are not included in these tables but those included should serve as a guideline to advisors. References to poorly and moderately drained soils do for example not include moderately drained soils. Similarly high pH is a relative indication. There are also different degrees of toxicity, leaching and volatilization.

Table 1. Prescription for the use of different N sources.

N Source	**Recommended applications**
LAN/AN/CAN	Pre-plant band placed or broadcast on poorly drained soils; Plant mixtures; After planting band placed or broadcast on all soils.
Ammonium sulphate	Supplemental to other N Sources: Before, at and after planting; Pre-plant, broadcast on well-drained soil with high pH.
Urea/UAN	Pre-plant band placed or broadcast, soil incorporated on poorly drained soils; After planting band placed or broadcast, soil incorporated or washed in; Aerial applications.
Ammonia	Pre-plant band placed on well drained and poorly drained soils.
MAP	Pre-plant band placed or broadcast, soil incorporated; As part of plant mixtures.
DAP	Pre-plant band placed or broadcast, soil incorporated.
$Ca(NO_3)_2$, KNO_3	After planting to optimize Nitrate-N : Ammonium-N ratio.

Table 2. Unfavourable conditions for the use of specific N sources.

N Source	Applications to be avoided
LAN/AN/CAN	Very high concentrations close to the seed – moderately toxic; Pre-plant applications on well drained soils – 50% immediately leachable.
Ammonium sulphate	Band placement in large quantities – toxic; Broadcast applications, not soil incorporated under alkaline conditions – volatilization.
Urea/UAN	Pre-plant applications on well drained soils – 100% immediately leachable; Band placement in plant mixtures – toxic and leachable; Broadcast applications not soil incorporated or washed in – volatilization; For rectifying severe N-deficiencies rapidly after planting – conversions slow.
Ammonia	Very dry and very wet soils – volatilization and toxicity; At and after planting – toxic.
MAP	Band placed in large quantities as a plant mixture – toxic.
DAP	Not to be left on the soil surface – volatilization; Band placement at planting close to the seed in high concentration – toxic.
$Ca(NO_3)_2$, KNO_3	Not to be applied in large quantities before or at planting – leaching.

CONCLUSIONS

Nitrate-N : ammonium-N ratios in the soil should be optimized around 75:25.

Pre-plant band placed applications of LAN, urea and NH_3 at low N rates, on poorly drained soils should result in similar yields provided that the soil is not waterlogged for a considerable length of time.

Pre-plant broadcast applications of ammonium sulphate under well drained conditions should result in higher yields compared to LAN and urea primarily due to less leaching of ammonium sulphate.

LAN/AN broadcast or band placed applications after planting should result in 3.0 to 14.5% higher yields compared to urea over localities and years. This is explained by less volatilization, less leaching and by supplying nitrate and ammonium closer to the preferred ratio.
Exceptional conditions which favour both the washing in and volatilization of fertilizers might result in higher yields for urea compared to AN/LAN/CAN provided that urea is not washed out of the profile. Adequate watering immediately after applications followed by a dry spell should be conducive of such conditions.

Cost effectiveness between N sources should in addition be considered since higher concentration products are usually cheaper per unit of N delivered on farm.

Nitrification inhibitors should only be considered when severe leaching is expected. Yield increases can be expected in very wet seasons on well drained soils but lower yield in wet seasons on poorly drained soils. Lower yield can be expected during dry seasons on all soils.

Urease inhibitors may increase yield when urea is surface applied especially with plant residue on the soil but not when urea is soil incorporated or washed in. Surface applications of LAN, is expected to outperform urea + urease inhibitor surface applications.

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reaching new frontiers

Efficacy and application of Nitrogen Sources

Dr. F. G. Adriaanse - Sasol Nitro

Basis of Comparisons Between N Sources

- Crop Requirements
- N Fertilizers + Conversion processes in soils:
  1. Nitrification of Ammonium + inhibitor
  2. Hydrolysis of Urea + inhibitor
- Toxicity Effects
- Potential Losses:
  1. Leaching
  2. Volatilization
- Yield Responses to N Sources
- Indications and contra indications for N sources
- Conclusion

Crop requirement

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All nutrients at optimum supply; regular pH control

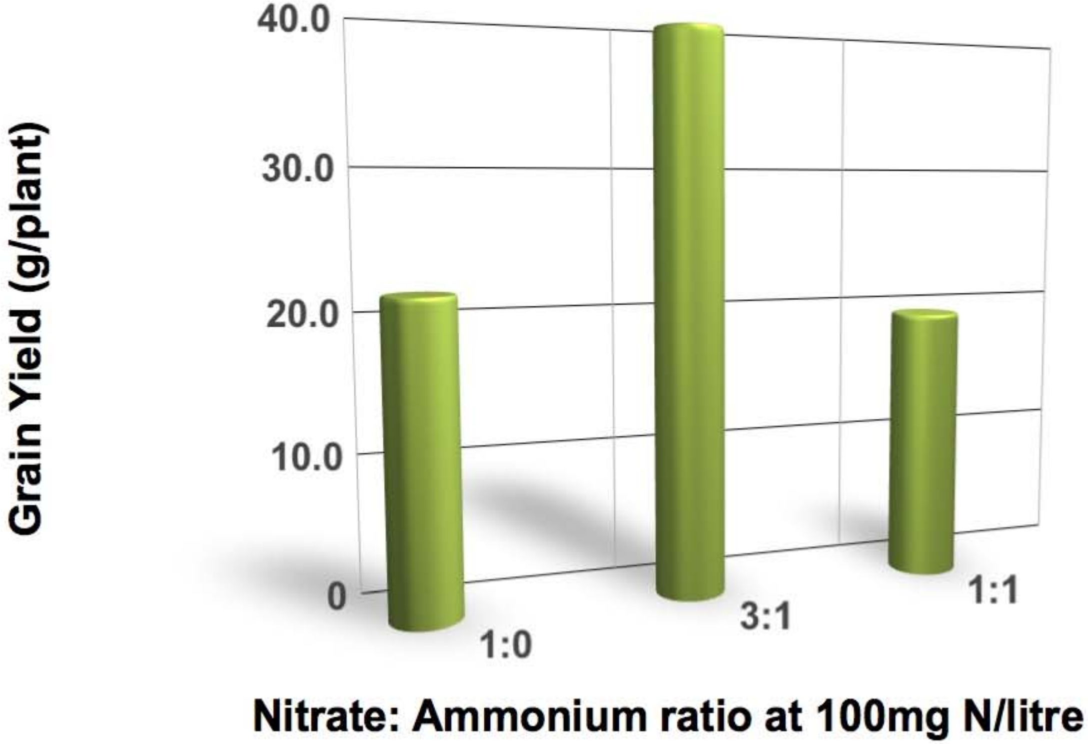
Yara Research Centre Hanninghof Germany (2007)

Crop requirements

Optimum Nitrate N : Ammonium N ratio of 3:1 for maize grain yield in hydroponics

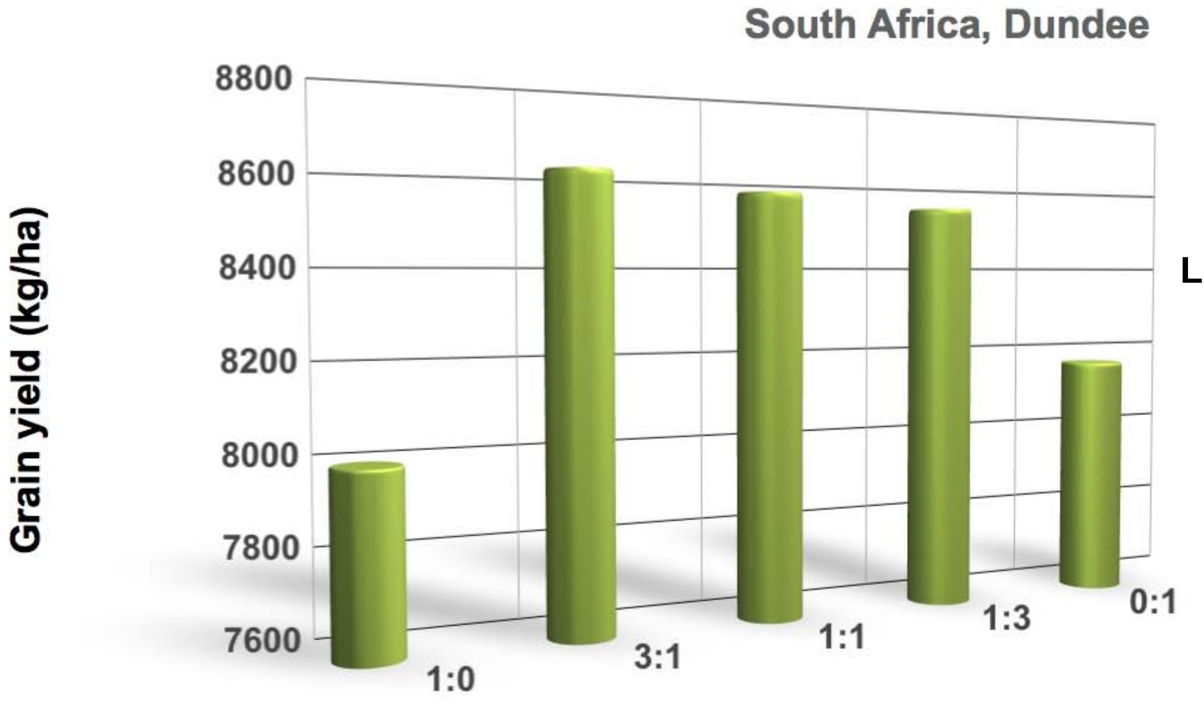
Average over 10 maize inbred lines

LSD Tukey (0.05) = 9.39 g/plant



Ref: Adriaanse F.G., 1985, ARC-GCI

Optimum Nitrate N : Ammonium N ratio of 3:1 for maize grain yield on a sandy soil and high rainfall



LSD(0.05) = 586 kg/ha

Nitrate : Ammonium ratio averaged over three N rates

Ref: Adriaanse F.G., 1991, ARC-GCI

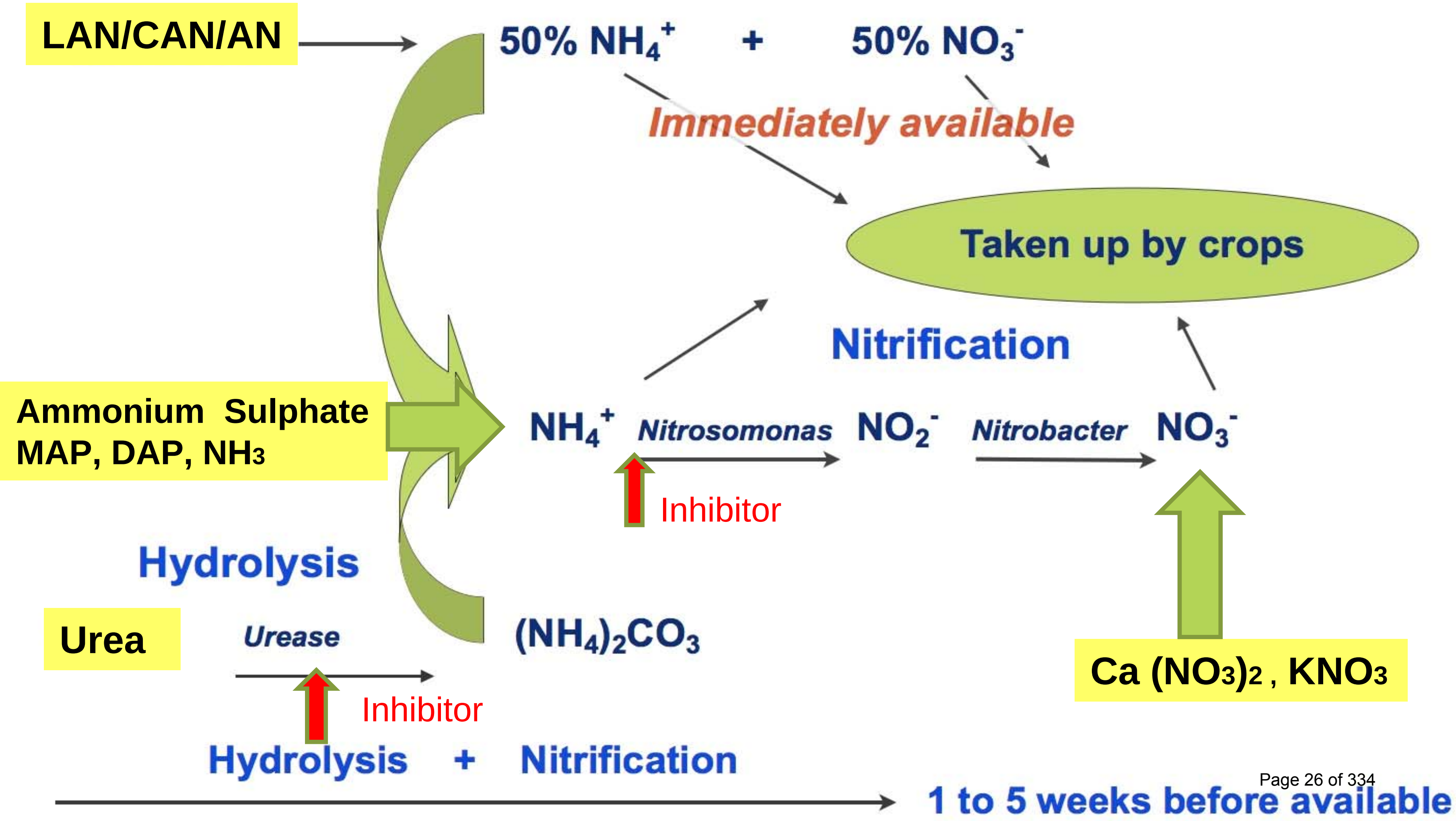
Crop requirement

To much Ammonium N

Inorganic N in soil = 63 kg/ha
Ammonium N = 35%

Inorganic N in soil = 123 kg/ha
Ammonium N = 81%

Conversion processes in soils



LAN/CAN/AN

$50\%\ NH_4^+$ + $50\%\ NO_3^-$

Immediately available

Taken up by crops

Nitrification

Ammonium Sulphate
MAP, DAP, NH_3

$NH_4^+ \xrightarrow{\textit{Nitrosomonas}} NO_2^- \xrightarrow{\textit{Nitrobacter}} NO_3^-$

Inhibitor

Hydrolysis

Urea

$\xrightarrow{\textit{Urease}}$ $(NH_4)_2CO_3$

Inhibitor

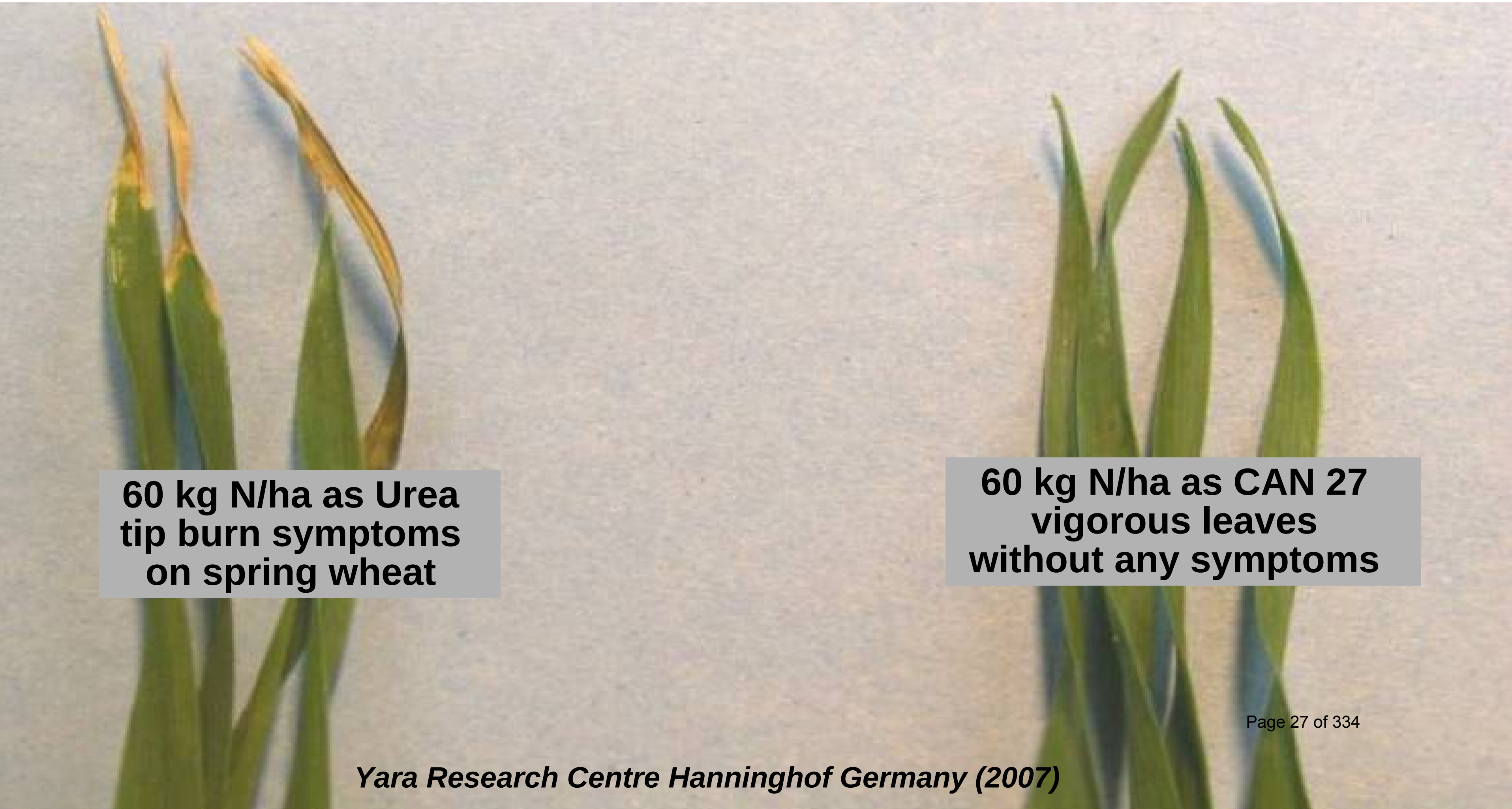
$Ca(NO_3)_2$, KNO_3

Hydrolysis + Nitrification

1 to 5 weeks before available

Toxicity effects

Urea toxicity on wheat



60 kg N/ha as Urea
tip burn symptoms
on spring wheat

60 kg N/ha as CAN 27
vigorous leaves
without any symptoms

Yara Research Centre Hanninghof Germany (2007)

Toxicity effects

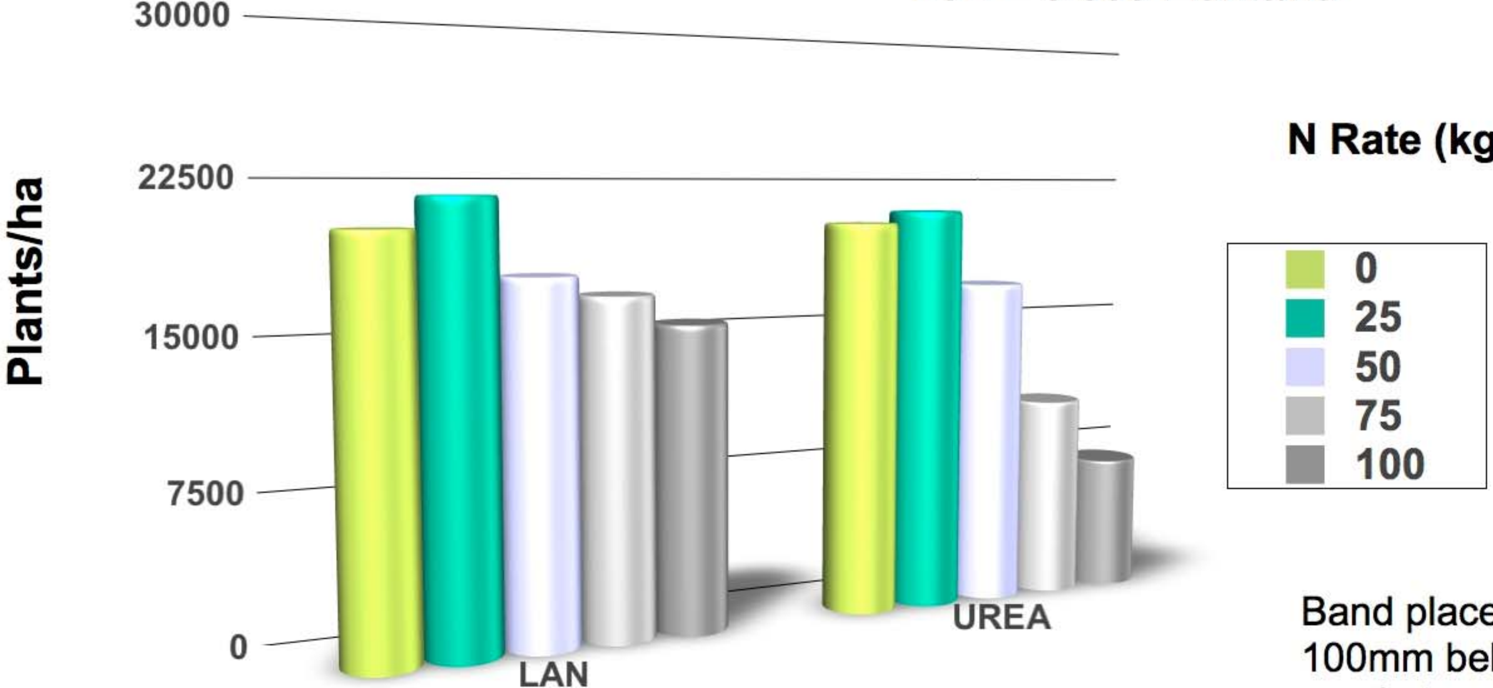
Urea mortality effects on maize seedlings

Yara Research Centre Hanninghof Germany (2007)

Toxicity effects

Urea mortality rate more severe than LAN when band placed

LSD = 3 300 Plants/ha

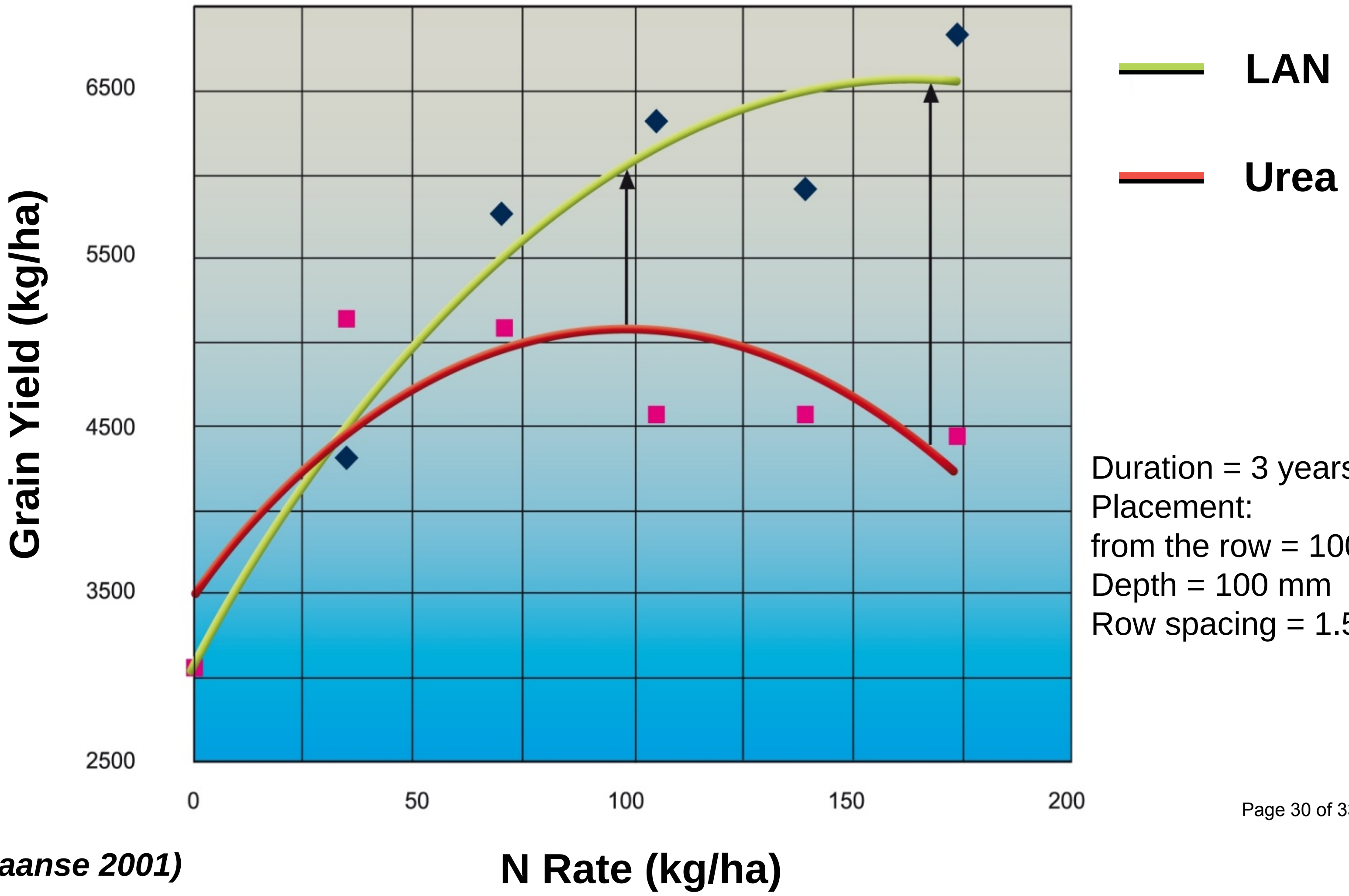


Band placed 50 to 100mm below the seed at row widths of 1.5m

Ref: Adriaanse F.G., 1991, ARC-GCI

Toxicity effects

Urea toxic compared to LAN on grain yield when band placed 100 to 150 mm from the row at planting



Duration = 3 years
Placement:
from the row = 100 – 150 mm
Depth = 100 mm
Row spacing = 1.5 m

(Adriaanse 2001)

Potential losses: leaching in clay soil

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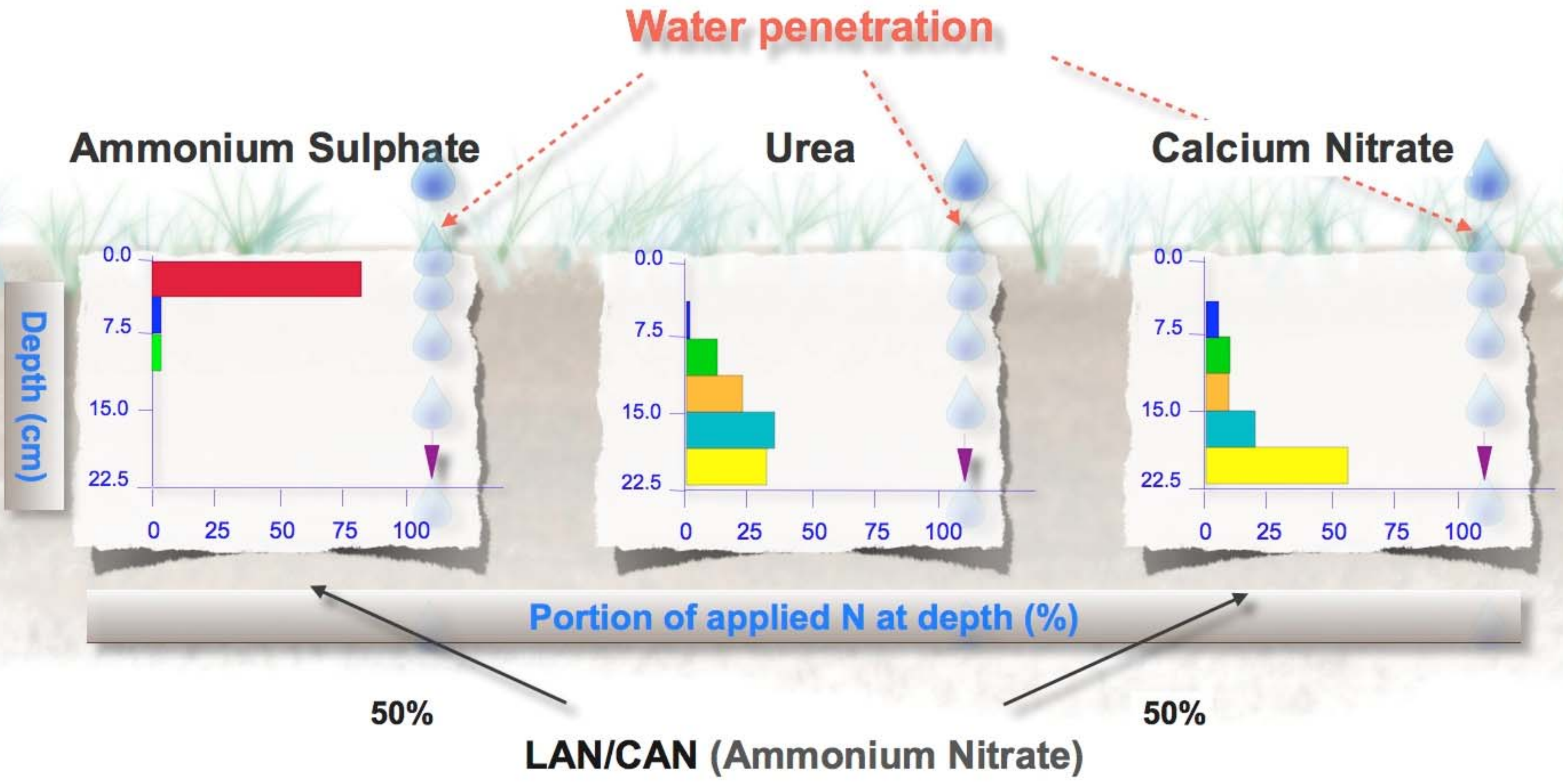


Water penetration

Ammonium Sulphate

Urea

Calcium Nitrate

Portion of applied N at depth (%)

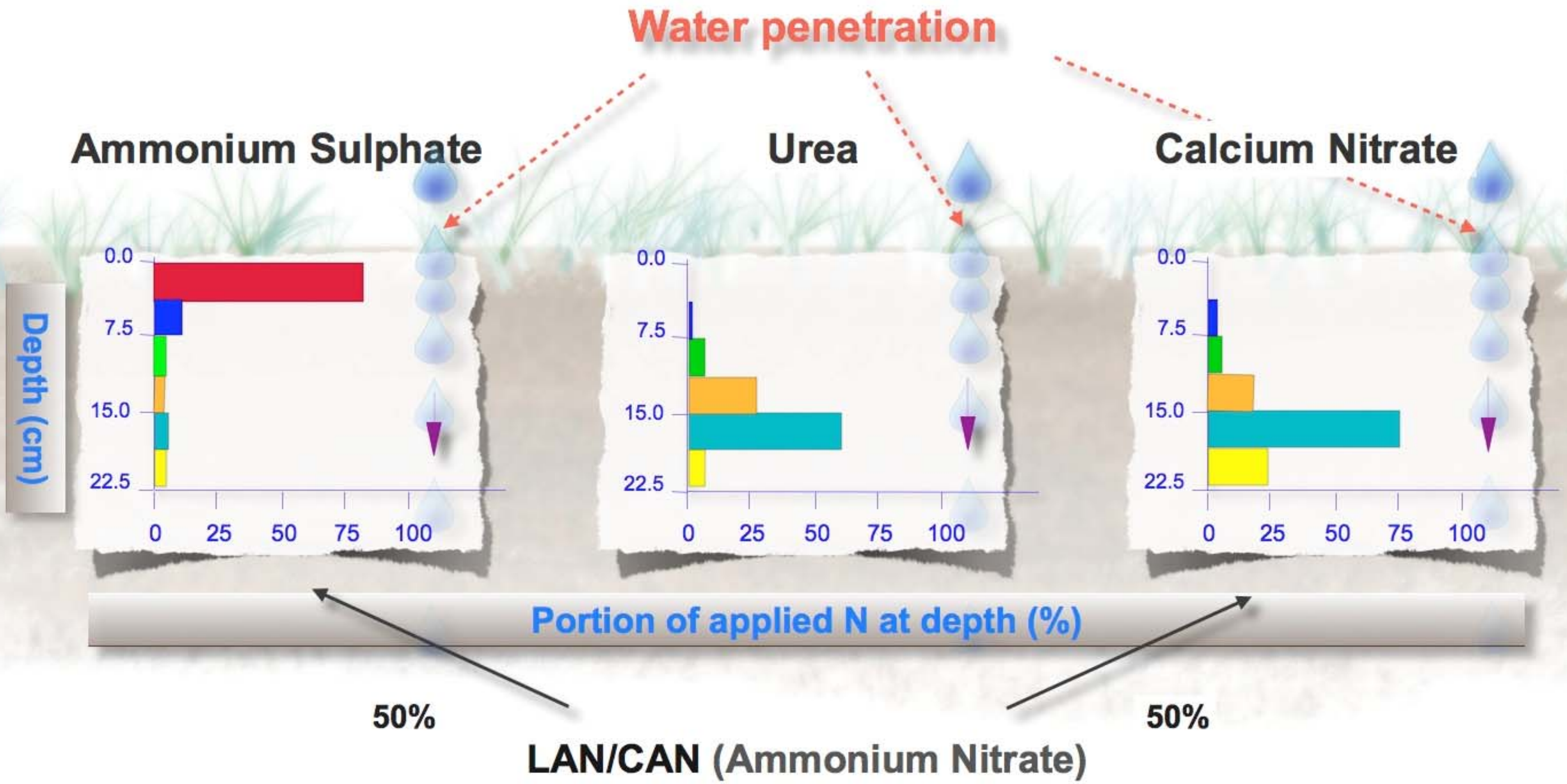
50%

50%

LAN/CAN (Ammonium Nitrate)

Ref: Broadbent et al.,1958

Potential losses: leaching in sandy loam soil


Water penetration

Ammonium Sulphate

Urea

Calcium Nitrate

Portion of applied N at depth (%)

50%

50%

LAN/CAN (Ammonium Nitrate)

Ref: Broadbent et al.,1958

Potential losses : leaching

63 kg N/ha as LAN
2 weeks before planting

40kg N/ha at planting

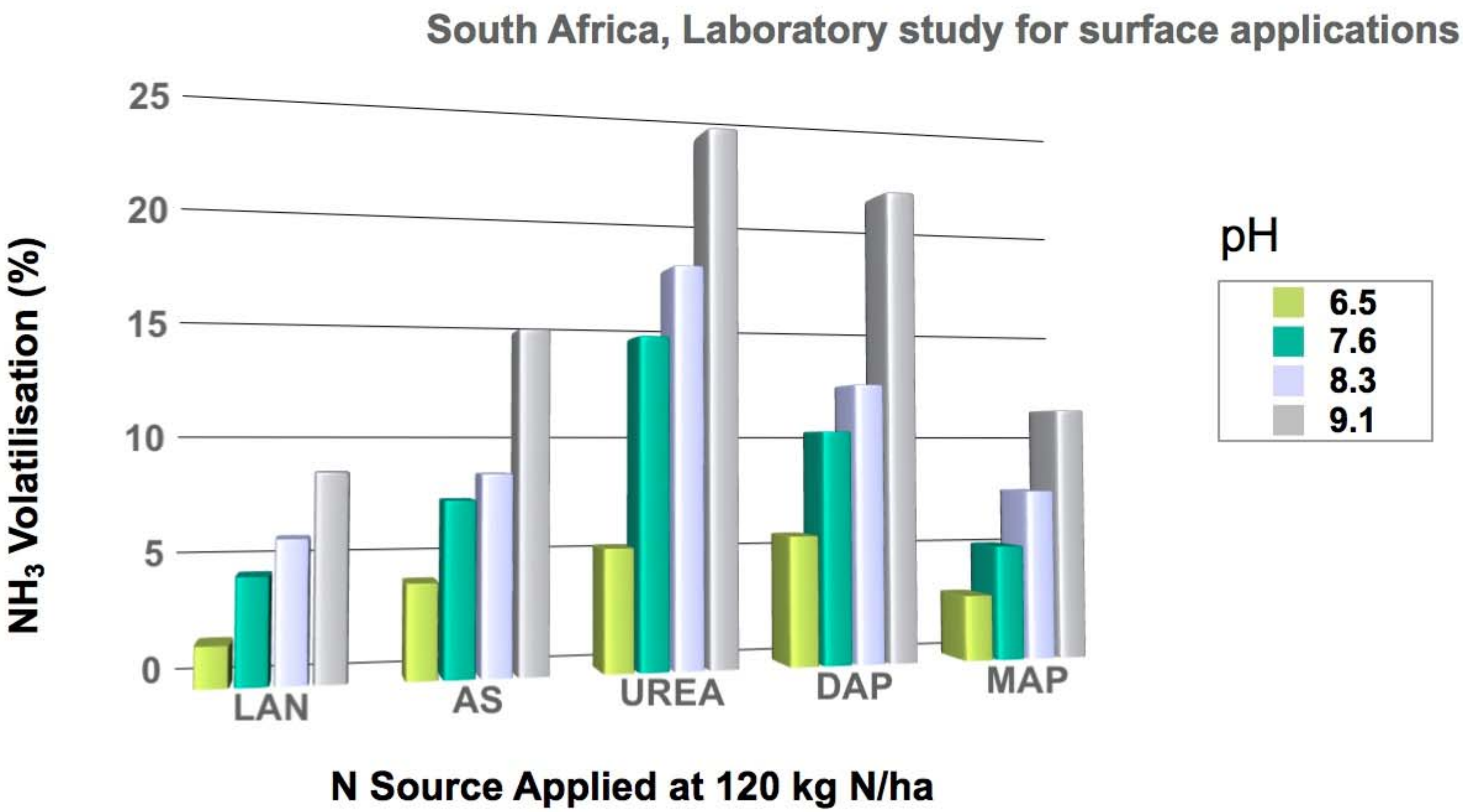
More than 100mm rain
shortly after planting

Well drained sandy soil

Adriaanse 2010

Potential losses: volatilisation

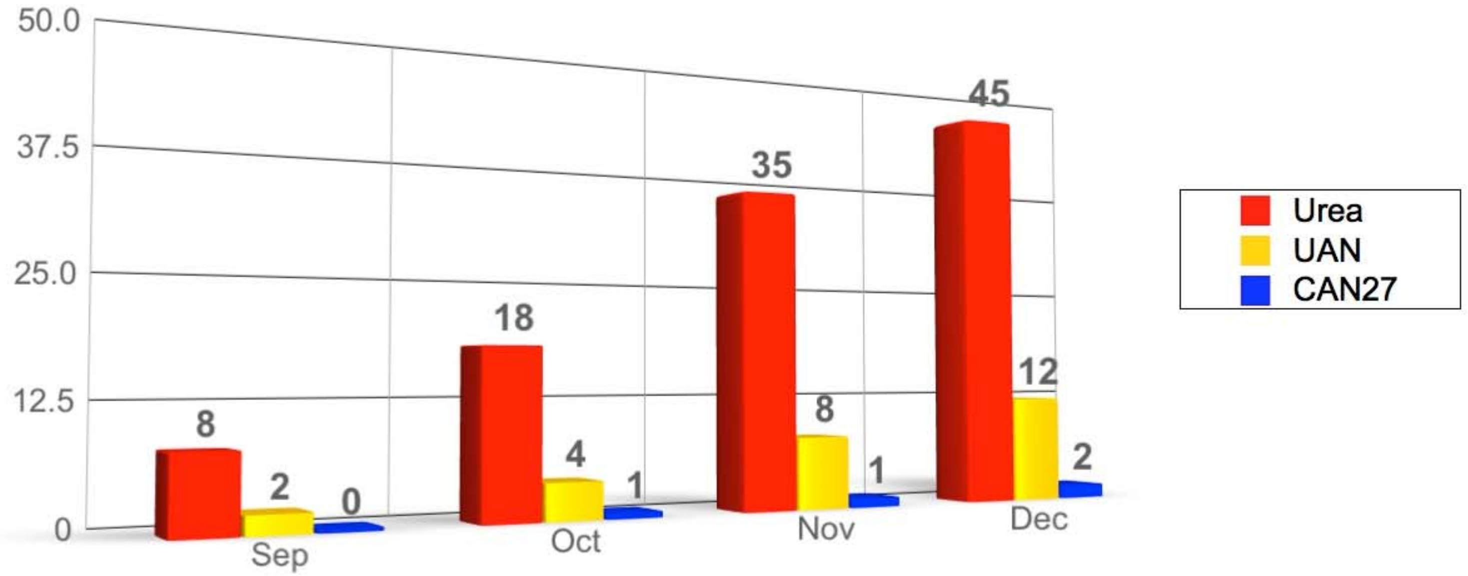
Volatilisation of Ammonium Sulphate is less than Urea but more than LAN at high pH



Ref: du Preez, C. C. and Burger R. du T., 1986

Potential losses: Volatilization

N loses are much more for Urea and UAN compared to LAN/CAN – larger differences with rising temperatures



Argentina

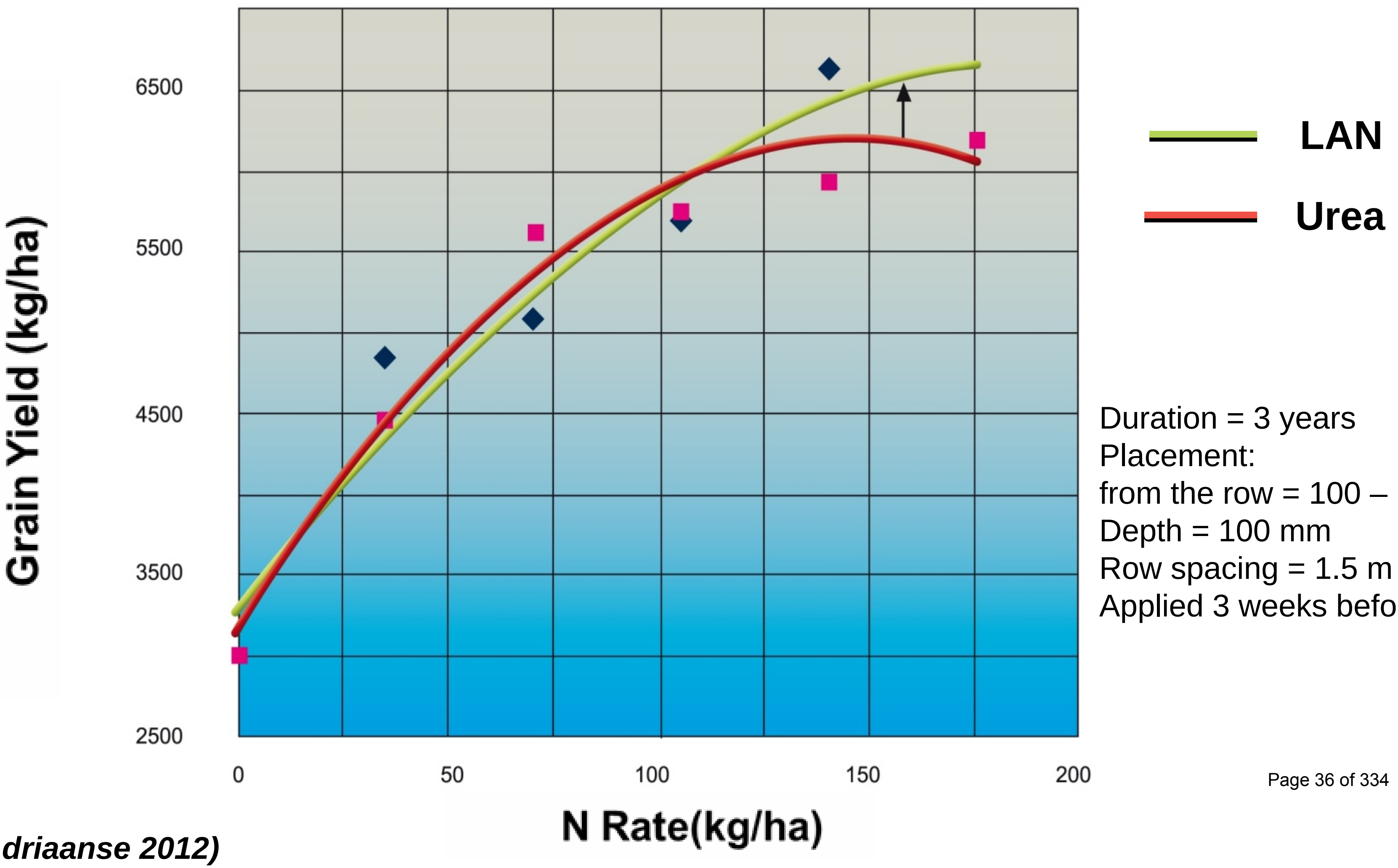
NH_3 losses as % of applied N

REF: H.Fontanetto - INTA

Yield response to N sources

reaching new frontiers

Similar yield responses to pre-plant band placed LAN and Urea at low N rates on a water table soil



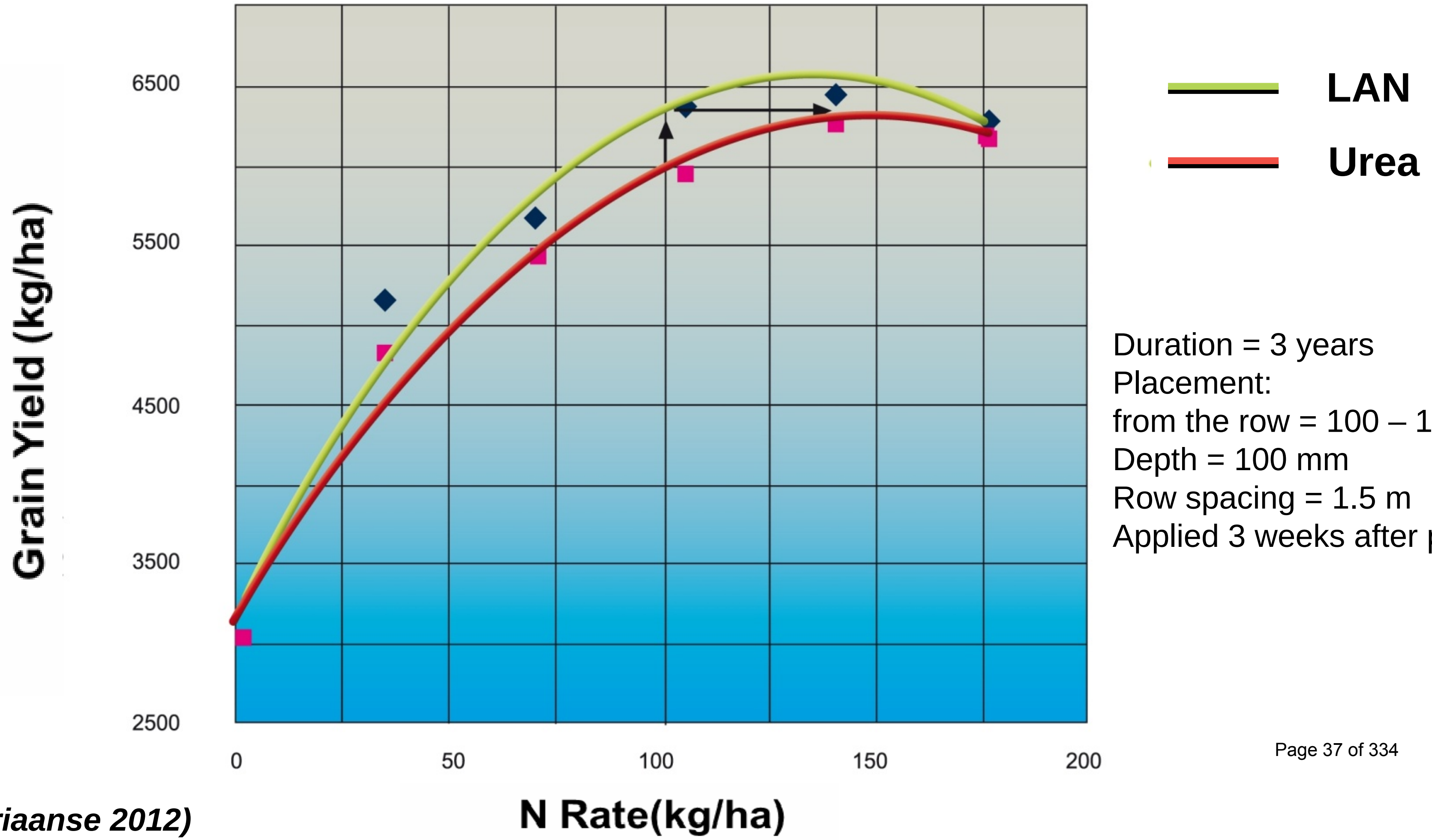
Duration = 3 years
Placement:
from the row = 100 – 150 mm
Depth = 100 mm
Row spacing = 1.5 m
Applied 3 weeks before planting

(Adriaanse 2012)

Yield response to N sources

sasol
reaching new frontiers

Ammonium Nitrate results in 5.8% higher maize yield than Urea, knifed in as a topdressing



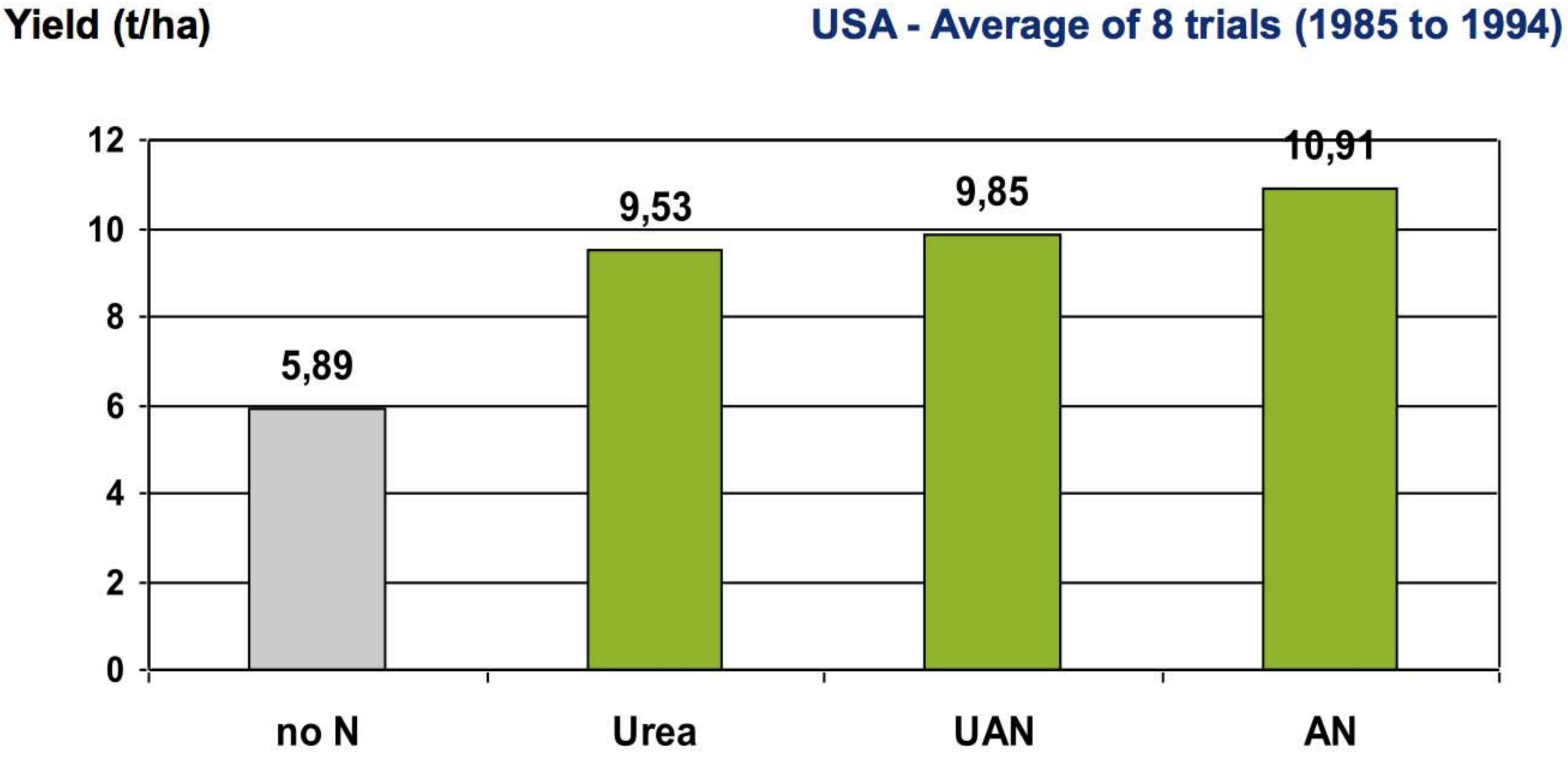
Duration = 3 years
Placement:
from the row = 100 – 150 mm
Depth = 100 mm
Row spacing = 1.5 m
Applied 3 weeks after planting

(Adriaanse 2012)

Yield response to N sources

sasol
reaching new frontiers

Ammonium Nitrate results in 14.5% higher maize yield than Urea

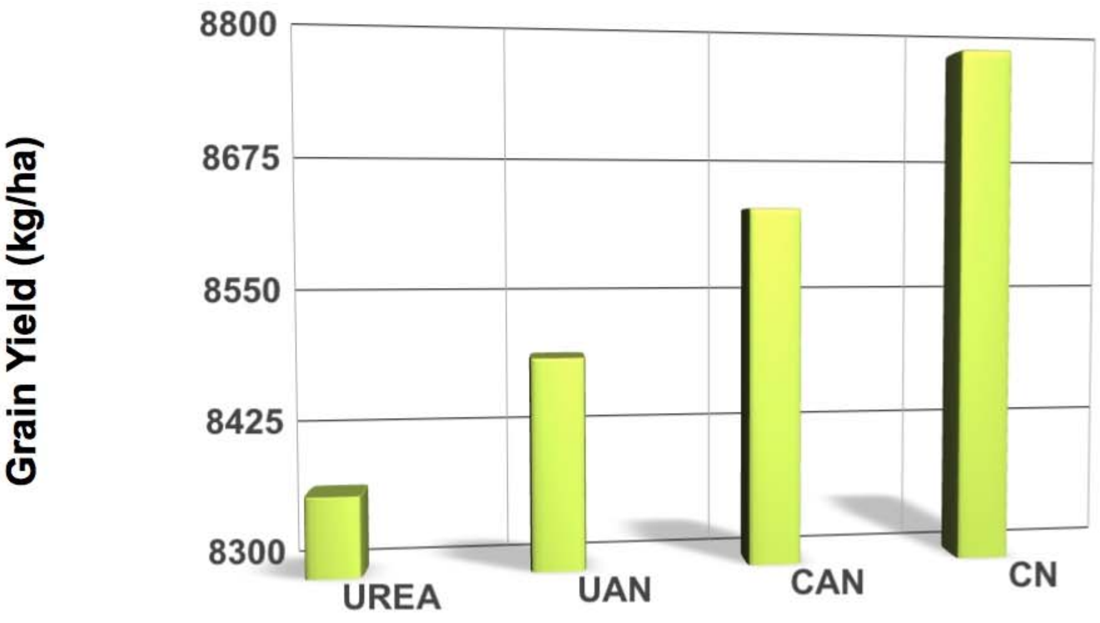


REF: Penchant, Mann, Mangle and Hawkins, Purdue, Univ., USA

Yield response to N sources

CAN results in 3.03% higher winter wheat yields than Urea

UK Average over 15 years

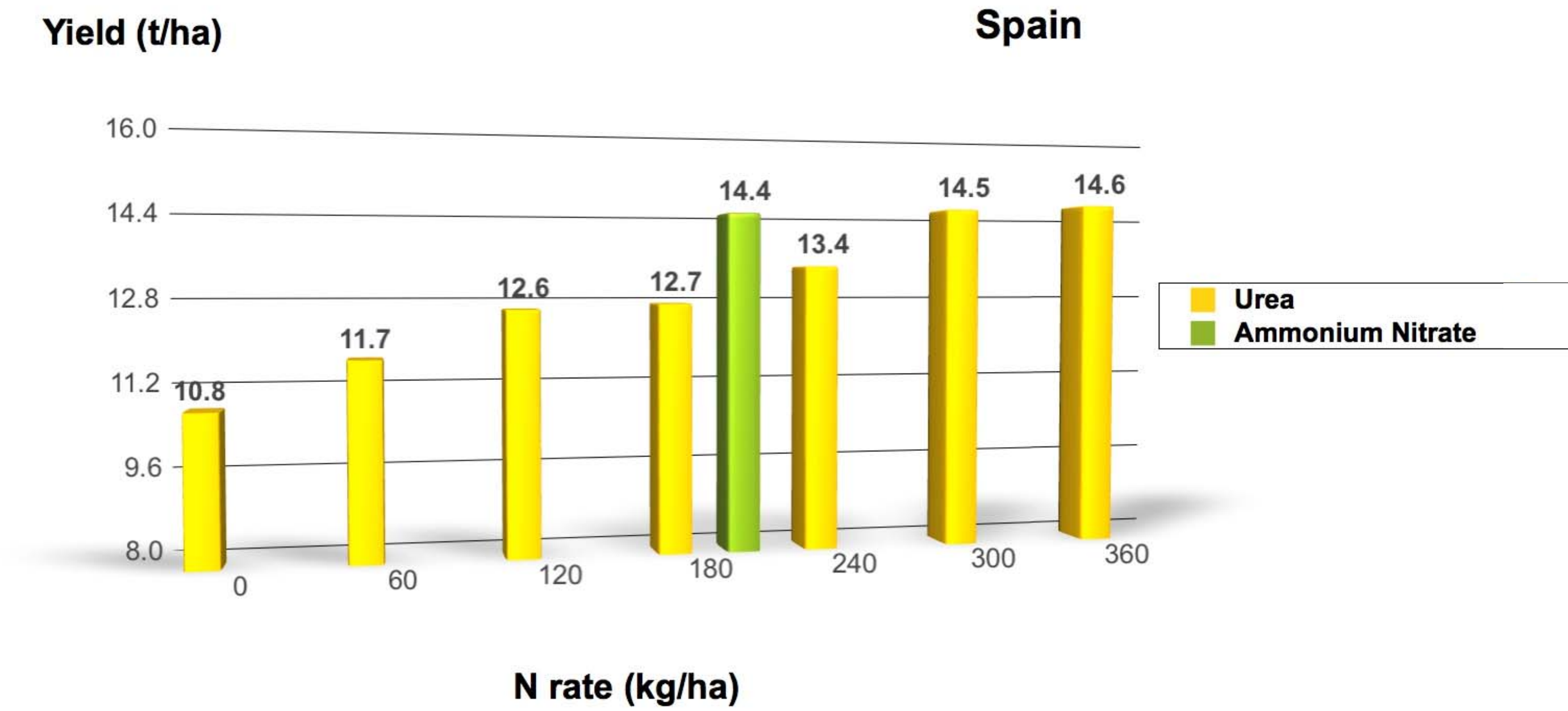


N Source at 160kg N/ha

(Ref: Levington Agriculture, UK)

Yield response to N sources

Ammonium Nitrate results in 13.4% higher maize yield than Urea

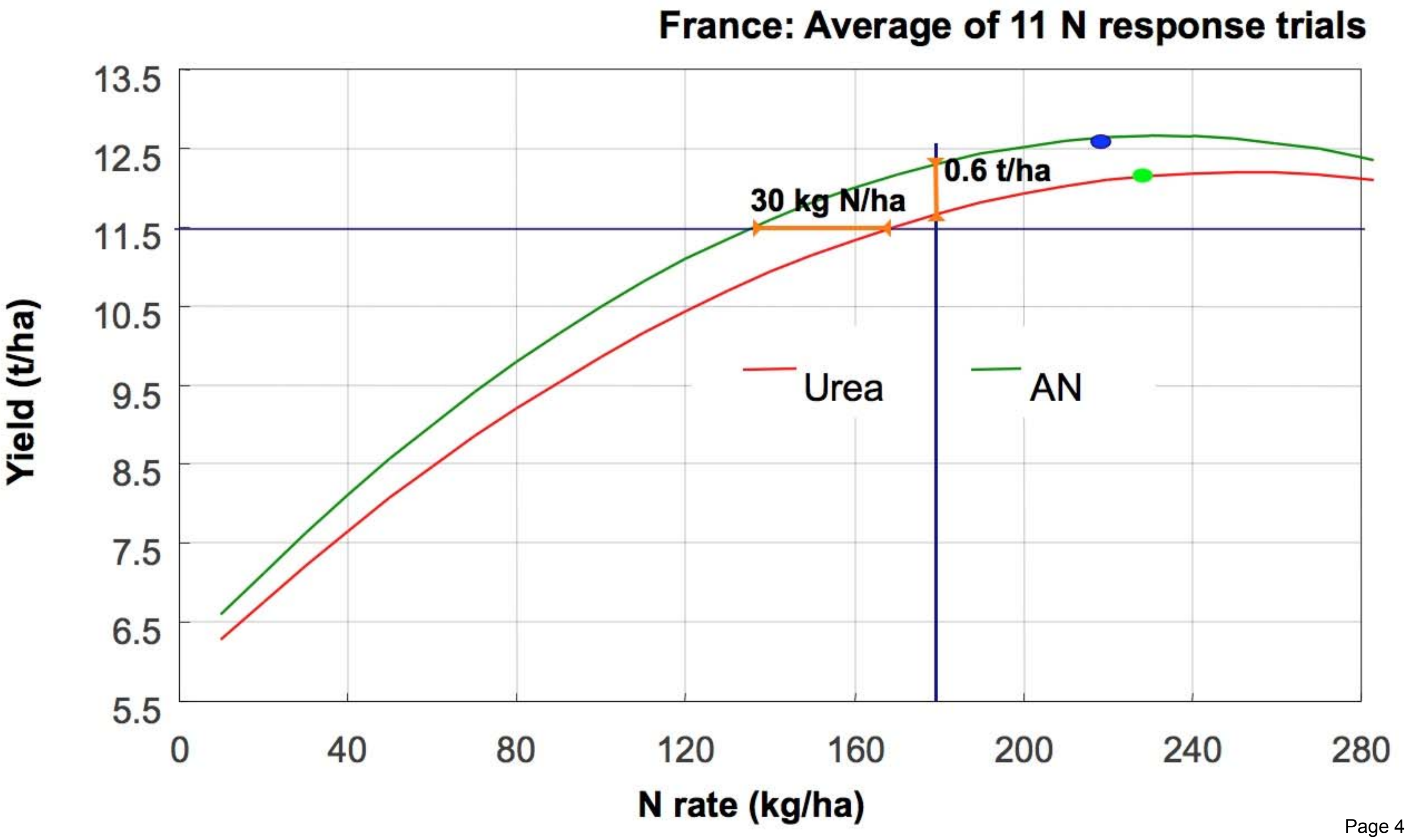


REF: ITGC (2004) - Instituto Técnico de Gestión del Cereal

Yield response to N sources

sasol
reaching new frontiers

Ammonium Nitrate results in 5.2% higher maize yields than Urea

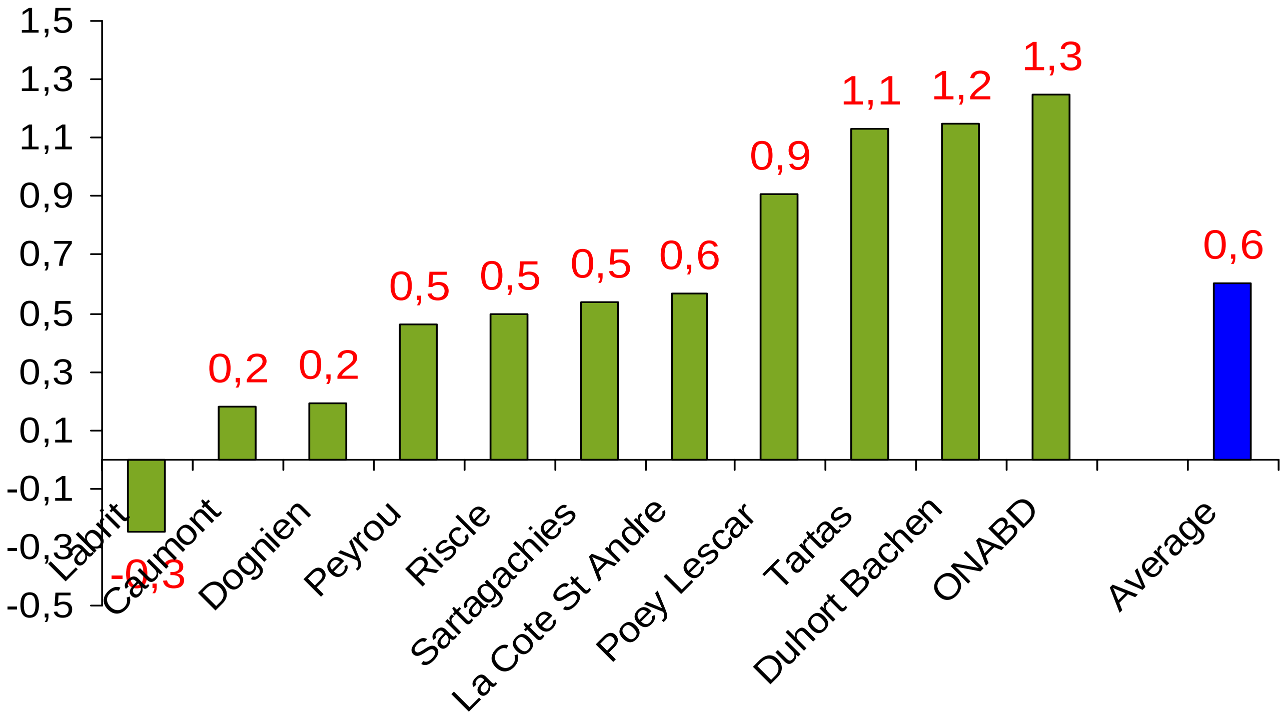


REF: Avails (1998) – Official advisory service, France

Yield response to N source

Relative Preference of Ammonium Nitrate over Urea is Site Specific - France

Yield difference (t/ha) = AN treatment minus Urea

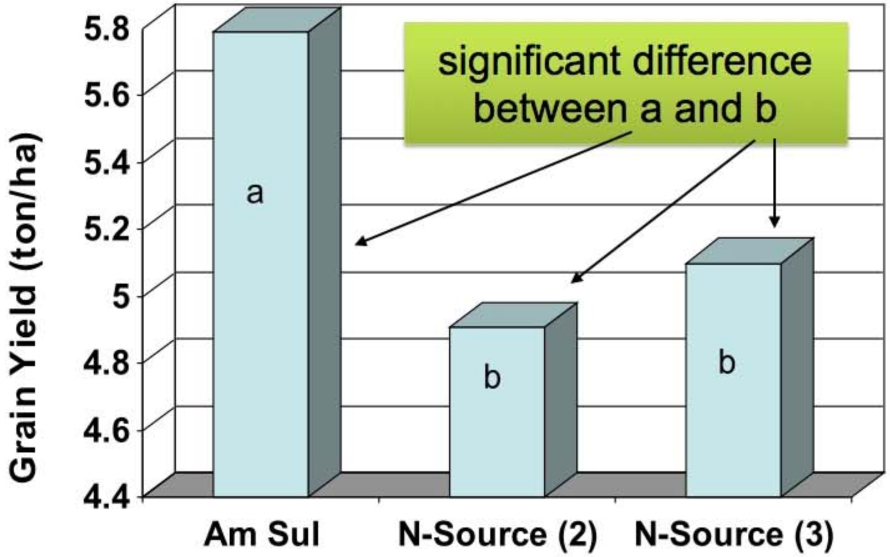


11 single site comparisons at 180 kg N/ha

(Ref: Avails (1998) – Official advisory service, France)

Higher yields under specific conditions

Higher wheat yield with Ammonium Sulphate compared to LAN or Urea under irrigation



	Am Sul	N-Source (2)	N-Source (3)
kg N/ha	140	140	140
kg S/ha	160	0	0

Explanation for higher yields:

- **Less leaching**
- **S Supply**

Conditions:

- **Hutton Soil Form**
- **Mangano Soil Series**
- **9.3% clay to a depth of 750mm**
- **pH (H_2O) = 6.4**
- **N sources were broadcasted and ploughed in prior to planting**

Ref: P.J.; du Toit Burger, R; Laker, M.C; 1985

Indications for N Sources

N Source	Recommended applications
Ammonium sulphate	Supplemental to other N sources: Before, at and after planting. Pre-plant, broadcast on well drained soil with high pH.
LAN/AN/CAN	Pre-plant band placed or broadcast on poorly drained soils. Plant mixtures. After planting band placed or broadcast on all soils.
Urea/UAN	Pre-plant band placed or broadcast, soil incorporated on poorly drained soils. After planting band placed or broadcast, soil incorporated or washed in. Aerial applications.
Ammonia	Pre-plant band placed on well drained and poorly drained soils.
MAP	Pre-plant band placed or broadcast, soil incorporated. As part of plant mixtures.
DAP	Pre-plant band placed or broadcast, soil incorporated.
$Ca(NO_3)_2$ KNO_3	After planting to optimize nitrate-N : Ammonium-N ratio.

Contra-indications for N Sources

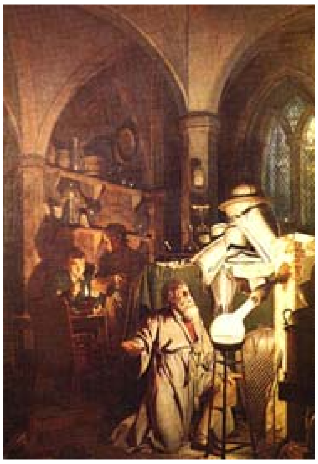
N Source	Applications to be avoided
Ammonium sulphate	Band placement in large quantities – toxic. Broadcast applications , not soil incorporated under alkaline conditions – volatilization.
LAN/AN/CAN	Very high concentrations close to the seed – moderately toxic. Pre plant applications on well drained soils – leachable.
Urea/UAN	Pre-plant applications on well drained soils – leachable. Band placement in plant mixtures – toxic and leachable. Broadcast applications not soil incorporated or washed in – volatilization. For rectifying severe N-deficiencies rapidly after planting – conversions slow.
Ammonia	Very dry and very wet soils – volatilization and toxicity. At and after planting – toxic.
MAP	Band placed in large quantities as a plant mixture – toxic.
DAP	Not to be left on the soil surface – volatilization. Band placement at planting close to the seed in high concentration – toxic.
$Ca\ (NO_3)_2$ KNO_3	Not to be applied in large quantities before or at planting – leachable,

Conclusions

- Nitrate-N : Ammonium-N ratios should be optimized around 75:25 in the soil.
- Pre-plant band placed applications of LAN, Urea and NH_3 at low N rates, on poorly drained soils should result in similar yields.
- Pre-plant broadcast applications of Ammonium Sulphate under well drained conditions should result in higher yields compared to LAN and Urea.
- LAN/AN broadcast or band placed applications after planting should result in 6 to 13.4% higher yields compared to urea over localities and years.
- Cost effectiveness between N sources should in addition be considered.
- Nitrification inhibitors should only be considered when severe leaching is expected.
- Urease inhibitors may increase yield when Urea is surface applied especially with residue on the soil but not when Urea is soil incorporated or washed in. LAN surface applications is expected to outperform Urea + Urease inhibitor.

THE EFFICACY OF PHOSPHATE SOURCES AND THEIR APPLICATION “TURNING OLD AND NEW BONES”

J.J. Bornman
General Manager: Strategic Agricultural Services,
Omnia Fertilizer



The discovery of Phosphorous.
The artist Joseph Wright’s depiction of
“The Alchymist”, 1771

ABSTRACT

Even before its discovery in 1669 the value of phosphorous has been known as a plant nutritional element, hence it is generally known today as the “noble fertilizer element”. The world will soon use approximately 23 million tons of phosphorous per annum of which 3 million tons are consumed in food. Fortunately there are enough resources to supply the world demand for many years to come, but the fact remains that phosphorous is a non renewable resource. It is actually described by some as “life’s bottleneck”. Hence it is of utmost importance that it is carefully managed for optimum use and minimum waste to the environment, especially in agriculture, which uses 82% of the resource for fertilizer production. To achieve the aforementioned, and to support the escalating food demand, it is important that the characteristics of phosphate fertilizer sources and their related efficacy are well understood. In this paper the production of various primary phosphate fertilizer sources are discussed and their relative agronomic efficiency compared under different conditions. The environmental dangers of phosphorous sources and their misuse as well as new trends regarding additives are briefly addressed.

THE DISCOVERY OF PHOSPHOROUS

In 1669, Hennig Brandt, a Hamburg alchemist, like most chemists of his day, was trying to make gold. He let urine stand for days in a tub until it purified. Then he boiled it down to a paste, heated this paste to a high temperature, and drew the vapours into water where they could condense - to gold. To his surprise and disappointment, however, he obtained instead a white, waxy substance that glowed in the dark (Toy and Walsh, 1987).

There is a strong probability that Arabian alchemists already discovered phosphorous from urine in the 12th century, but the credit is given to Hennig Brandt.

The word phosphorous is of Greek origin and means “the bearer of light” (Childs, 2012a). Phosphorous is indeed known as the “noble fertilizer element” (ISMA, 1977)

A BRIEF HISTORY OF PHOSPHATE FERTILIZERS

As early as 2,000 years ago, Chinese farmers applied calcined or lime-treated bones to their fields. The Greeks and Romans also realized the benefit of bone residues to crops, for instance, encouraging the establishment of orchards near old battlefields (Palgrave, 1991; Beaton, 2012).

The German chemist Justus von Liebig (1803-1873) is considered by many to be the father of agricultural chemistry and the fertilizer industry (Sauchelli, 1965). Although Von Liebig showed that treatment of bones with a strong acid, such as sulphuric acid, would increase the availability of phosphorus, he developed a fertilizer in which the phosphate and potash salts were fused with lime and as a result it was a failure (Beaton, 2012).

The credit of beginning the synthetic fertilizer industry is given in literature to John Bennett Lawes when he started making phosphate fertilizers in 1842 at Deptford in England. However, that is not quite the origin of phosphate fertilizers, which also has an Irish dimension (Childs, 2012b).

In 1817 James Murray, a doctor in Dublin and discoverer of “milk of Magnesia”, first reacted calcium phosphate with sulphuric acid to produce a fertilizer (Childs, 2012b).

James Murray's main competitor was John Bennett Lawes, an Englishman who turned out to be a better businessman. In 1846 he bought Murray's patent and came to be known as the father of the fertilizer industry (Childs, 2012b).

THE LEGEND OF LAWES

Sir John Bennett Lawes (1814-1900) was born at Rothamsted, Hertfordshire. In 1841/2 he patented a method of making superphosphate from bones, extended his process to mineral phosphates (coprolites) and later to imported apatite (calcium phosphate) with sulphuric acid. He started manufacturing fertilizers in 1844 in Deptford, London (Beaton, 2012).

The brisk demand for bones in England in the early 1800s, lead to the importation of bones from the Continent, already starting in 1815 and reaching a high of 30,000 tons annually. Justus von Liebig actually criticized the English for collecting bones from old battlefields and burial sites such as the catacombs of Sicily (Beaton, 2012).

For more than 100 years superphosphate was the world’s leading phosphate fertilizer. It dominated in the US from 1870 to 1964 and peaked in 1952. Triple (concentrated) superphosphate was initially produced in Germany in 1872. Ammonium phosphates, which are now the dominant phosphate sources world wide, were first produced commercially in the U.S. in 1916. By 1974, diammonium phosphate (DAP) became the most widely used phosphate fertilizer across the world (Beaton, 2012).

WORLD DEMAND AND SUPPLY OF PHOSPHOROUS (“LIFE’S BOTTLENECK”)

A prominent science writer, Isaac Asimov said the following in 1974: “*We may be able to substitute nuclear power for coal, and plastic for wood, and yeast for meat, and friendliness for isolation - but for phosphorous there is neither substitute nor replacement. Phosphorous is life’s bottleneck*”.

By the middle of this century the world population will have reached 9 billion people. Amongst others, the general dietary shift to meat preference and crop based bio-energy demand, further contributes to fertilizer phosphorous demand, besides that to produce needed crops for basic food production. Currently 3 million tonnes of phosphorous (P) are consumed in food by the world population per year (Schröder, Cordell, Smit & Rosemarin, 2010).

It is estimated that the world increase in phosphate demand will exceed a compounded growth rate of 2% from 2011 to 2015. This translates to 20 to 23 million tonnes of phosphorous (P) demand per annum. Eighty two per cent of this quantity is for fertilizer production. Fifty five per cent will be in Asia, 29% in America, 8% in Europe and 4% in Africa and Oceania. It is foreseen that supply will exceed demand by 6% in 2015 (Schröder *et al.*, 2010; FAO, 2011).

Although phosphorous is the 11th most abundant element in the Earth's crust only a small percentage is present in high enough concentrations to be utilized by humans for producing fertilizers (ISMA, 1977).

Phosphate rock like oil is a non-renewable source and high grade reserves are becoming increasingly scarce. There is currently an active debate regarding the reserves available. Estimates differ vastly (mainly because of definitions), but it is estimated to last between 60 and 130 years. The fact that 85% of world reserves are based in 5 countries being Morocco, China, South Africa, Jordan and the United States further adds to the dilemma. This could lead to geopolitical constraints of availability (Schröder *et al.*, 2010; FAO, 2011).

Some scientists have proposed the "peak theory" claiming that peak production capability of prime resources will be reached before mid current century (2035). Production costs will rise and even become uneconomical because of escalated demand by developing countries and cost of mining and beneficiation of poorer less accessible sources (Schröder *et al.*, 2010). The International Fertilizer Industry Association (IFA), for instance, do not agree with this view (IFA, 2012).

Nevertheless, everybody is in agreement that phosphorous use should be optimized and losses to the environment minimized, hence this paper on phosphorous sources and their relevant efficiency.

THE PRODUCTION OF THE CLASSIC FERTILIZER PHOSPHATES

To better understand the efficacy of the different fertilizer phosphate sources, the production thereof needs to be explained as these production methods lend such sources their characteristics.

In the following discussion on the manufacture of different fertilizer phosphates, the following primary references were used: Sauchelli (1965), Engelstad, 1990, Palgrave (1991) and UNIDO & IFDC (1998).

The production of most phosphorous fertilizer products begins with phosphoric acid as base material. Phosphoric acid is produced today primarily by means of the so called "wet process" where phosphate rock, whether in sedimentary or igneous form, is attacked by acid and mostly in the form of sulphuric acid. Phosphoric acid is also produced by an electric and blast furnace process, but these processes will not be discussed in this paper.

The basic chemical reaction of sulphuric acid with rock phosphate (usually as fluoroapatite) is as follows:

$$Ca_{10}F_2(PO_4)_6 + 10H_2SO_4 + nH_2O \rightarrow 10CaSO_4.nH_2O + H_3PO_4 + 2HF$$

During the wet process phosphoric acid containing some 23% of P is produced with by products of gypsum and usually some hyfrofluoride gas (hydrofluoric acid in water), depending on the rock type.

Most rock phosphate sources contain "impurities" like aluminium, iron and magnesium. Depending on the purity of the acid and the specific purity the acid takes on a characteristic colour. Very pure sources are white in colour while most commercial sources are either green or black (Fowles & Kruger, 2000).

Ordinary, normal or single superphosphate (containing 8.0% to 8.7% P) is manufactured in exactly the same way as phosphoric acid, but the acidulation is incomplete. The reaction is as follows:

$$Ca_3(PO_4)_2 + 2H_2SO_4 + H_2O \rightarrow Ca(H_2PO_4)_2.H_2O + 2CaSO_4$$

During the process carbon dioxide (CO_2) is formed which gives superphosphate its characteristic porous structure, making it an ideal matrix to absorb ammonia in the production of ammoniated superphosphates.

If phosphoric acid is used instead of sulphuric acid to react with phosphate rock, double, concentrated or triple superphosphate (containing 20% citric soluble P) is formed in the following reaction:

$Ca_3(PO_4)_2 + 4H_3PO_4 + H_2O \rightarrow 3Ca(H_2PO_4)_2.H_2O$

Note the absence of sulphur in the form of gypsum in the final product.

Ammonium orthophosphates are manufactured by ammoniating phosphoric acid in a mole ratio of ammonia to phosphoric acid of 1:1 or 2:1 to form mono ammonium phosphate (MAP) and di-ammonium phosphate (DAP), respectively. MAP contains 11% N and 22% P while DAP contains 18% N and 20% P. MAP has an acid reaction in soil giving a pH of approximately 3.5 to 4.5 around the granule while DAP has an alkaline reaction of above pH 8 (usually 8.5) around the granule.

THE MANUFACTURE OF POLYPHOSPHATE BASED FERTILIZERS

Polyphosphate containing fertilizers are manufactured firstly by concentrating fairly pure phosphoric acid (preferably low in especially magnesium and also iron) by driving off normal and crystal water, reaching a concentration of above 30% P (usually 31% P). This process of heating and distillation is energy intensive. During this process orthophosphate is polymerized to pyro- (2 units), tripoly- (3 units) and longer chains. Super phosphoric acid or super acid could contain up to 60% of the total P as polyphosphate, although it is usually manufactured containing 20% to 30% polyphosphate P.

This acid is usually ammoniated to form ammonium polyphosphate to produce a 10% nitrogen and 15% phosphorous containing liquid product. This product is very popular as a clear liquid fertilizer, as is, or to be used as a phosphate raw material at liquid plants (clear or suspension).

Ammonium polyphosphate can be granulated to form an 11% N and 24% containing granule.

A urea ammonium polyphosphate is also produced by combining a melt of urea with a melt of granulated ammonium polyphosphate to form products like 28:12:0 or 35:8:0.

Super acid is also used in granulation processes.

THE PRODUCTION OF NITROPHOSPHATES

When producing nitrophosphate, rock phosphate is reacted with nitric acid in stead of the usual sulphuric acid. It requires much less energy for production and is environmental friendly as no gypsum is generated as by-product. The chemical reaction is as follows:

$Ca_3(PO_4)_2 + 6HNO_3 \rightarrow 3Ca(NO_3)_2.H_2O + 2H_3PO_4$

Combinations of nitric with sulphuric or phosphoric are also used. If the resultant solution of the reaction of nitric acid with phosphate rock is directly ammoniated and granulated, without removing the calcium nitrate, the product will be water insoluble dicalcium phosphate that is highly hygroscopic due to the large calcium nitrate presence. There are three primary processes to prevent this:

- Removing the calcium nitrate by cooling and crystallization (the classic Odda Process).
- The re-addition of phosphoric acid and/or sulphuric acid to precipitate most of the calcium.
- The addition of sulphate salts to precipitate calcium as gypsum.

After total or partial removal of calcium the solution is ammoniated and granulated giving the so-called nitrophosphate product. Depending on the process, nitrophosphates are water soluble in a range from 25% to as high as 98%. To be agronomical feasible it is agreed by scientists that nitrophosphates should be at least 60% water soluble. The European Union requires at least 75% solubility in 2% citric acid.

OTHER PHOSPHATE SOURCES

DIRECT APPLICATION OF PHOSPHATE ROCK AND PARTIALLY ACIDULATED ROCK PHOSPHATES (PAR)

Direct application of finely pulverized phosphate rock (sedimentary rock) has been utilized from near the beginning of fertilizer practice. It is of course the lowest cost material, but its agronomic effectiveness depends on the chemical and mineralogical nature of the rock, pH and other characteristics of the soil, as well as the crop produced (see discussion below). North Carolina (US) and Gafsa (Tunisia) rock have the highest reactivity and is suitable for direct application.

Rock phosphates are also partially acidulated, usually with sulphuric acid and mixtures of superphosphate and rock phosphate are also prepared and compacted or granulated. Much literature is available regarding the evaluation of the agronomic effectiveness of these sources (Chien, Prochnow, Tu & Snyder, 2010). See comments under the heading “The efficacy of other fertilizer phosphate sources” below.

CALCINED PHOSPHATES, RHENANIA PHOSPHATE, BASIC SLAG AND FUSED MAGNESIUM PHOSPHATE (FMP)

These phosphate sources originate or are derived from thermal processes.

Ores consisting mainly of hydrated aluminium phosphate minerals are useful for direct application after being calcined at controlled temperature. Calcining (heating at high temperature, 400-600°C) not only removes the combined water and enhances the grade, but also destroys crystallinity in the phosphate minerals, thereby improving reactivity. Calcined products are usually 75% citrate soluble and contain 12 to 15% P, but also substantial amounts of aluminium (17-19%).

Rhenania phosphate was produced in substantial quantities and exported from Germany and is a calcium sodium phosphate. Phosphate rock is calcined in the presence of silica and sodium carbonate at 1260 °C. Rhenania phosphate contains approximately 12 to 13% P.

Basic slag is a by-product from the steel industry. Lime is added to the steel melt to remove phosphorous. The extract, also known as Thomas slag contains up to 7% P.

Fused calcium magnesium phosphate is a most interesting product made by an electric furnace-type operation. It is manufactured by the addition of a magnesium source (olivine or serpentine) along with phosphate rock in a furnace to produce a melt. The glassy product is cooled and pulverized to improve availability to plants. It usually contains approximately 9% P and 9% magnesium.

POTASSIUM PHOSPHATES

Potassium phosphates are excellent fertilizers but expensive to produce. Most potassium phosphates are produced by reacting phosphoric acid with potassium hydroxide or carbonate.

Typical products are:

Monopotassium phosphate (23% P, 26% K)
Dipotassium phosphate (17% P, 45% K)
Tetra potassium pyrophosphate (19% P, 47% K)
Potassium metaphosphate (26% P, 33% K)

UREA PHOSPHATES

When producing urea phosphate or urea superphosphate (USP), urea is melted and reacted with pure phosphoric acid or mixtures of phosphoric acid and sulphuric acid. The mole ratios are specific because of eutectics. The resultant melts are either directly prilled to produce urea phosphate (UP) or it is further reacted with superphosphate to form USP which is granulated in a number of ways. UP contains 18% N and 19% P and is completely water soluble. USP contains 21% N and 4.4% P which are all citrate soluble.

These products are highly acidic and are often used under calcareous soil conditions especially in nutrient solutions used for fertigation.

PHOSPHATES IN ORGANIC SOURCES

There is much debate regarding the efficiency of phosphates from organic sources. As all manures and composts are not the same regarding water soluble phosphorous content, mineralization rates and other constituents, it is difficult to predict its phosphorous efficiency. In general, it is stated that approximately 60% to 75% of P will be available from organic sources or that P availability from manures and other organic sources are indeed equal to or slightly less than from fertilizer sources. Regardless, availability still depends on said mineralization rate, microbial immobilization, P reaction with manure constituents and direct soluble P content (Bundy, 2012).

Reactive sedimentary rock phosphate sources are often blended with organic sources as they themselves are regarded as organic. It is postulated that the reactivity of such rock phosphates are enhanced by the organic material as calcium within the phosphate source is chelated by organic acids, freeing up phosphate for plant use (Chien *et al.,* 2010).

Many researchers have indicated that inorganic P applied to soils that contain a significant quantity of organic matter is more efficient than if applied to organic deficient soils (Johnston, 2000; Syers, Johnston & Curtin, 2008).

THE EFFICACY OF FERTILIZER PHOSPHATE SOURCES

Note: In this discussion where there is referred to the relative agronomic efficiency (RAE) of phosphorous sources, and if not specifically otherwise stated, the initial slope of the response curve is used as basis of comparison as explained by Chien, Sale and Friesen (1990). Logarithmic response functions were used where possible.

DIRECT APPLICATION OF PHOSPHATE ROCK (SEDIMENTARY)

Certain sedimentary rock phosphates show high citric acid or citrate analysis values regarding P, which makes it suitable for direct application. If such sources are available near the site of production it could be a viable source of phosphate. Such sources are North Carolina and Tunisian rock phosphates which show a citrate solubility of P as high as 7%.

However, the direct application of certain rock phosphates, especially those of igneous origin with low citrate or citric solubility is questioned. Such an example is Phalaborwa rock phosphate, which only contains 0.68% citric acid soluble P (Krumm, 1969).

Much work has been done in South Africa with a sedimentary rock phosphate sourced near Langebaan on the West Coast, North of Cape Town, containing 3% citric acid soluble P (Krumm, 1969; Thibaud, Farina, Hughes & Johnston, 1991).

Thibaud *et al.* published two papers in 1991 and 1992 discussing extensive work done with maize in greenhouse trials, testing the RAE of Langebaan rock phosphate vs. superphosphate. Different acid soils were used with and without liming. Mixtures of Langebaan rock phosphate and TSP were also evaluated. Thibaud *et al.* (1991) reported RAE's of Langebaan rock phosphate of between 5% and

39% depending on soil acidity and P fixing capability with single and multiple cropping after application. They also studied the effect of liming with the application of the phosphate sources and confirmed substantial reduced response with the rock phosphate due to the common ion effect of calcium and the impact of pH increase.

A trial was done by AECI in the Western Cape with wheat over a term of six years where different phosphorous sources were applied once off at different rates to a slightly acid clay soil near Malmesbury (Bornman & Bester, 1998). The plots were split with a maintenance treatment of 20 kg ha^{-1} P equivalent with the particular source initially applied and no maintenance application. The sources evaluated included triple superphosphate and commercially available Langebaan rock phosphate. Both in the first year of response and over a six year period of wheat on wheat cumulative production the Langebaan rock phosphate gave a RAE value of approximately 60% vs. triple superphosphate. Most of this response is attributed to the liming effect of the rock phosphate. However, if the maintenance plots were compared, the RAE of Langebaan rock phosphate drops to 10%. This is explained by the fact that an increased presence of P, calcium and carbonate suppresses the dissolution and solubilisation of the sparsely soluble rock phosphate, similar to that found by Thibaud *et al.* (1992) with liming.

A web based model provided by IFDC (www.iswam.iaea.org/dapr/srv/en/home) is available to evaluate the RAE of a particular rock phosphate. It considers the rock source, soil parameters and crop capability (Smalberger, Singh, Chien Henau & Wilkens, 2006). Using this model the RAE of Langebaan rock phosphate is evaluated as 30% in a typical Malmesbury acid soil (if a liming effect is excluded) using wheat as crop.

PHOSPHORIC ACID AND RELATED LIQUID FERTILIZERS

Phosphoric acid is often used in direct applications but is most popular for its use in acid clear liquid and suspension fertilizers. Already in the early eighties, scientists from TVA (Tennessee Valley Authority), the institute best known for its development of liquid fertilizers, reported superior response of crops to liquid phosphorous containing fertilizers as compared to granular superphosphates, especially if such acid fertilizers are used on calcareous soils. An enhancement of efficiency of 10% was mentioned and ascribed to the enhanced mobility of a liquid in soil and the solution of other nutrients such as calcium, magnesium and trace elements (Achorn, 1984; Palgrave, 1991; Bornman & Van Niekerk, 1995).

A trial was conducted by AECI in the Western Cape with wheat over a term of six years, mentioned above (Bornman & Bester, 1998), where different phosphorous sources were applied once off at different rates to a slightly acid clay soil near Malmesbury. Phosphoric acid showed a RAE of 108% if the cumulative yield response of the acid is compared to triple superphosphate on the non maintenance plots. In the first year of response the RAE was 133%. The once off phosphoric acid treatment yielded a significant 0.8 tons per ha more wheat grain vs. the superphosphate over the six years at the optimum soil P level.

In a one year trial done with alfalfa on a calcareous soil at the experimental farm of the Department of Agriculture at Cradock, phosphoric acid outperformed triple superphosphate yield wise with an RAE of 137% (Bornman & Van Niekerk, 1995).

Polyphosphate containing liquid fertilizers give similar RAE’s as phosphoric acid. In a recent study in Australia where polyphosphate and phosphoric acid liquids were evaluated against triple superphosphate (TSP) granular with wheat as test crop in soils with a range of soil pH (McBeath, Armstrong, Lombi, McLauchlin & Holloway, 2005), RAE’s of between 110% and 120% were noted of the liquid fertilizers against TSP granular.

THE RELATIVE EFFICACY OF SUPERPHOSPHATES AND AMMONIATED PHOSPHATES

Before the relative efficacy of these phosphates can be discussed some clarity needs to be given to the basic reaction monocalcium phosphates (MCP or superphosphates) undergo in soil.

Lindsay (1979) described the reaction of MCP as follows:

When MCP dissolves in soil solution, it is hydrolyzes to dicalcium phosphate and phosphoric acid in a metastable triple-point solution. The reaction may be written as shown below:

$Ca(H_2PO_4)_2.H_2O + H_2O \rightleftarrows CaHPO_4.H_2O + H_3PO_4$

The released phosphoric acid can lower soil pH to below 1.5 and thus dissolves iron and aluminium minerals and even clays, which, in turn, will react with the phosphates precipitating as less or even unavailable aluminium and iron phosphates.

In acid lateritic soils the RAE of superphosphates may therefore be substantially lower than the ammoniated phosphates like MAP and DAP as Bouldin and Sample (1959) demonstrated. A RAE of MAP and DAP relative to Supers of 150% were demonstrated on an acid soil with a pH (water) of 5.2.

In acid soils deficient in calcium and sulphur the benefit of the addition of these nutrients with superphosphates may outweigh the negative effect of P sorption or precipitation. Bennett and Adams (1970) illustrated a RAE of single superphosphate against DAP of 130% for pastures and even 300% for cotton production on an acid calcium deficient soil. The negative effect of DAP was also ascribed to ammonium toxicity.

On near neutral, alkaline and free lime containing soils, superphosphates do much better than ammoniated phosphates, because of the continuous release of phosphoric acid into an alkaline environment. Lu, Chien, Henau and Sompongse (1987) confirmed RAE's of between 125% and 200% for maize grown on alkaline soils (pH 8 in water) for single superphosphate against DAP. MAP, being slightly acid itself (pH in solution of approximately 4.5), is also quite soluble in alkaline soils. Superphosphate is 7 times more soluble than DAP in an alkaline soil (pH 8.3 in water), as reported by Bouldin and Sample (1959). However, superphosphate still outperforms MAP with a RAE of 117% with maize as test crop on a soil with pH 7.8 (water) (Lu *et al*., 1987).

THE EFFICACY OF NITROPHOSPHATES

Not much is available from literature on this topic. It is generally assumed that nitrophosphates would give similar RAE as ammoniated phosphates, provided its phosphate water solubility exceeds 60% (Khurana, Suroa & Vig, 2004). In South Africa two sources of nitrophosphate may be available. One is an imported product that is produced by the classic Odda process where all calcium nitrate is removed from slurry after reaction of nitric acid with phosphate rock. It contains up to 25% of its P content as polyphosphate and is 60% to 65% water soluble. Various claims are made regarding this phosphorous source, amongst others its enhanced solubility and mobility in soil and hence its higher availability and efficiency. The ability of polyphosphates to chelate trace elements, making it more available, is also mentioned (Yara Nitrophosphate NPK Fertilizer Manual, 2005).

Torres-Dorante, Claassen, Steingrobe and Olfs (2006) studied such polyphosphate containing products and evaluated its relative agronomic effectiveness against orthophosphate. The study revealed varied response in different soils. As polyphosphates need to be hydrolysed to orthophosphate before it is plant-available, the biological activity of the soil, especially regarding phosphatase presence, will determine the efficiency of polyphosphate containing sources. It is also postulated that as polyphosphates might show some slow release effect it might offer some protection against fixation. In a silty loam soil the authors report an increase "P fertilizer use efficiency" in production of maize (pot trial) with polyphosphates against orthophosphate of 7%, while on a sandy soil, low in phosphatase, a significant decrease of efficiency of 5% was observed with a pyrophosphate source.

The second nitrophosphate available in South Africa is locally produced in a double acid process. All calcium nitrate is not extracted from the product and sulphuric acid is also reintroduced with ammonia via a pipe reactor to stabilize it. The result is a 97% water soluble and 100% citric acid soluble product containing more than 6% each of sulphur and calcium. It also contains some magnesium. It does not contain any polyphosphates. This intermediate nitrophosphate is used as raw material in further granulation.

Recent greenhouse studies with the mentioned local nitrophosphate by the University of the Free State (Coetzee, ‘A Bear & Bornman, 2011) revealed RAE’s as evaluated against MAP of between 116% and 122% (dry and wet mass respectively) using wheat as a test crop on two different soils varying in texture. Preliminary evaluation of the data indicates that the primary reason for such increased RAE is the enhanced uptake of sulphur, calcium and magnesium especially at early growth stages. Significant increased calcium uptake (gram pot^{-1}) and increased chlorophyll measurements of the nitrophosphate treated plants seem to confirm this observation.

Data from a greenhouse trial done with spinach in a near neutral sandy soil (pH 6.2 measured in KCl) further supports the above findings (Mthandazo, ‘A Bear & Bornman, 2012). In this trial MAP significantly outperformed nitrophosphate at the first level of application but it actually depressed the yield of spinach at levels of P application above 15 kg ha^{-1}. A RAE of 176% was calculated for nitrophosphate to MAP if the slopes of response (dry mass pot^{-1}) were compared. At 30 kg ha^{-1} P application, nitrophosphate significantly increased the dry mass yield of spinach tops to twice that achieved with the MAP treatment and at 45 kg ha^{-1} P application more than three times the dry mass yield reached by MAP. Phosphorous-, sulphur-, calcium- magnesium uptake and chlorophyll measurement values followed the same trend as the dry mass yields. All these parameters were highly significantly increased with the nitrophosphate treatments as measured with analysis of variance (probability levels for source by level interaction were all less than 0.01). A trial with lettuce run parallel with the spinach trial confirms the trends, but nitrophosphate also tended (not significantly) to depress the yields of lettuce at the highest level of P application.

From these initial trials it is postulated that the presence of secondary elements in the nitrophosphate causes the better response per unit P. It would also seem that at higher P rates ammonium from MAP has a depressing effect due to direct toxicity and/or osmotic effect and/or inhibition of uptake of cations as reported by other researchers (Bennett & Adams, 1970, Dowling, 2001). It must be mentioned that this suppressing effect was evident despite the application of 200 mg kg^{-1} potassium as potassium nitrate in a supplementing nutrient solution in the last trial mentioned.

THE EFFICACY OF FUSED MAGNESIUM PHOSPHATE

International comparative data with this phosphate source is hard to come by, but during the middle nineties a fused magnesium phosphate (FMP) was produced in South Africa, from a factory based in Roodepoort. Questions arose as to whether it could be used as a commercial phosphate fertilizer source. The source (9.5% citric acid soluble P) was evaluated against chemically pure mono calcium phosphate (MCP) and commercially available triple superphosphate (TSP) in a contracted greenhouse trial at the University of Pretoria (Bornman, 1996). Dry bean plants were used as test crop. The sandy soil (10% clay) used was acid (pH 4.1 (KCl)), low in cations and relatively low in phosphorous (17 mg kg^{-1}, Bray 1).

Highly significant responses were achieved with all the sources applied at the different P levels (20, 40, 80 and 160 mg kg^{-1} soil), but the FMP significantly outperformed the other sources regarding dry biomass production. Although the TSP showed higher initial response to the first level of P application the response curves indicated a RAE of 151% of FMP against TSP.

The uptake of P, calcium and magnesium was highly significantly increased with the FMP and also significantly higher than the other sources at the two highest levels of application. The pH was also significantly increased with the FMP to a level of 4.38 (KCl) at the highest level of application while the other sources slightly decreased pH.

The increased RAE of FMP was primarily attributed to a liming effect in this soil and especially because of its magnesium nutrition contribution.

Some FMP is currently imported into South Africa, buts its RAE is yet unknown.

THE EFFICACY OF OTHER FERTILIZER PHOSPHATE SOURCES

Published data on other fertilizer phosphate sources besides those already discussed above is rather difficult to find. The classic phosphate sources are mostly dominant as raw material in the so called "other" sources discussed and therefore responses equivalent to those sources and their ratio could be expected.

ENVIRONMENTAL ASPECTS LINKED TO FERTILIZER PHOSPHATE SOURCES

No doubt, there is increasing concern over the use of phosphorous fertilizers, containing heavy metals, especially cadmium (Cd). Numerous greenhouse and field studies have been done and are still continuing to show the build up and adverse effects of cadmium. Quite a few review papers have also been published in this regard (Morvedt, 2005).

The source of Cd remains the phosphate rock used for production, and sources vary widely regarding their Cd content. The recent tendency is to report not only Cd content of a source itself but also to report the Cd content relative to the total P content of a source or product. As examples, South African Phalaborwa rock phosphate contains some of the lowest Cd concentration in the world i.e. 4 mg Cd kg^{-1} rock (23 mg Cd kg^{-1} P), Tunesian or Gafsa rock contains intermediate Cd content - 38 mg kg^{-1} rock (108 mg kg^{-1} P) and USA North Carolina rock contains large quantities of Cd - 47 mg kg^{-1} (311 mg kg^{-1} P), Chien *et al.* (2010).

Because of the actual rate of Cd application based on the rate of application of P fertilizers is rather low, gradual accumulation of Cd in soils takes place. To give an idea of accumulation rate, Bolan, Adriano, Naido, Mora and Santiago (2005) showed that it would take between 214 and 2,250 years to contaminate a soil with Cd to exceed a critical level of 3 mg Cd kg^{-1} soil.

Nonetheless, the threat remains, and various countries have introduced limits to regulate P fertilizers. It varies from fairly high, 300 mg Cd kg^{-1} P in Australia, to a relatively low level of 35 mg Cd kg^{-1} P in the Netherlands (Morvedt, 2005).

Another finger of accusation is pointed to P fertilizers regarding pollution and that is the problem of eutrophication. This means the unnatural enrichment of surface waters with a nutrient like P, stimulating aquatic life, like blue green algae (actually a bacteria). This bloom in bacteria growth causes depletion of oxygen leading to anaerobic conditions called hypoxia. This condition kills off other aquatic life and leads to impaired surface water quality.

Many surveys and studies have been conducted with different P sources to evaluate degree of loss of P from fields and to quantify differences of contribution from fertilizer sources Bundy, Andraski and Powell (2001); Withers, Nash and Laboski (2005). Data are conflicting relating to source effect as many aspects play a role like landscape, rainfall, management, placement and cropping systems. However, primary problem areas were identified like the risk of over application and surface broadcasting of especially highly water soluble P sources like DAP and TSP and even manures. Runoff from pastures also seems to be a common problem identified.

The solution to prevention of P loss into surface waters is to follow best management practices whereby fertilizer phosphates should be incorporated into soil and rates should be managed to maintain soils at the critical value for optimum crop production. As Maguire, Chardon and Simard (2005) stated: "*By managing P applications so that they remain near the agronomic optimum, it may be possible to maintain optimum crop growth while also protecting surface water quality*."

There is some concern about the radioactivity associated with phosphates, but it has been shown that it is of no consequence in practice regarding soil and plant build up (Johnston, 2000).

NEW ADDITIVES TO FERTILIZER PHOSPHATES

Chien, Prochnow and Cantarella (2009) have written a review paper on the recent enhancements of water soluble P sources, placing emphasis on polymer coatings. Unfortunately not much comparative data were available at the time. Many coatings from organic to inorganic have emerged over recent years, claiming enhanced and efficient use of water soluble phosphate sources. Claims include increased solubilisation by micro-organisms to protection against sorption by negatively charged agents. In particular the dicarboxylic copolymer type of coatings is showing promise (Tindall, 2007). However, Karamanos and Puurveen (2011) claim no significant benefit in using a commercially available product containing such coating. Only time and published scientific data will tell if enhanced agronomic effectiveness will justify additional cost using such coatings or enhancers.

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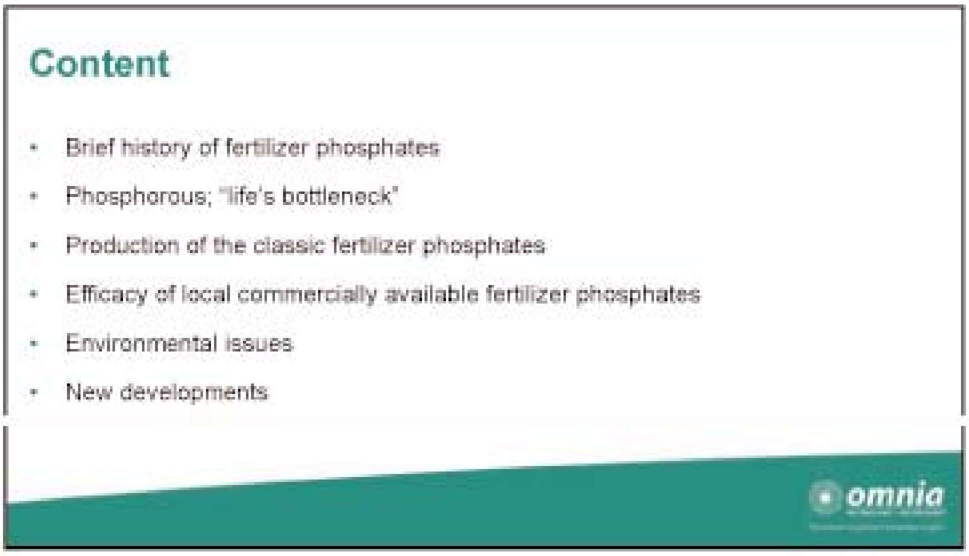
The efficacy and application of different Fertilizer Phosphate sources

"Turning old and new bones"

Koos Bornman, FSSA Technical Symposium

22 August 2012



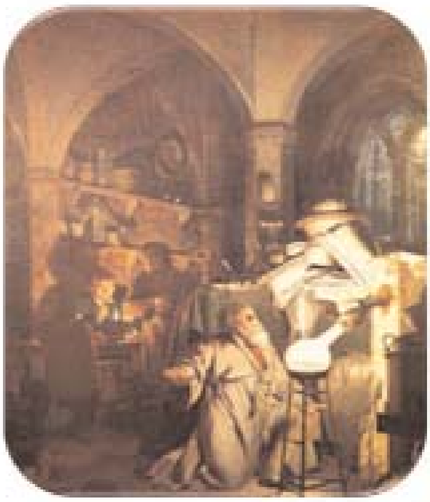
Content

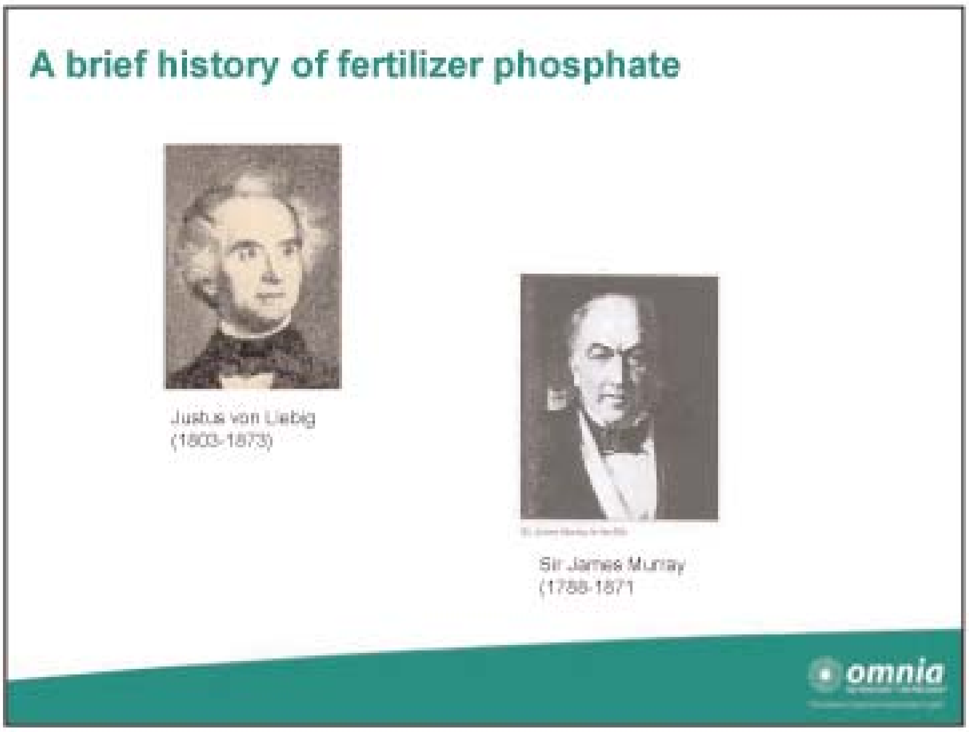
- Brief history of fertilizer phosphates
- Phosphorous; "life's bottleneck"
- Production of the classic fertilizer phosphates
- Efficacy of local commercially available fertilizer phosphates
- Environmental issues
- New developments

History

The discovery of Phosphorous by Hennig Brandt, 1669.

The artist Joseph Wright's depiction of "The Alchymist", 1771.





A brief history of fertilizer phosphate

Justus von Liebig
(1803-1873)

Sir James Murray
(1788-1871

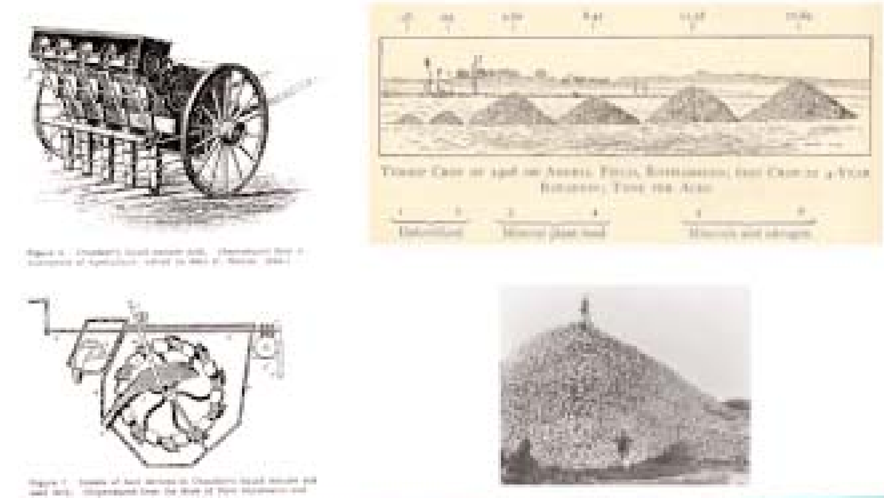
The recognized fathers of Superphosphate

Sir Joseph Henry Gilbert
(1817-1901)

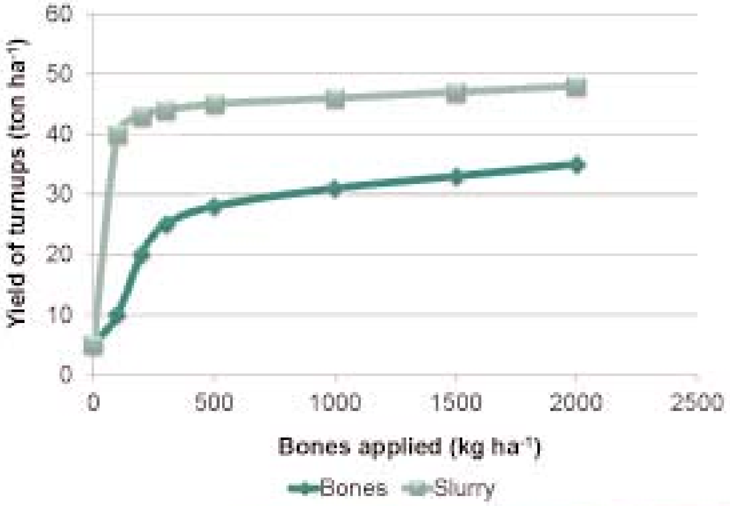
John Bennet Lawes
(1814-1900)

Lawes' works at Deptford London (1844)

History of fertilizer phosphates. The application of acidulated bone suspensions



Response of Turnips to phosphoric acid treated bones (1855) Norfolk; England (Palgrave, 1991)



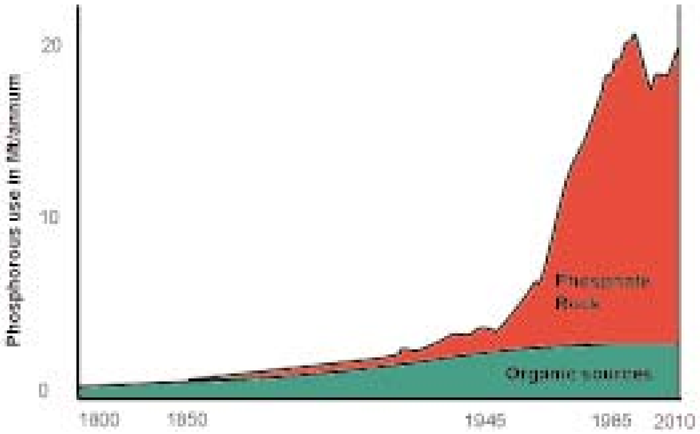
Phosphorous: "Life's Bottleneck"

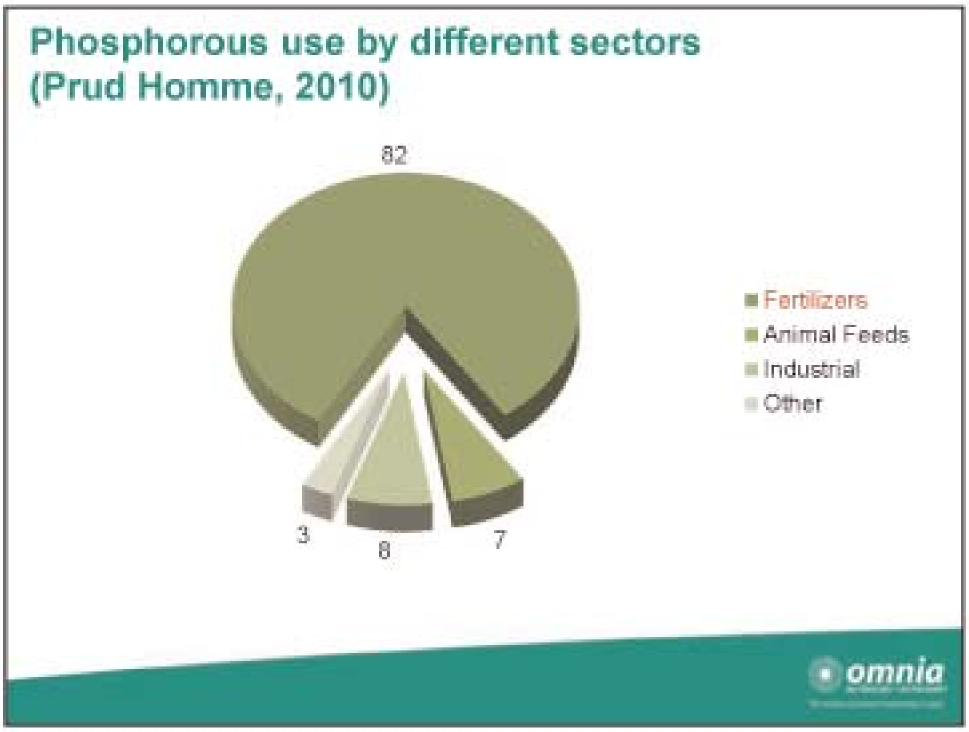
A prominent science writer, Isaac Asimov said the following in 1974;

"We may be able to substitute nuclear power for coal, and plastic for wood, and yeast for meat, and friendliness for isolation-- but for phosphorous there is neither substitute nor replacement. Phosphorous is life's bottleneck".

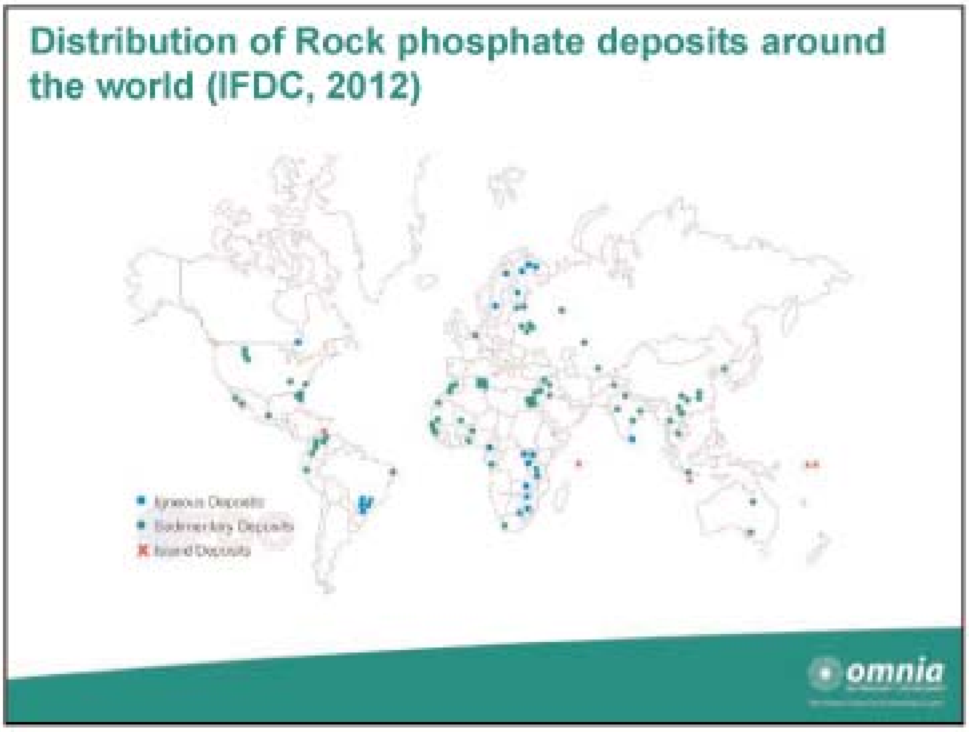
Estimates differ vastly but it is foreseen that phosphate rock reserves will last for another 60 to130 years

Historic sources of phosphorous (Redrawn from Cordell, 2010)

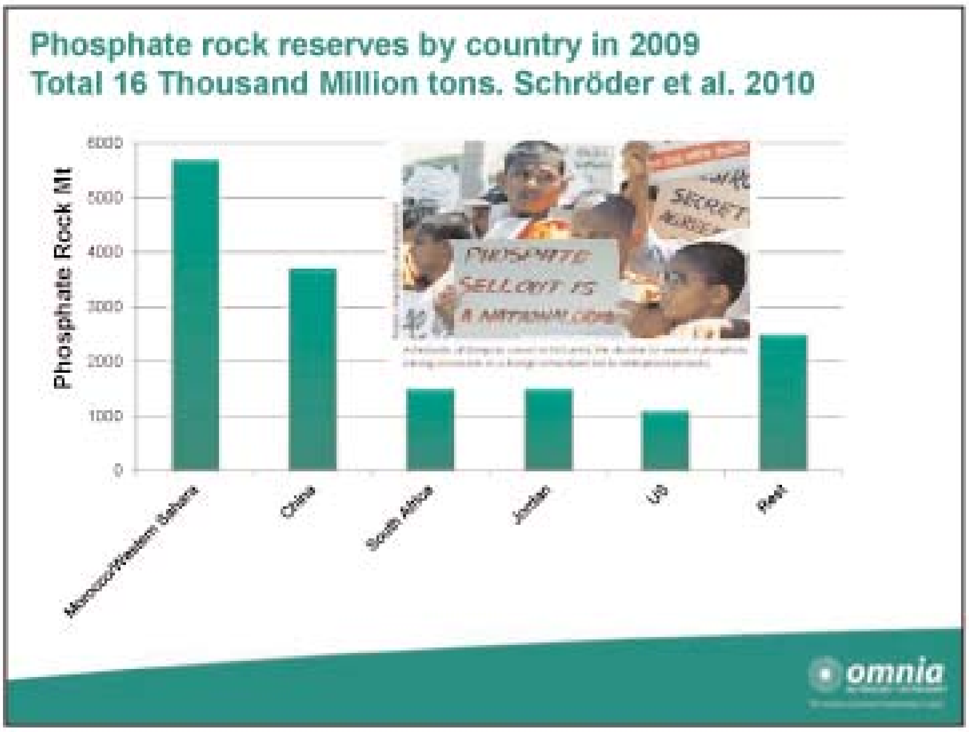




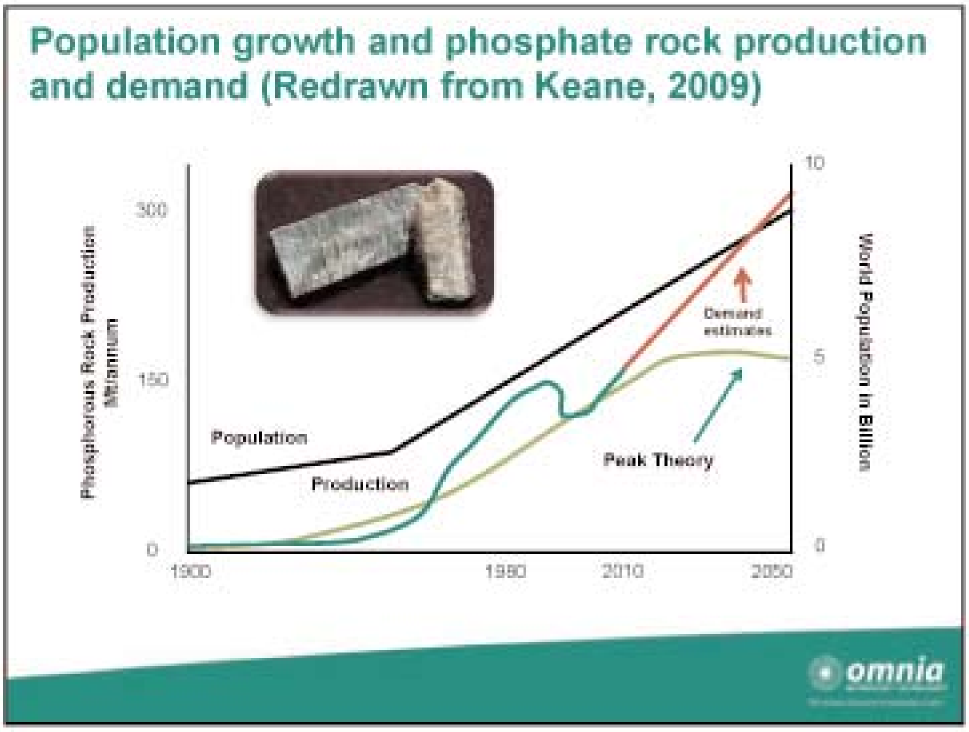
Phosphorous use by different sectors (Prud Homme, 2010)



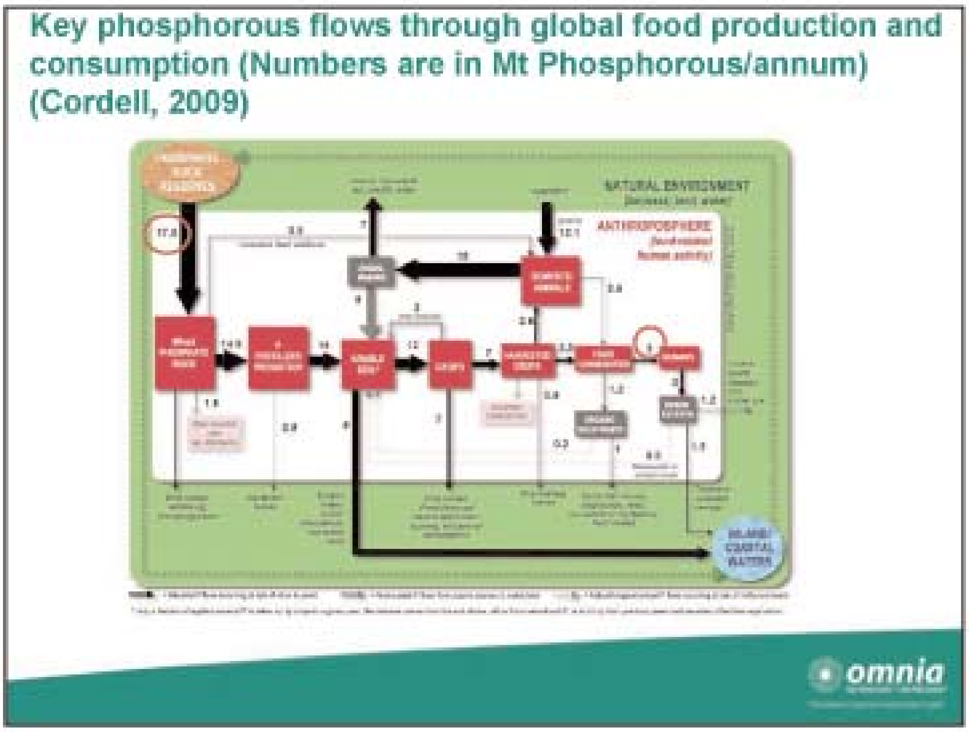
Distribution of Rock phosphate deposits around the world (IFDC, 2012)



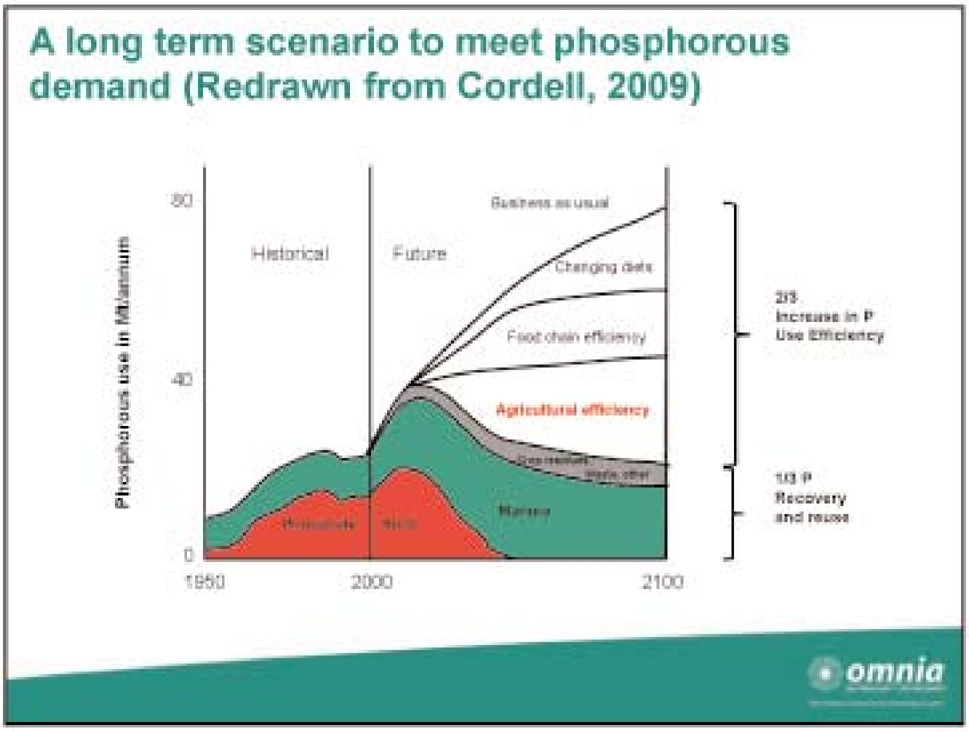
Phosphate rock reserves by country in 2009 Total 16 Thousand Million tons. Schröder et al. 2010



Population growth and phosphate rock production and demand (Redrawn from Keane, 2009)



Key phosphorous flows through global food production and consumption (Numbers are in Mt Phosphorous/annum) (Cordell, 2009)



A long term scenario to meet phosphorous demand (Redrawn from Cordell, 2009)

Production of the classic fertilizer phosphates

The production of the classic commercial Phosphate Fertilizers

Phosphate Rock

Sulphuric acid

Superphosphate

Ammonia

Ammoniated Superphosphate

Sulphuric acid

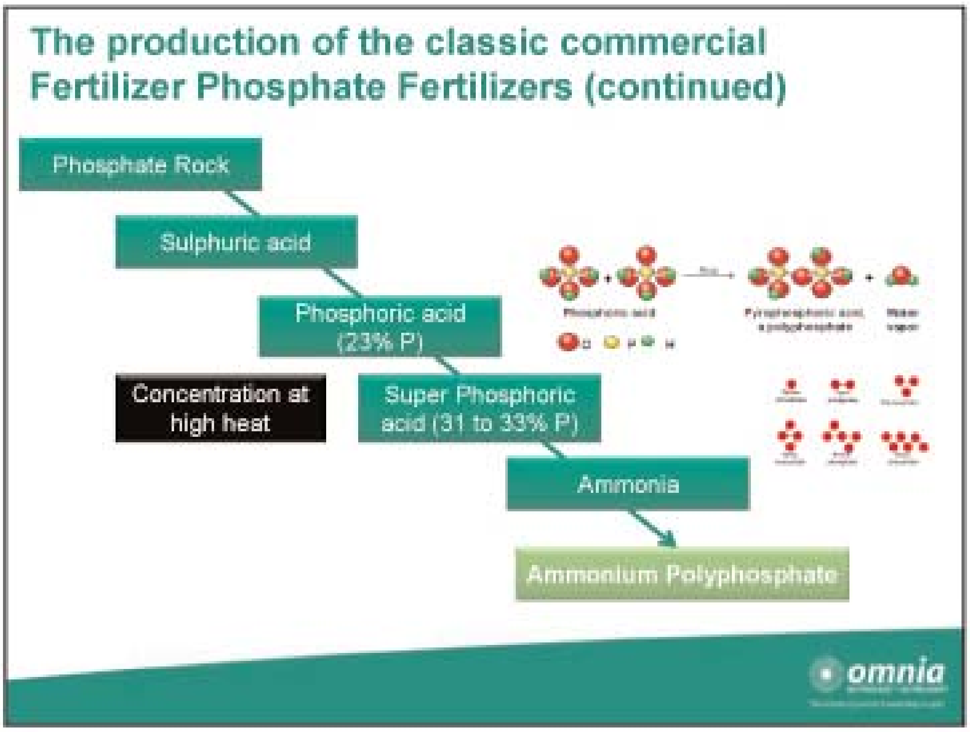
Phosphoric acid

Phosphate Rock

Triple Superphosphate

Ammonia

Ammonium Phosphates



The production of the classic commercial Fertilizer Phosphate Fertilizers (continued)

Phosphate Rock

Sulphuric acid

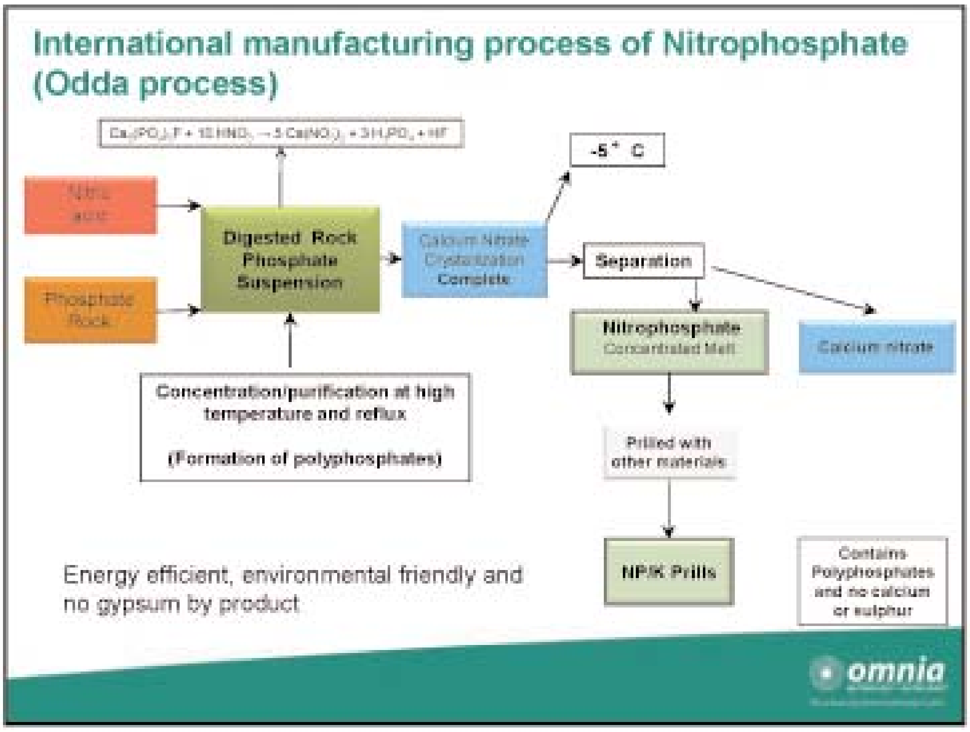
Phosphoric acid (23% P)

Concentration at high heat

Super Phosphoric acid (31 to 33% P)

Ammonia

Ammonium Polyphosphate



International manufacturing process of Nitrophosphate (Odda process)

$Ca_5(PO_4)_3F + 10\,HNO_3 \rightarrow 5\,Ca(NO_3)_2 + 3\,H_3PO_4 + HF$

Nitric acid

Phosphate Rock

Digested Rock Phosphate Suspension

Concentration/purification at high temperature and reflux

(Formation of polyphosphates)

Calcium Nitrate Crystallization Complete

-5 ° C

Separation

Nitrophosphate Concentrated Melt

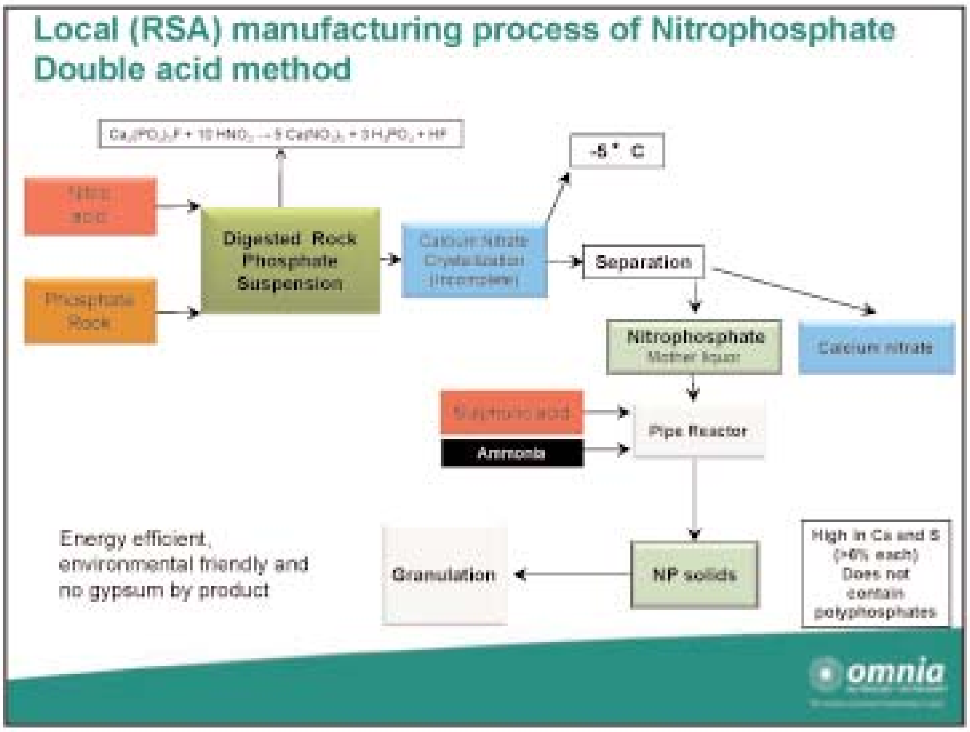
Calcium nitrate

Prilled with other materials

NP/K Prills

Contains Polyphosphates and no calcium or sulphur

Energy efficient, environmental friendly and no gypsum by product

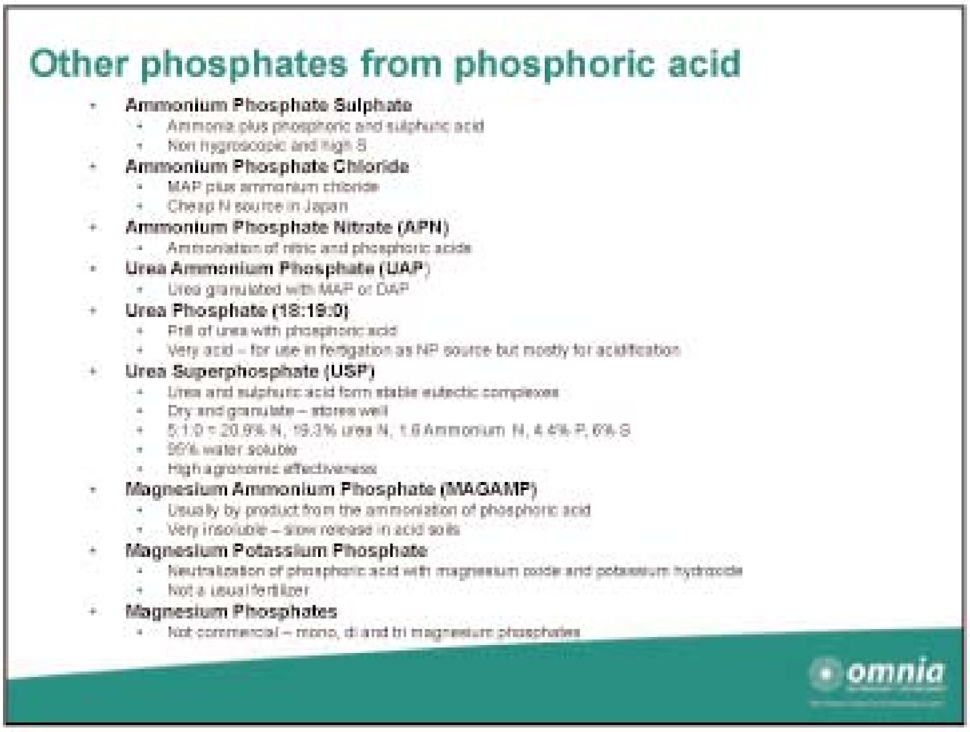


Local (RSA) manufacturing process of Nitrophosphate Double acid method

$Ca_5(PO_4)_3F + 10\,HNO_3 \rightarrow 5\,Ca(NO_3)_2 + 3\,H_3PO_4 + HF$

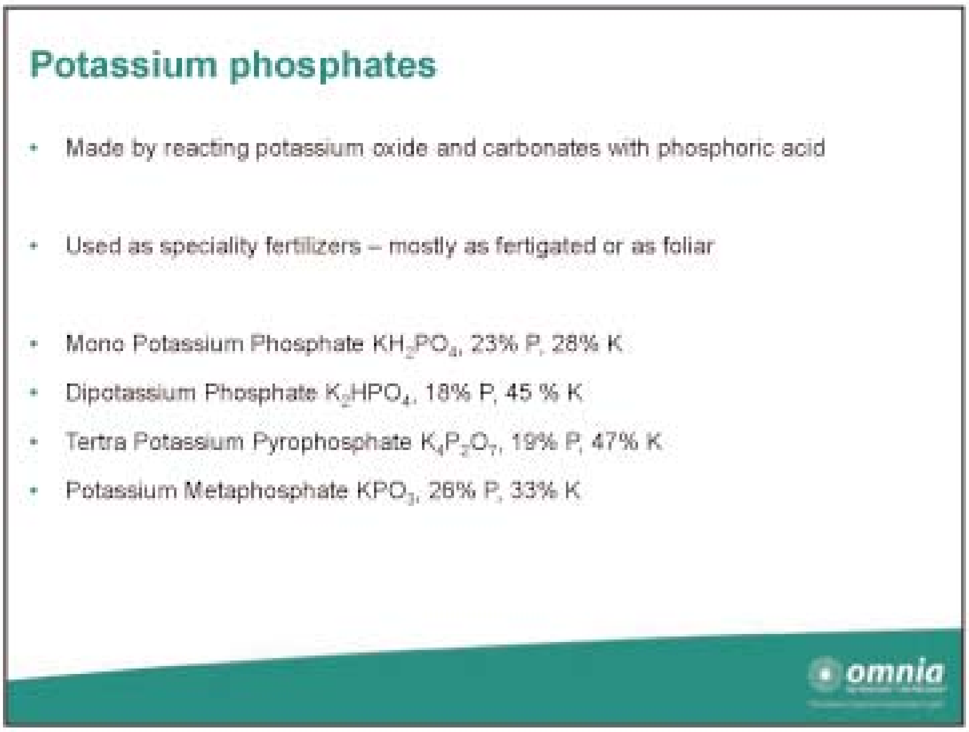
High in Ca and S (>6% each)
Does not contain polyphosphates

Energy efficient, environmental friendly and no gypsum by product



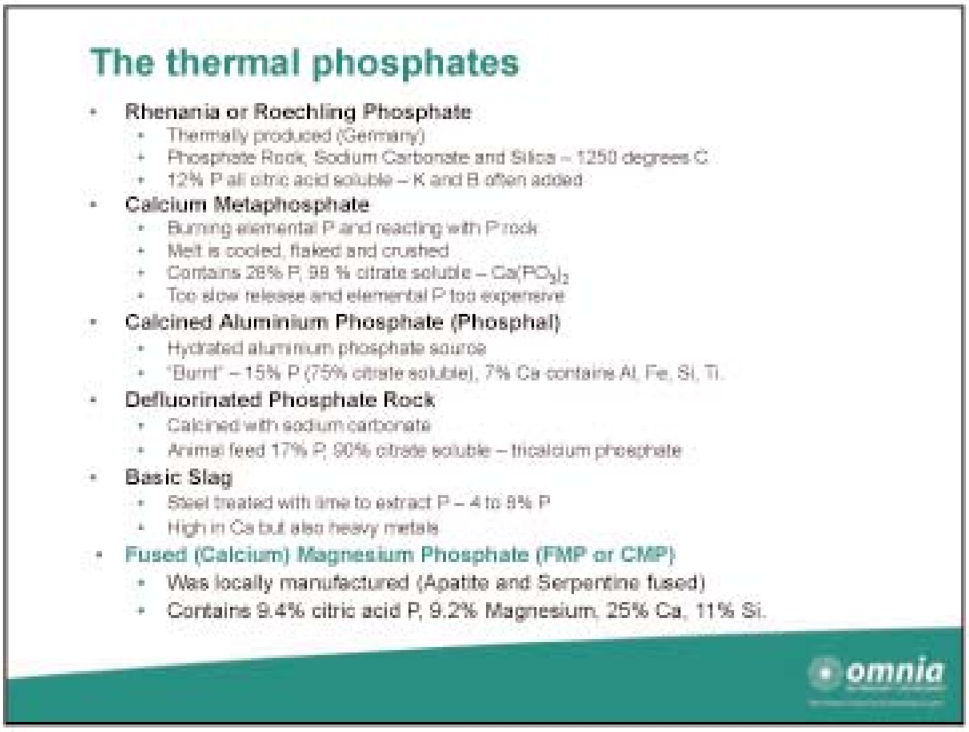
Other phosphates from phosphoric acid

- **Ammonium Phosphate Sulphate**
  - Ammonia plus phosphoric and sulphuric acid
  - Non hygroscopic and high S
- **Ammonium Phosphate Chloride**
  - MAP plus ammonium chloride
  - Cheap N source in Japan
- **Ammonium Phosphate Nitrate (APN)**
  - Ammoniation of nitric and phosphoric acids
- **Urea Ammonium Phosphate (UAP)**
  - Urea granulated with MAP or DAP
- **Urea Phosphate (18:19:0)**
  - Prill of urea with phosphoric acid
  - Very acid – for use in fertigation as NP source but mostly for acidification
- **Urea Superphosphate (USP)**
  - Urea and sulphuric acid form stable eutectic complexes
  - Dry and granulate – stores well
  - 5:1:0 = 20.9% N, 19.3% urea N, 1.6 Ammonium N, 4.4% P, 6% S
  - 95% water soluble
  - High agronomic effectiveness
- **Magnesium Ammonium Phosphate (MAGAMP)**
  - Usually by product from the ammoniation of phosphoric acid
  - Very insoluble – slow release in acid soils
- **Magnesium Potassium Phosphate**
  - Neutralization of phosphoric acid with magnesium oxide and potassium hydroxide
  - Not a usual fertilizer
- **Magnesium Phosphates**
  - Not commercial – mono, di and tri magnesium phosphates



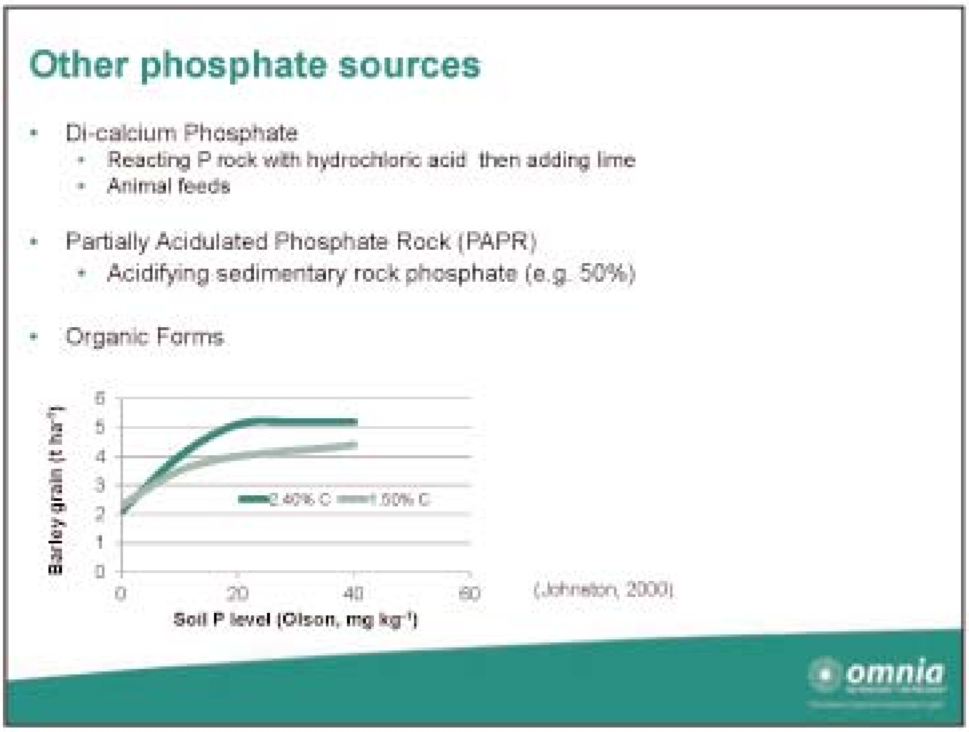
Potassium phosphates

- Made by reacting potassium oxide and carbonates with phosphoric acid
- Used as speciality fertilizers – mostly as fertigated or as foliar
- Mono Potassium Phosphate KH_2PO_4, 23% P, 28% K
- Dipotassium Phosphate K_2HPO_4, 18% P, 45 % K
- Tertra Potassium Pyrophosphate $K_4P_2O_7$, 19% P, 47% K
- Potassium Metaphosphate KPO_3, 26% P, 33% K



The thermal phosphates

- **Rhenania or Roechling Phosphate**
  - Thermally produced (Germany)
  - Phosphate Rock, Sodium Carbonate and Silica – 1250 degrees C
  - 12% P all citric acid soluble – K and B often added
- **Calcium Metaphosphate**
  - Burning elemental P and reacting with P rock
  - Melt is cooled, flaked and crushed
  - Contains 28% P, 98 % citrate soluble – $Ca(PO_3)_2$
  - Too slow release and elemental P too expensive
- **Calcined Aluminium Phosphate (Phosphal)**
  - Hydrated aluminium phosphate source
  - "Burnt" – 15% P (75% citrate soluble), 7% Ca contains Al, Fe, Si, Ti.
- **Defluorinated Phosphate Rock**
  - Calcined with sodium carbonate
  - Animal feed 17% P, 90% citrate soluble – tricalcium phosphate
- **Basic Slag**
  - Steel treated with lime to extract P – 4 to 8% P
  - High in Ca but also heavy metals
- **Fused (Calcium) Magnesium Phosphate (FMP or CMP)**
  - Was locally manufactured (Apatite and Serpentine fused)
  - Contains 9.4% citric acid P, 9.2% Magnesium, 25% Ca, 11% Si.

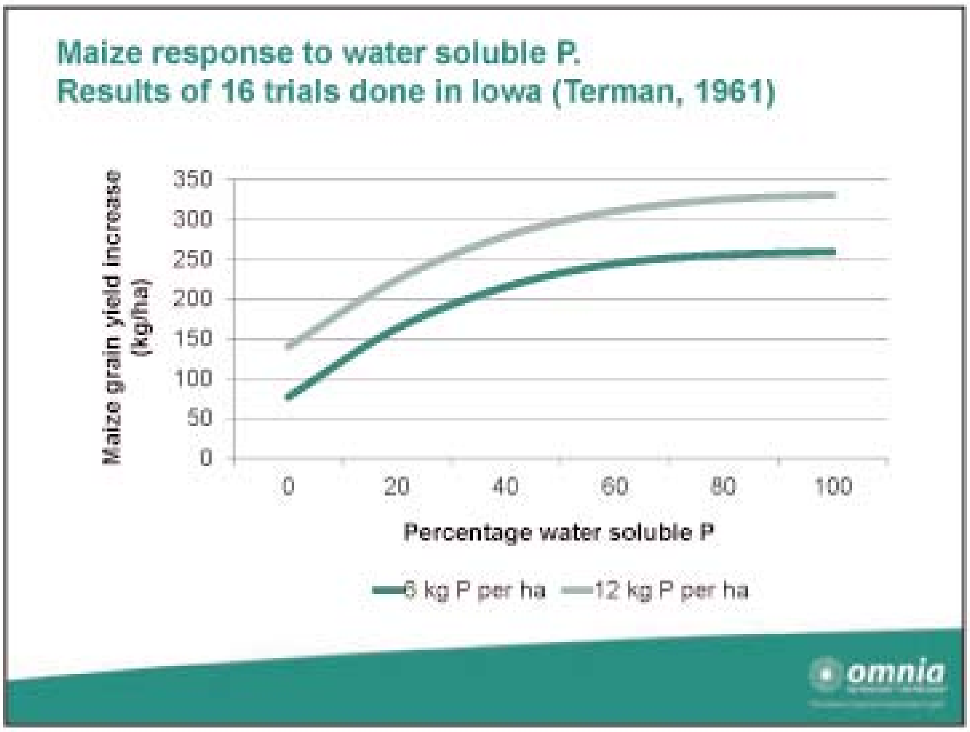


Other phosphate sources

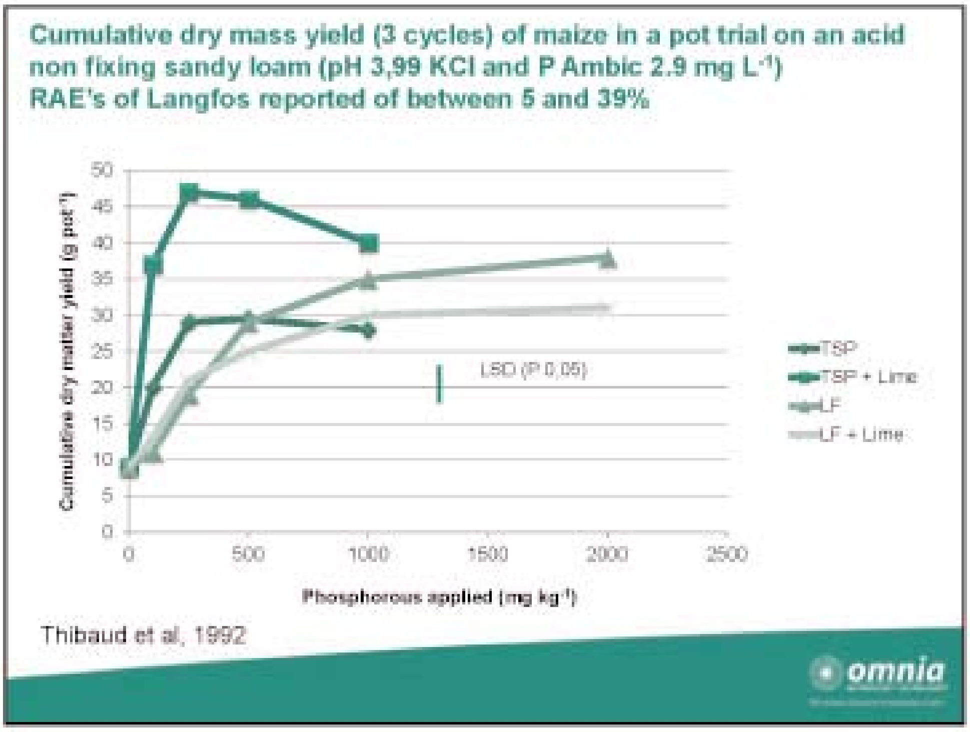
- Di-calcium Phosphate
  - Reacting P rock with hydrochloric acid then adding lime
  - Animal feeds
- Partially Acidulated Phosphate Rock (PAPR)
  - Acidifying sedimentary rock phosphate (e.g. 50%)
- Organic Forms

(Johnston, 2000)

The efficacy of prominent local commercially available fertilizer phosphates

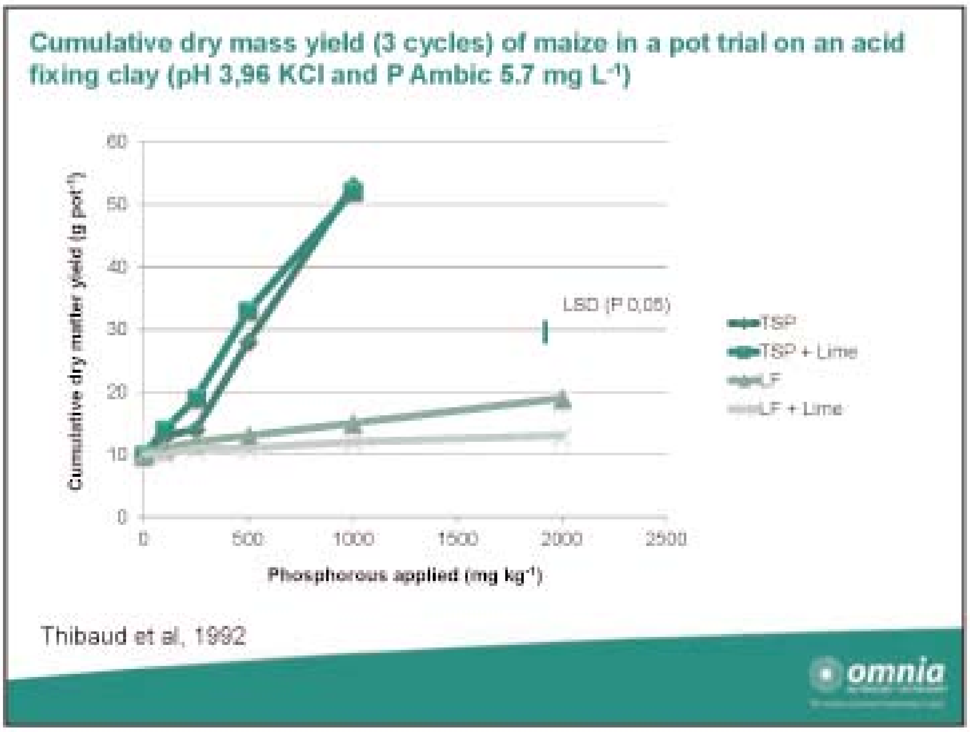


Maize response to water soluble P.
Results of 16 trials done in Iowa (Terman, 1961)



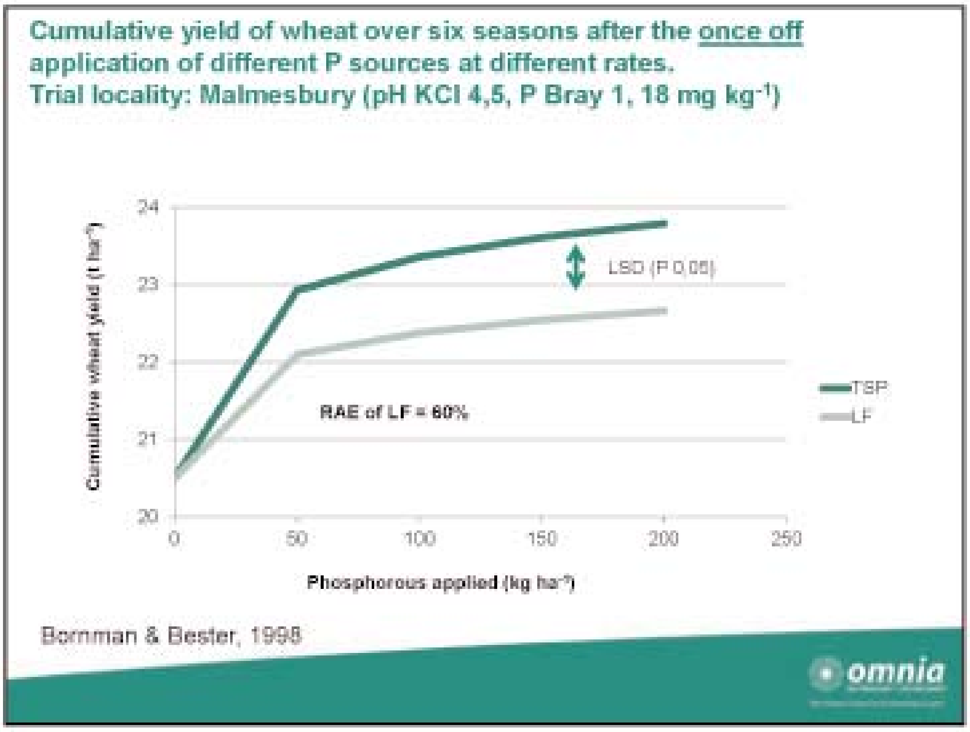
Cumulative dry mass yield (3 cycles) of maize in a pot trial on an acid non fixing sandy loam (pH 3,99 KCl and P Ambic 2.9 mg L^{-1}) RAE's of Langfos reported of between 5 and 39%

Thibaud et al, 1992



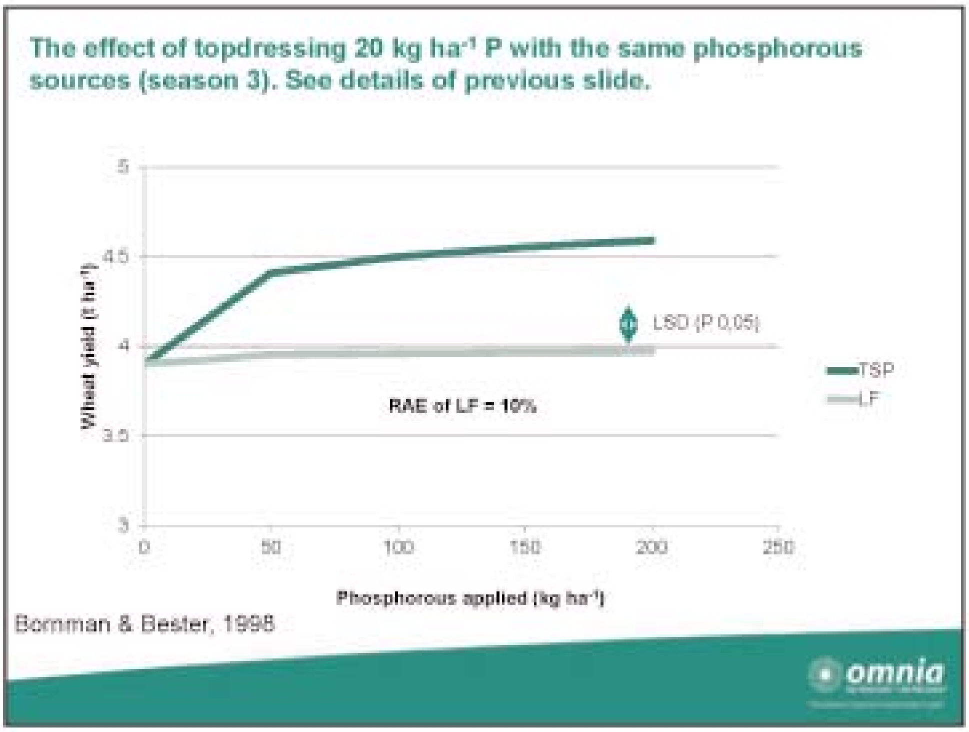
Cumulative dry mass yield (3 cycles) of maize in a pot trial on an acid fixing clay (pH 3,96 KCl and P Ambic 5.7 mg L^{-1})

Thibaud et al, 1992



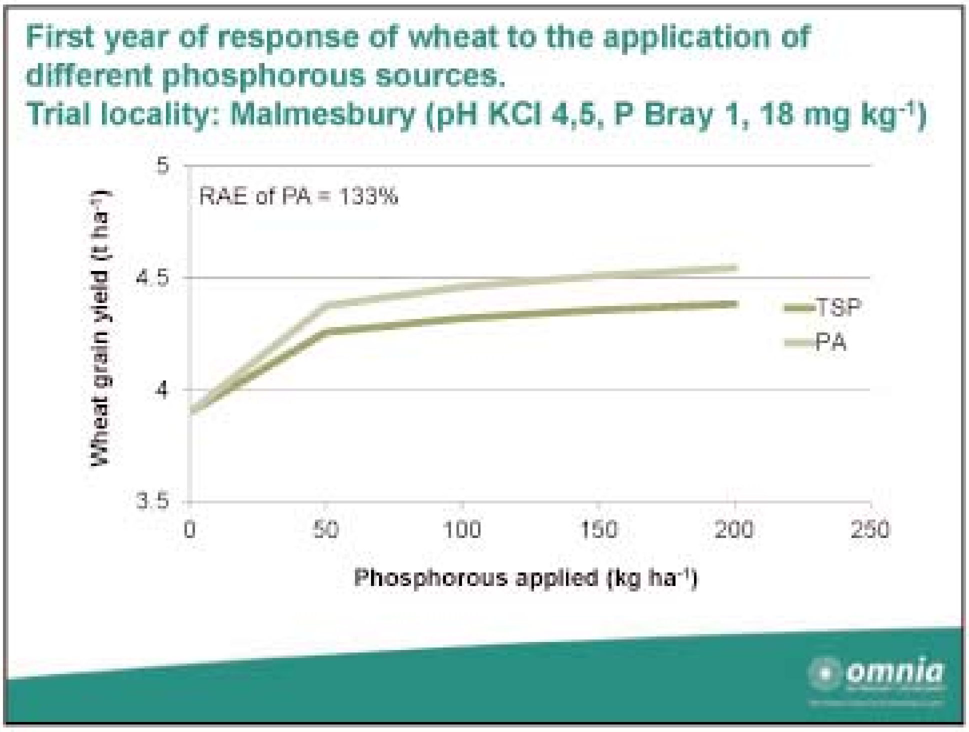
**Cumulative yield of wheat over six seasons after the once off application of different P sources at different rates.
Trial locality: Malmesbury (pH KCl 4,5, P Bray 1, 18 mg kg^{-1})**

Bornman & Bester, 1998

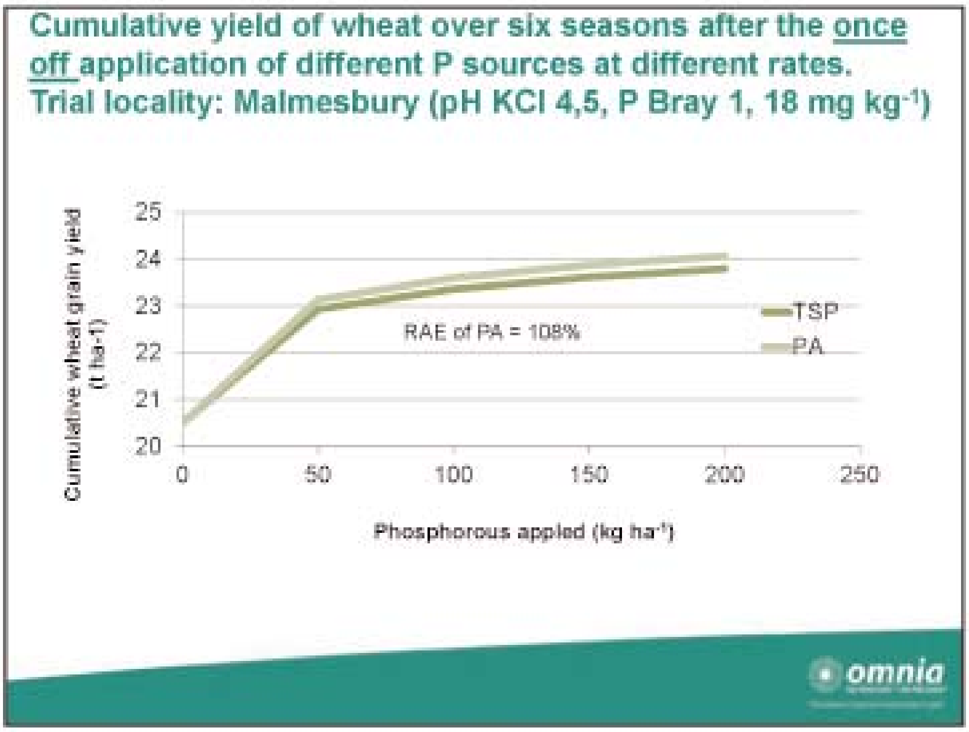


The effect of topdressing 20 kg ha^{-1} P with the same phosphorous sources (season 3). See details of previous slide.

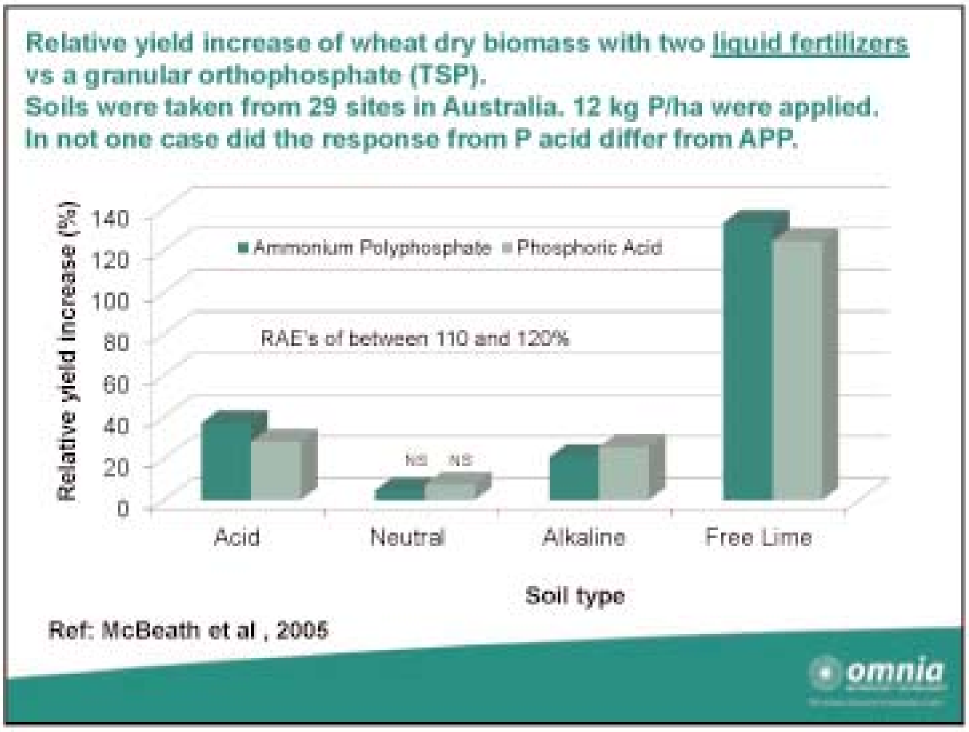
Bornman & Bester, 1998



First year of response of wheat to the application of different phosphorous sources. Trial locality: Malmesbury (pH KCl 4,5, P Bray 1, 18 mg kg^{-1})

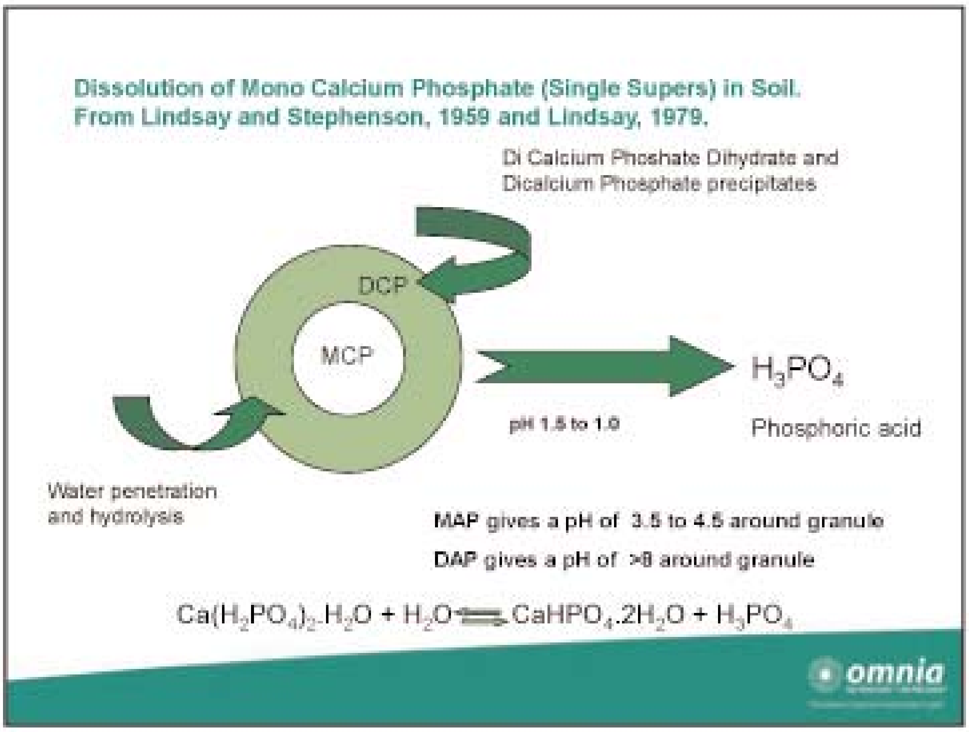


Cumulative yield of wheat over six seasons after the once off application of different P sources at different rates.
Trial locality: Malmesbury (pH KCl 4,5, P Bray 1, 18 mg kg^{-1})



Relative yield increase of wheat dry biomass with two liquid fertilizers vs a granular orthophosphate (TSP).
Soils were taken from 29 sites in Australia. 12 kg P/ha were applied.
In not one case did the response from P acid differ from APP.

Ref: McBeath et al , 2005



Dissolution of Mono Calcium Phosphate (Single Supers) in Soil.
From Lindsay and Stephenson, 1959 and Lindsay, 1979.

Di Calcium Phoshate Dihydrate and
Dicalcium Phosphate precipitates

H_3PO_4

Phosphoric acid

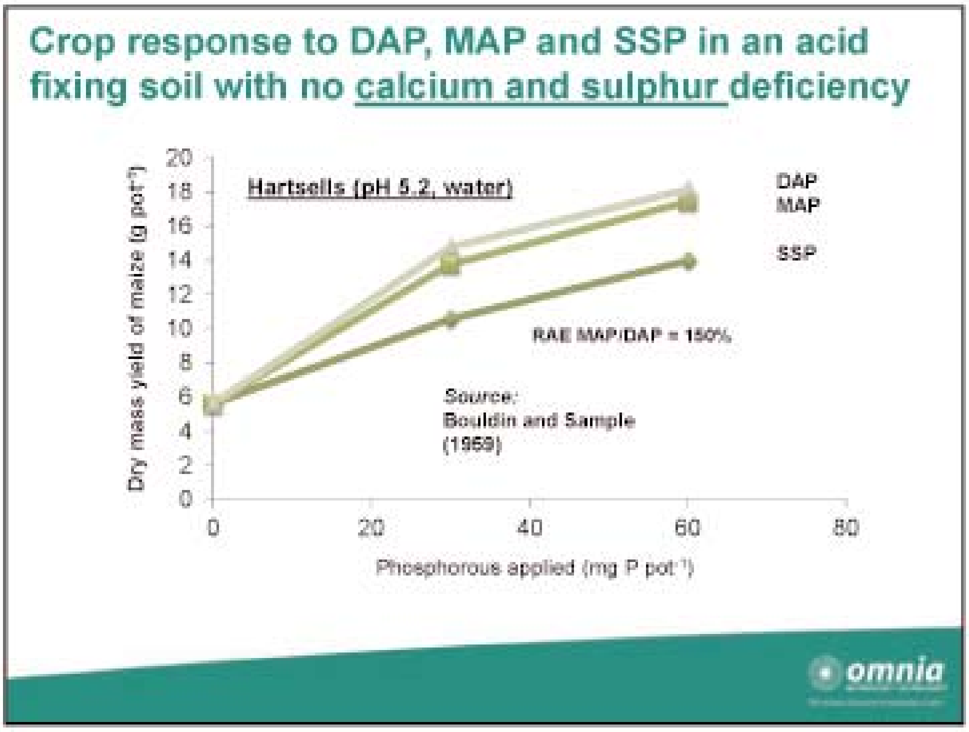
pH 1.5 to 1.0

Water penetration
and hydrolysis

MAP gives a pH of 3.5 to 4.5 around granule

DAP gives a pH of >8 around granule

$$Ca(H_2PO_4)_2.H_2O + H_2O \rightleftharpoons CaHPO_4.2H_2O + H_3PO_4$$



Crop response to DAP, MAP and SSP in an acid fixing soil with no calcium and sulphur deficiency

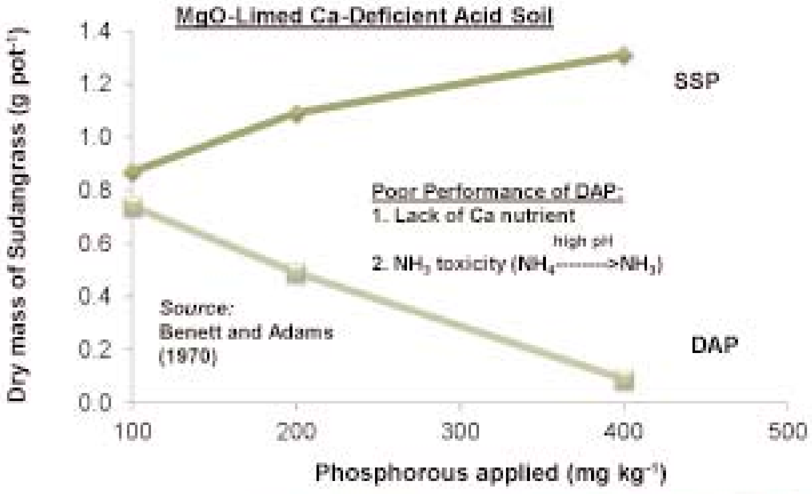
RAE MAP/DAP = 150%

Source:
Bouldin and Sample
(1959)

The efficiency of SSP in a sandy (2% clay) near neutral soil due to the presence of calcium and sulphur.

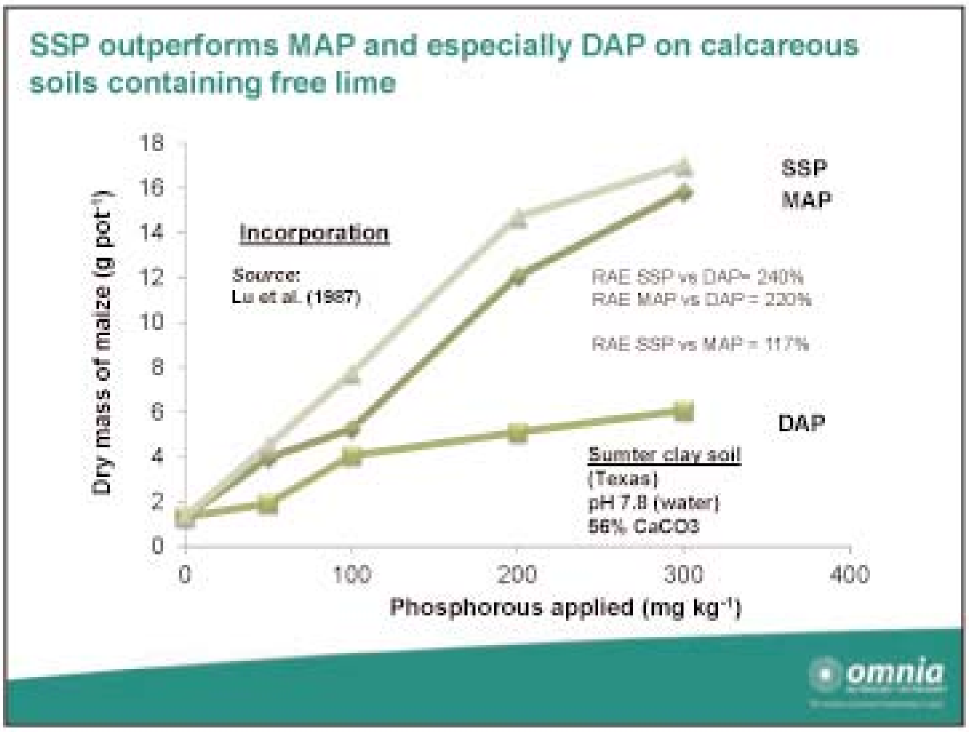
Ref: Khan et al, 2010

Response of Sudangrass to SSP and DAP in a calcium deficient soil.



Poor Performance of DAP:
1. Lack of Ca nutrient
2. NH_3 toxicity ($NH_4 \xrightarrow{\text{high pH}} NH_3$)

Source:
Benett and Adams
(1970)



SSP outperforms MAP and especially DAP on calcareous soils containing free lime

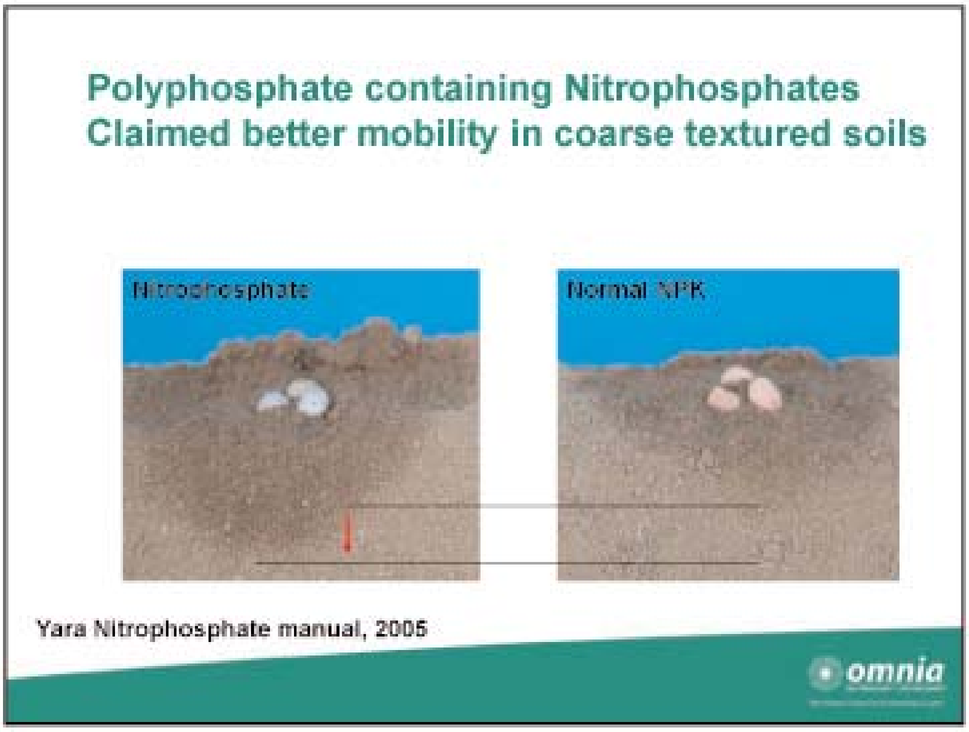
Incorporation

Source:
Lu et al. (1987)

RAE SSP vs DAP= 240%
RAE MAP vs DAP = 220%

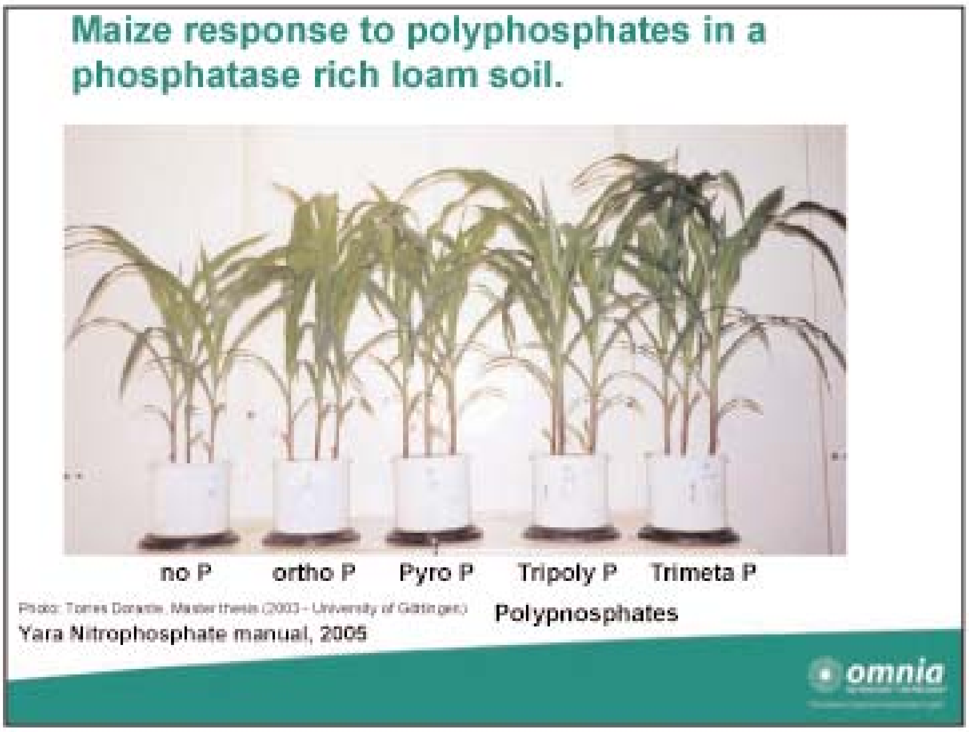
RAE SSP vs MAP = 117%

Sumter clay soil
(Texas)
pH 7.8 (water)
56% CaCO3



Polyphosphate containing Nitrophosphates Claimed better mobility in coarse textured soils

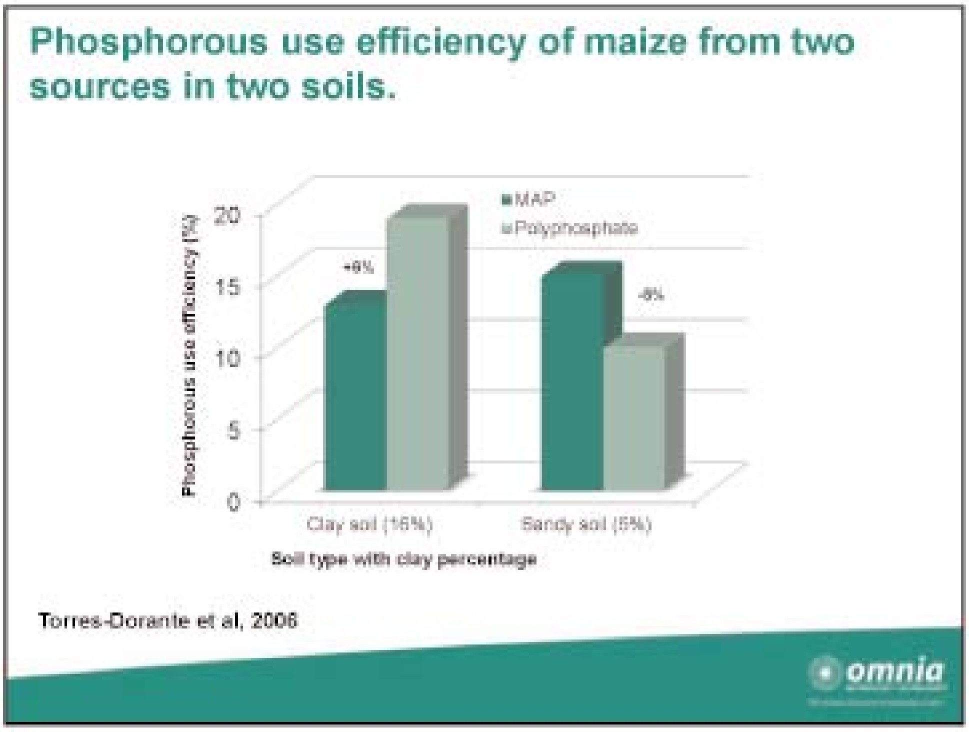
Yara Nitrophosphate manual, 2005



Maize response to polyphosphates in a phosphatase rich loam soil.

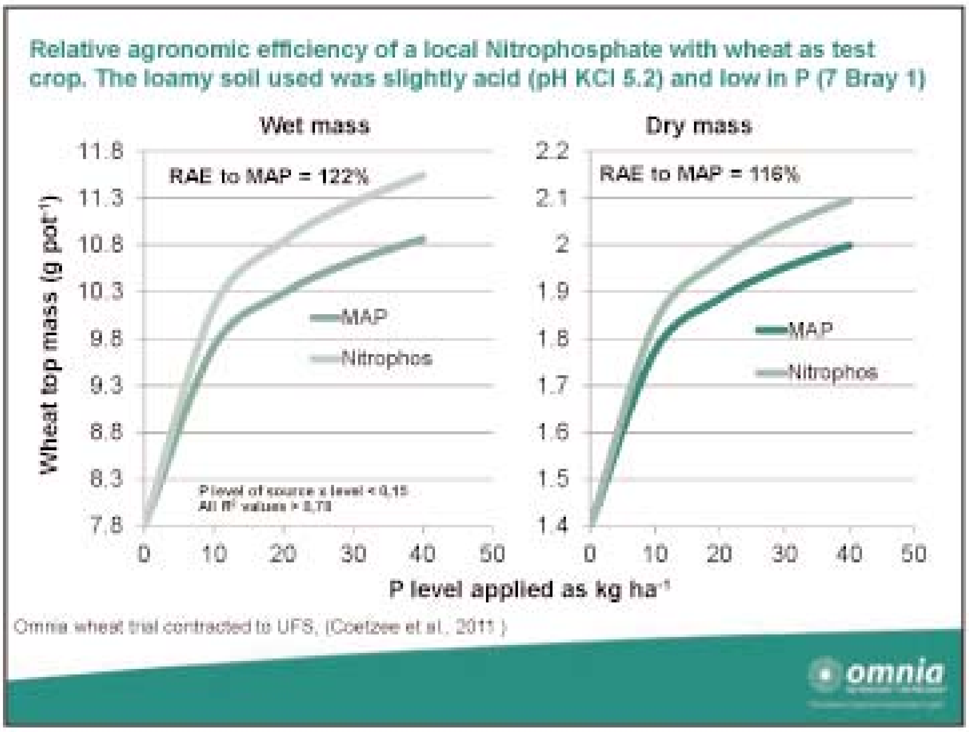
Photo: Torres Dorante, Master thesis (2003 - University of Göttingen)

Yara Nitrophosphate manual, 2005



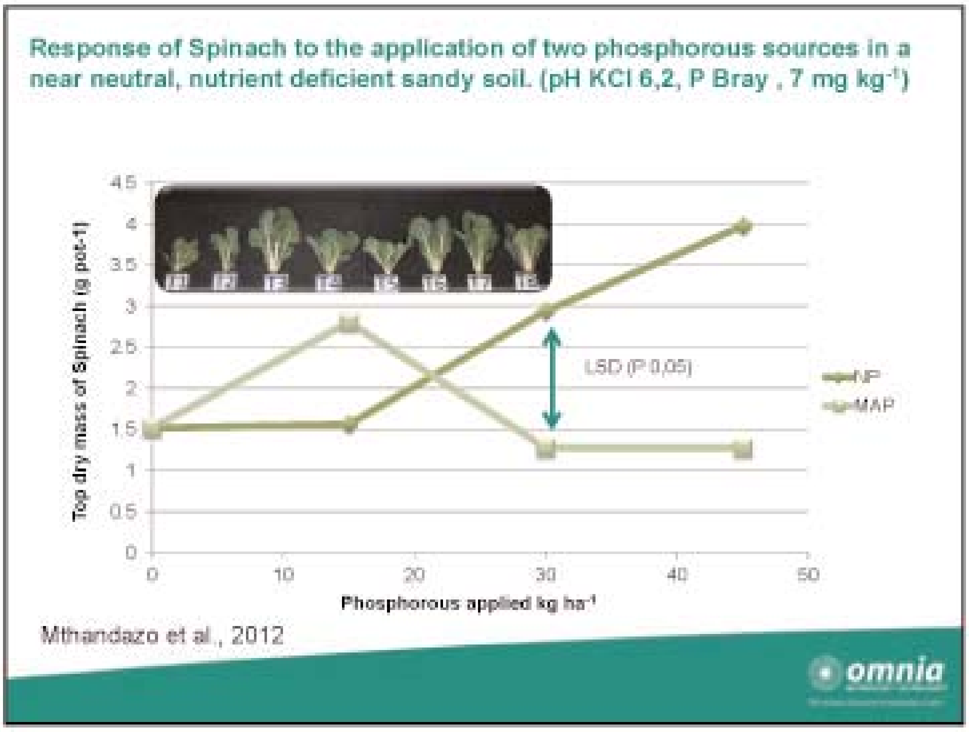
Phosphorous use efficiency of maize from two sources in two soils.

Torres-Dorante et al, 2006



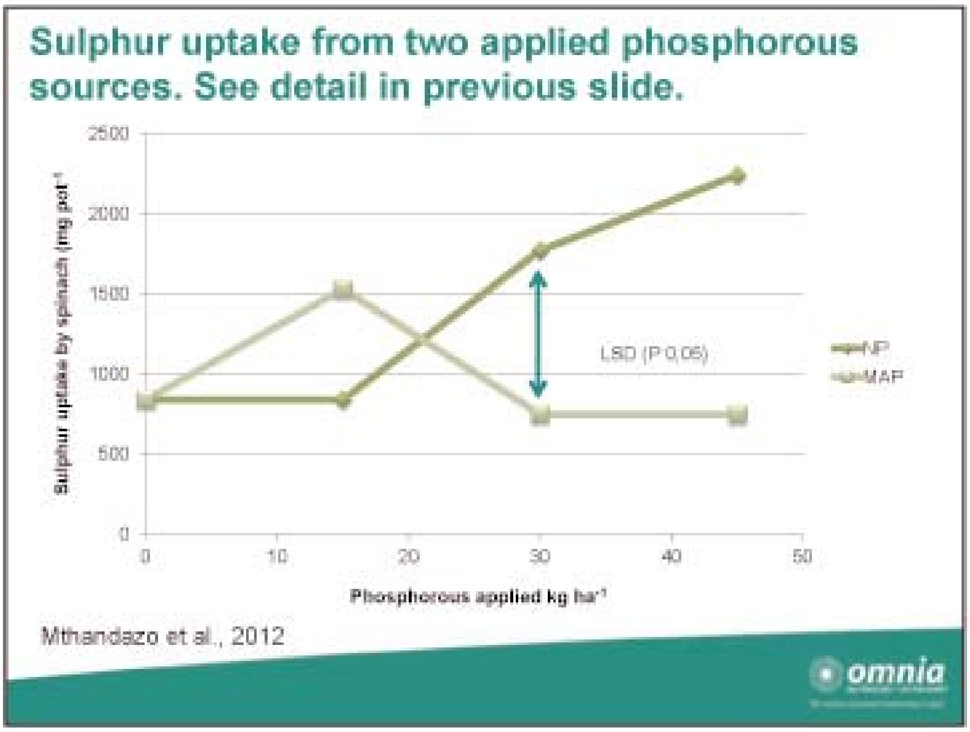
Relative agronomic efficiency of a local Nitrophosphate with wheat as test crop. The loamy soil used was slightly acid (pH KCl 5.2) and low in P (7 Bray 1)

Omnia wheat trial contracted to UFS, (Coetzee et al., 2011)



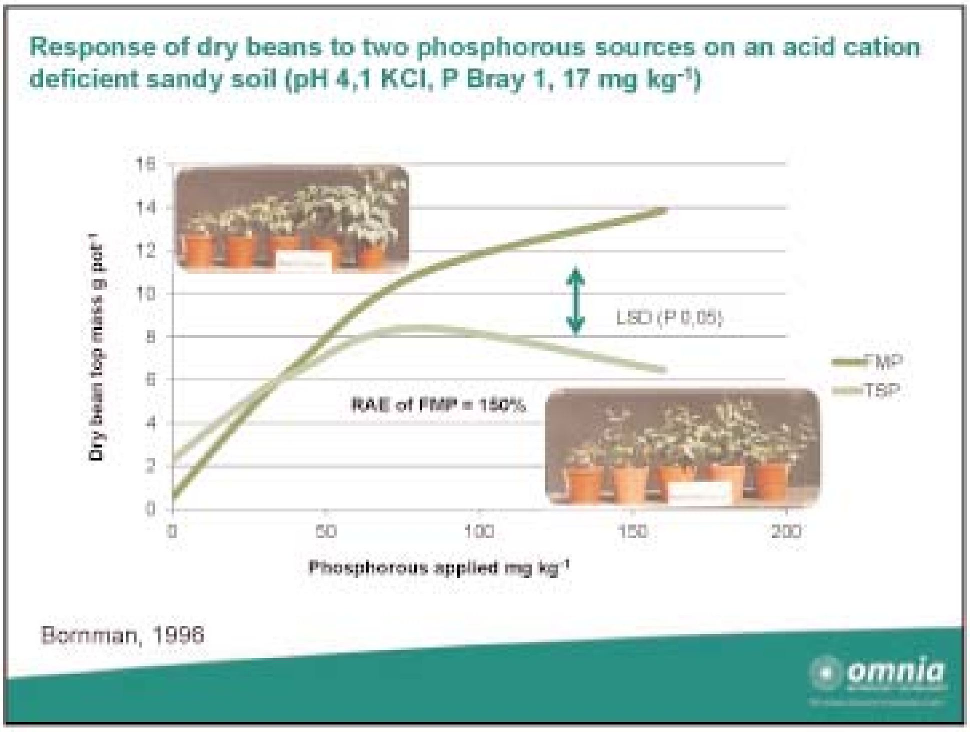
Response of Spinach to the application of two phosphorous sources in a near neutral, nutrient deficient sandy soil. (pH KCl 6,2, P Bray , 7 mg kg⁻¹)

Mthandazo et al., 2012



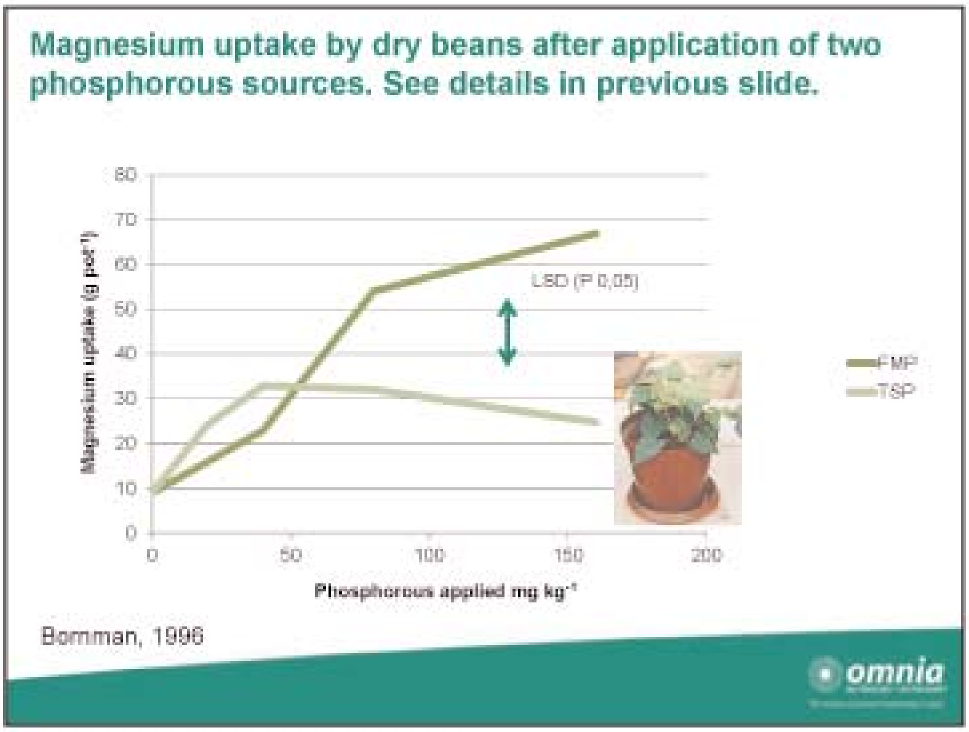
Sulphur uptake from two applied phosphorous sources. See detail in previous slide.

Mthandazo et al., 2012



Response of dry beans to two phosphorous sources on an acid cation deficient sandy soil (pH 4,1 KCl, P Bray 1, 17 mg kg⁻¹)

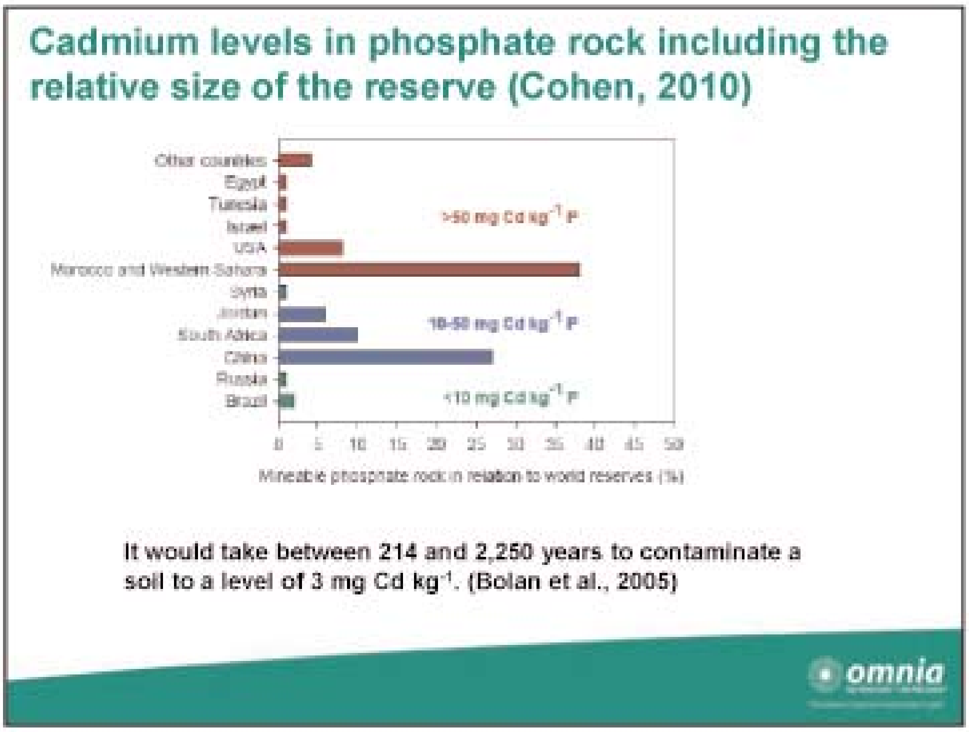
Bornman, 1998



Magnesium uptake by dry beans after application of two phosphorous sources. See details in previous slide.

Bornman, 1996

Environmental issues



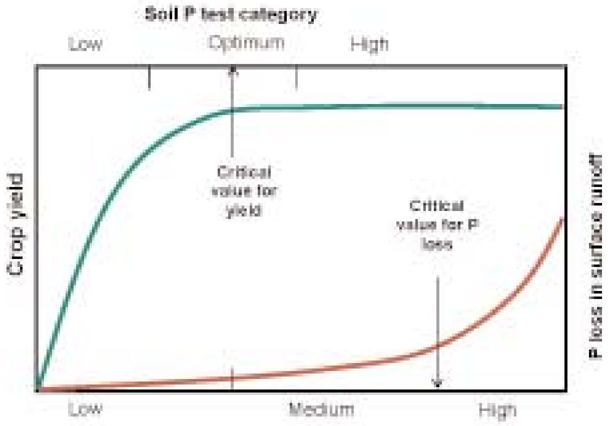
Cadmium levels in phosphate rock including the relative size of the reserve (Cohen, 2010)

It would take between 214 and 2,250 years to contaminate a soil to a level of 3 mg Cd kg^{-1}. (Bolan et al., 2005)

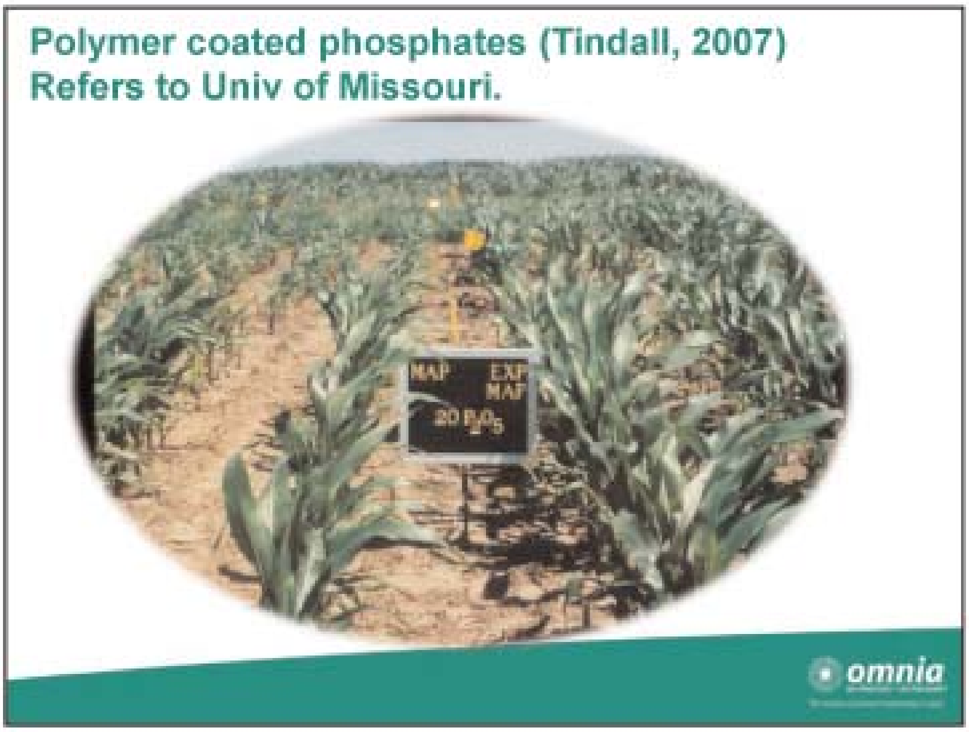
The danger of eutrophication

Cyanophycota

Maguire et al., 2005: Influence of soil test phosphate on crop yield and P loss in runoff.



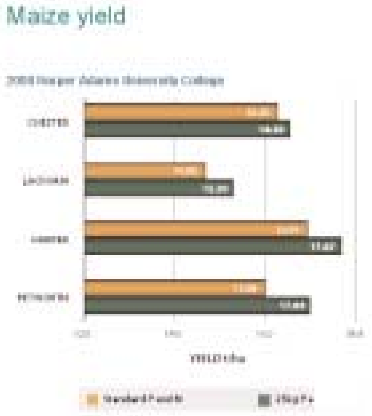
New developments



Polymer coated phosphates (Tindall, 2007)
Refers to Univ of Missouri.

Preventing fixation and enhancing efficiency
Private company web based advertisement

Private company web based advertisement


Maize yield

However, Karamanos & Puurveen, 2011 could find no beneficial effect

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End

POTASSIUM REQUIREMENTS AND SOIL ACIDITY MANAGEMENT FOR SUGARCANE

Neil Miles[1,2]

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INTRODUCTION

Sugarcane is an important crop on the eastern seaboard and lowveld of South Africa. The current area under production is estimated to be 378 000 hectares. Of considerable concern is evidence that production per unit area has during the past two to three decades either reached a plateau or declined. Similar trends have been reported in overseas countries, including Australia and the USA. This disturbing trend in crop productivity has led to an increased focus on the range of agronomic practices applied in the industry. In terms of crop nutrition, interrogation of soil test databases relating to sugarcane fields in South Africa reveals widespread potential limitations, and in particular excessive soil acidity, low levels of basic cations (Ca, Mg and K) and micronutrient (Zn and Cu) deficiencies (Van der Laan & Miles, 2010). This paper provides a cursory overview of the K nutrition of the sugarcane crop, together with soil acidity limitations and the management of soil acidification under sugarcane production.

POTASSIUM NUTRITION OF SUGARCANE

POTASSIUM IN THE PHYSIOLOGY OF SUGARCANE

Potassium (K) is the nutrient usually taken up in largest amounts by sugarcane. In the mature crop, about 45% of the K is in the leaves and trash, with the remainder being in the stem. Potassium is extremely mobile in the plant and redistributes rapidly from older leaves to newer ones.

Marschner (1995) has listed the numerous functions of K in plant growth. Of particular importance in terms of the sugarcane crop are its roles in photosynthetic processes, the translocation of sugars, water use efficiency, reduction in lodging and cold tolerance.

With K being mobile in the plant, deficiency symptoms appear in the older leaves initially. Symptoms include reddish spots in the central vein of the leaf and necrosis of leaf margins which gradually spread inwards over the leaf.

POTASSIUM REMOVALS, SOIL TESTS AND RECOMMENDATIONS

Data reported in the literature on the amounts of K removed in harvested stalks are characterized by considerable variability, with removals in a 100 t crop ranging between 53 and 343 kg of K (Table 1).

Table 1. Potassium removals in harvested stalks for specified yields.

Country	Stalk Yield (t)	Removal (kg K)	Reference
Australia	80	164	Wood & Schroeder, 2004
Brazil	100	53 - 256	Rosetto *et al*., 2008
Florida	103	343	Coale *et al*., 1993
India	100	280	Gopalasundaram *et al.*, 2011
South Africa	100	150	Meyer, Jan, *pers comm*.(2007)

Threshold topsoil K test levels have been determined in a number of investigations. In South African studies, Meyer and Wood (1985) found that on light-textured soils, responses could be expected when soil exchangeable K was below 125 mg/kg. However, on high base-status heavy textured soils a threshold of 225 mg/kg was indicated. Critical soil test levels established in trials on highly-weathered soils in Brazil, range from 47 to 91 mg/L (Orlando Filho, 1985; Rossetto *et al*., 2008). The Australian sugar industry has recently introduced a K recommendation system based on soil texture and exchangeable and non-exchangeable (slowly available) K levels (Schroeder *et al*., 2007).

A particular concern with respect to the application of critical soil test values as a basis for making recommendations is that there is generally little cognisance of potential subsoil K contributions to crop growth. Sugarcane is a deep-rooted crop and is able to extract nutrients from depths of up to a meter or more (Smith *et al*., 2005). In recent times, prohibitively low soil exchangeable K levels in many subsoils of the South African industry point to marked exploitation of subsoil K reserves by the crop. Conceivably, therefore, as subsoil K reserves are diminished with successive crops, higher topsoil thresholds may be appropriate in order to maintain production. It would seem that this largely overlooked aspect warrants attention in research programmes.

Potassium recommendations are generally based on soil tests and anticipated yields. Recommendations vary widely between countries. In South Africa, recommendations for low base status soils generally range between 100 and 200 kg K/ha, with a maximum of 250 kg K/ha for soils that are severely depleted in this nutrient. For high base status soils, up to 300 kg K/ha is recommended. For the calculation of maintenance recommendations in the absence of supporting soil test data, yield-related removal factors in the range 1.6 to 2.1 kg K/t cane are used. Field trials in Brazil have shown continuous responses up to rates of 166 kg K/ha; however, recommendations are generally in the range 110 to 120 kg K/ha (Rossetto *et al*., 2008). Recommendations for K in Reunion are closely related to anticipated yields, with the range being from 100 kg K/ha for a yield of 60 t of stalks to 232 kg K/ha for a yield of 140 t (Fillols & Chabalier, 2007). In Australia, for both plant and ratoon crops the maximum K recommended is 120 kg/ha (Schroeder *et al*., 2007).

A vexing problem in the management of K for ratoon crops is the likelihood of K applied on the soil surface being rendered ‘positionally unavailable’ in loam and clay soils when the surface soil is in a dry state. This is less of a concern in soils with <15% clay, where downward movement of K by leaching has been observed. In order to circumvent this problem some growers incorporate fertilizer by tillage operations; however, this implies extra costs, and in any event, is not possible on steep land.

Interestingly, the sustainability of K fertilization practices has been questioned in several studies. Wood and Schroeder (2004) investigated the K budget for the Australian industry over the period 1996 to 2000, and found a major disparity between the amount of K applied as fertilizer and that removed by the crop. These workers reported that whereas an average of 1.5 kg of K was removed per ton of stalks harvested (this figure takes into account returns from cane trash and tops), only 0.89 kg K/t was applied in fertilizers. They concluded that “ongoing under-application of K …… is a major cause for concern”. In a trial spanning a plant and 10 ratoon crops at Pongola, South Africa, it was found that an application of 110 kg K/crop was insufficient to maintain soil exchangeable K levels, with soil K declining steadily with increasing ratoons (Meyer & Wood, 1985). Further evidence of under-fertilization with K in the South African industry is contained in a recent report on soil test levels in samples submitted by growers (van der Laan & Miles, 2010). It was found that on sands and loams, 30 to 40% of samples were deficient in K. There is, in fact, mounting evidence in this industry of unbalanced use of P and K, with many topsoils having higher P than K soil test levels.

LEAF ANALYSIS

Considerable research has been conducted into the use of leaf analysis as an aid in the management of the nutrition of sugarcane. Generally the central portion of the top visible dewlap leaf is used for foliar analysis purposes. Published adequate levels for K range from 1.05% to 2.0% (Malavolta, 1994; Fageria *et al*., 2011).

In a recent review of the use of foliar analysis in sugarcane, Miles (2010) drew attention to the impacts of variety, crop age and moisture stress on leaf nutrient concentrations, and the potential for incorrect interpretations where these factors are not taken into account. Furthermore, attention was drawn to the following aspects which impact on the interpretive process in the case of foliar K data:

- Nitrogen (N) has been found to promote the uptake of phosphorus (P), potassium (K) and sulphur (S), and possibly other nutrients as well. Consequently, reliable interpretation of sufficiency levels of these nutrients in the leaf is possible only where N concentrations are non-limiting.

- Marked seasonal effects on leaf K concentrations create particular difficulties in the interpretation of leaf K data. Indications are that in the South African industry, in both irrigated and rainfed sugarcane, only samples taken in the January to March period are likely to provide K values that are a reliable reflection of the adequacy of K supply to the crop.

POTASSIUM AND CROP QUALITY

The effect of K supply on the sucrose content of sugarcane has over the years received considerable attention. Varying trends have emerged from trials, and the reviews of Orlando Filho (1985), Meyer and Wood (2001) and Rossetto *et al*. (2008) conclude that K supply has no consistent effect on the accumulation of sucrose in the crop. Interestingly, Stewart (1969) found that on a soil with very low K levels, the depression in sucrose resulting from heavy applications of N could be arrested by applications of K.

Of concern, in terms of sucrose recovery, is the evidence that high K levels in juice decrease crystal yield and have a negative effect on the colour of refined sugar (Orlando Filho, 1985; Meyer & Wood, 2001).

SOIL ACIDITY AND ITS MANAGEMENT

THE NATURE OF THE SOIL ACIDITY PROBLEM

Under high rainfall regimes, soils acidify naturally over long periods of time due mainly to the action of percolating rainwater in which CO_2 is dissolved to form carbonic acid. In agricultural systems the major causes of soil acidification are N fertilizers containing or producing NH_4^+, the removal of bases in harvested products, and accelerated organic matter mineralization accompanying tillage operations.

It is well-established that for most crops, low soil pH *per se* does not pose a limitation for plant growth (Sumner & Yamada, 2002); rather, it is the chemical and sometimes biological factors associated with low pH which limit plant growth. These factors fall into four broad categories: metal toxicities, nutrient deficiencies, reduced cation exchange capacity (CEC) and reduced or modified biological activity.

Metal toxicities

As soil pH values drop below about 4.5 in 0.01 *M* $CaCl_2$ (about pH 5.2 in water), Al dissociates from the edges of clay minerals and aluminium oxides and hydroxides, and its solubility in the soil solution increases sharply (Figure 1). High levels of exchangeable and soluble Al, coupled with limited availability of cationic nutrients (Ca, Mg, K), are conditions that are inimical to root growth and function.

In soils with high levels of manganese oxides, Mn toxicities may also pose a limitation in acid soils. Where Mn toxicities occur in South Africa, they tend to be restricted largely to soils that have acidified anthropogenically (Dr. Alan Manson, *pers. comm.*).

Nutrient deficiencies

Severe deficiencies of macro and micro-nutrients frequently occur in acid soils, and in particular in those in which acidity is natural and not induced by farming practices. Phosphorus deficiency and high P fixation are frequent problems on highly-weathered Oxisols and Ultisols, and the correction of P problems invariably poses particular challenges from an economic perspective.

Deficiencies of S and micronutrients, in particular Zn and Mo, are widespread in acid soils. In the case of Mo, the deficiency is usually pH-induced, with supplies of this nutrient becoming more favourable following the elevation of pH by liming.

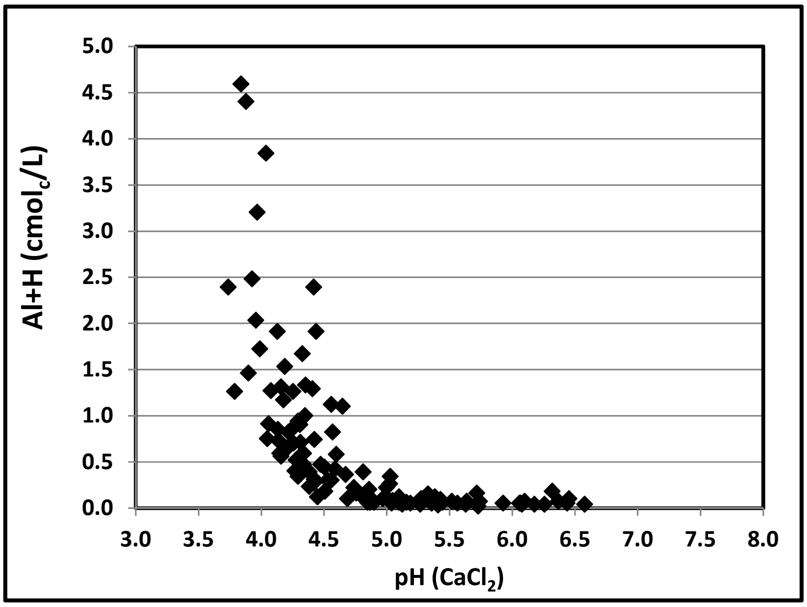

Figure 1. Relationship between pH ($CaCl_2$) and exchangeable Al+H in soils of the South African sugar industry.

A widespread deficiency on naturally acid soils is that of Si. Soil profiles with very low reserves of plant-available Si are the end result of desilication arising from the combined effects of weathering and leaching in high rainfall environments. Silicon is of particular importance to the sugarcane crop, with it being linked to yield responses (Korndörfer & Lepsch, 2001) and improved resistance to the stalk borer, *Eldana saccharina* (Keeping & Meyer, 2006).

Reduced cation exchange capacity

An oft overlooked factor in the soil acidity conundrum is the sharp reduction in CEC with decreasing soil pH. This is illustrated in Table 2 for a Griffin soil (Ultisol) treated with increasing rates of calcium hydroxide. Raising pH from 4.23 to 5.90 resulted in a three-fold increase in effective cation exchange capacity (ECEC).

Although on higher clay soils, as in the example presented in Table 2, the impact of acidity on exchange capacity is possibly of limited practical consequence, in sandy soils the low CEC under acid conditions limits the retention of the cationic nutrients, Ca, Mg and K (Sumner, 1997), with potential consequences for crop growth. Fox *et al*. (1991) present striking data on the impact of lime on retarding K leaching in a highly weathered Hawaiian soil. There is mounting evidence that the low CEC's on sandy, low organic matter soils are a growth limiting factor over large areas of the sugar industry in South Africa.

Biological activity

As soils acidify, both the activity and composition of the soil biota are modified. Fageria and Baligar (2008) note that in acid soils the activities of beneficial bacteria and mycorrhizal fungi are suppressed, while Syers and Springett (1984) found that earthworm populations diminish under acid soil conditions, and rapidly increase following liming. Evidence of the latter is in the form of often vastly increased mole activity in limed fields. Further visible evidence of reduced biological activity under acid soil conditions is the slow rate of decomposition of surface residues.

Table 2. Variations in chemical properties of a Griffin soil (Ultisol; 60% clay) following treatment with increasing amounts of calcium hydroxide.

Soil pH ($CaCl_2$)	Ca	Al+H	ECEC	Acid Sat
	----- mg/L -----	------------ cmol$_c$ /L -------------		%
4.23	591	2.34	6.08	38.3
4.85	1608	0.35	9.21	3.5
5.90	3236	0.21	16.97	1.0

THE OCCURRENCE OF ACID SOILS IN THE SOUTH AFRICAN SUGAR INDUSTRY

Excessive soil acidity is confined largely to the coastal and inland higher rainfall areas of the KwaZulu-Natal province. Affected soils include both those that are naturally acidic and those acidified by long-term agricultural practices. Of particular concern is mounting evidence of severe subsoil acidity and associated Ca deficiencies in many sugarcane fields in KwaZulu-Natal. Data from a soil profile in the Stanger area (Table 3) provide fairly typical evidence of the nature and severity of this problem. Figure 2 shows the restricted rooting resulting from the chemical and nutritional limitations in the same subsoil. Clearly, lack of accessibility to subsoil moisture and nutrient reserves as a result of poor rooting has major implications in terms of crop yields and the profitability of operations.

Table 3. Selected properties of the soil profile of a sugarcane field in the Stanger area of KwaZulu-Natal.

Depth	pH ($CaCl_2$)	P (Truog)	K	Ca	Mg	Al+H	Acid Sat	Zn	Si	Clay
cm		------------------ mg L^{-1} --------------------				cmol$_c$ L^{-1}	%	----- mg L^{-1} ------		%
0 – 20	3.73	29	57	104	20	1.74	66.7	0.06	1.9	15
20 – 40	3.65	17	26	69	12	2.41	81.7	0.28	2.2	17
40 – 60	3.71	5	22	51	10	2.74	86.4	0.34	3.9	21
60 - 80	3.84	3	23	68	8	1.76	78.6	0.01	3.4	19

RESPONSES OF SUGARCANE TO LIME AND GYPSUM

Sugarcane responses to lime on acid soils have been studied in numerous greenhouse and field trials in South Africa and overseas. A common finding from these studies is that although significant yield responses usually occur, sugarcane's tolerance of soil acidity far exceeds that of other row crops such as maize and soybean.

Meyer (1970) reported massive yield increases in cane growing on soils where wattle brush had been burnt, compared to the surrounding area. Greenhouse studies aimed at elucidating the factors implicated in this response showed that yields were optimised at pH_w of 5.2 to 5.5. In that pH range, exchangeable Al was reduced to very low levels. A noteworthy finding of the study was that with increasing exchangeable Al in the soil, root growth of sugarcane was decreased significantly more than top growth.

Figure 2. Sugarcane root development in a field near Stanger (soil properties of the profile are listed in Table 3).

In field trials on a Clovelly soil (pHw = 4.8, Ca = 104 mg/kg), Moberly (1974) applied 5.6 t/ha of dolomitic lime and reported yield responses in the plant and first two ratoon crops of 29%, 22% and 45%, respectively. In field trials spanning plant crops and numerous ratoons on severely acid humic soils in the KwaZulu-Natal midlands and south coast, Nixon *et al*. (2003) noted that the variety N12 was more tolerant of soil acidity than the varieties N16 and NCo376. Responses in the trials ranged from 5 to 39% (Table 4). In trials on three soils in Australia with lime rates of 10 to 15 t/ha, Quinan and Wood (1989) measured yield responses (four to five crops) of 17 to 25%.

A noteworthy finding in both Australian and South African research is that the magnitude of responses to soil acidity ameliorants generally increases with age of ratoons, particularly at higher application rates (Quinan & Wood, 1989; Mallawaarachchi *et al*., 1998; Noble & Hurney, 2000; Nixon *et al*., 2003). Data presented in Figure 3 clearly illustrate this effect. In that trial there was essentially no response to lime applications in the plant and first ratoon crops, but massive responses in subsequent ratoons. Acidity build-up with successive cropping no doubt contributes to this pattern of response. In terms of the longevity of lime effects, Noble and Hurney (2000) reported that significant increases in sugarcane yields were still being recorded 18 years after a single application of 5 t/ha of lime. In that study, the 5 t/ha of lime resulted in approximately 366 t of additional cane relative to the unlimed treatment over the 18 year period, thereby implying a huge economic benefit from liming.

Table 4. Responses of sugarcane varieties to lime and gypsum in trials at Paddock (plant + 5 ratoons) and Dalton (plant + 4 ratoons). Pre-treatment soil properties at Paddock (clay = 26%) pHw = 4.4 and Al saturation = 80%; Dalton (clay = 59%) pHw = 4.2 and Al saturation = 84% (Nixon *et al*., 2003)

Variety	Paddock (14 t lime/ha)	Dalton (10 t lime/ha)	Dalton (5 t lime + 5 t gypsum)
	---------- % sucrose yield response relative to control ---------		
N12	14.6	4.8	10.7
N16	32.2	32.8	39.0
NC0376	28.5	-	-

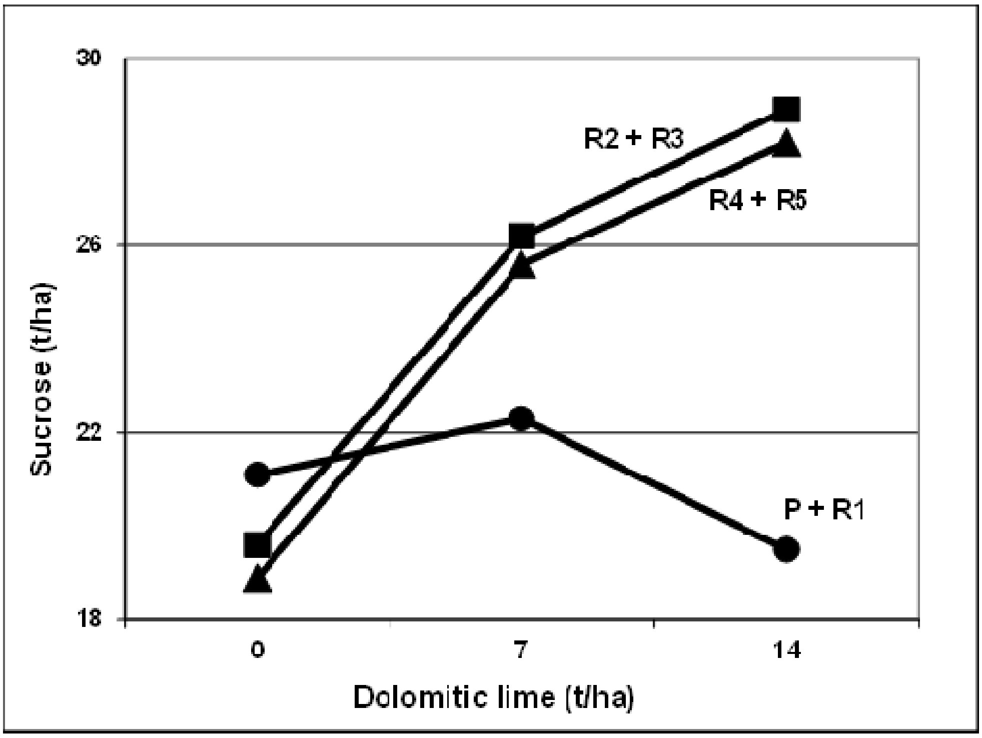

Figure 3. Responses of sugarcane variety NCo376 to lime at Paddock (P+R1 = plant + 1st ratoon, R2+R3 = 2nd + 3rd ratoons, R4+R5 = 4th + 5th ratoons). Pre-treatment soil properties are listed in Table 4 (Nixon **et al*****., 2003).***

Both Brazilian and South African research has shown that the best yields are obtained from combinations of gypsum and lime (Table 4; Nixon *et al*, 2003; Sumner 2012). In a recent review of Brazilian research data (Sumner, 2012), cane yield responses to combinations of lime and gypsum were found to range between 5 and 53%. Brazilian work has clearly demonstrated the benefits of gypsum in promoting root development throughout the soil profile, and thereby increasing available moisture for crop growth.

CURRENT RECOMMENDATIONS FOR THE MANAGEMENT OF SOIL ACIDITY

The remarkable tolerance of sugarcane to acid soil conditions has, both in South Africa and overseas (Mallawaarachchi *et al*., 1998), proved a barrier to the adoption of appropriate ameliorative practices. However, in this country anecdotal evidence of very profitable responses to heavy applications of lime and gypsum by some leading farmers, coupled with an increasing emphasis by scientists and extensionists on the deleterious effects of acidity, have served to engender widespread interest in the more rigorous management of soil acidity problems.

A major consideration in the management of soil acidity under sugarcane is that once established, the crop typically is in production for some 10 to 20 years before it is eradicated and re-established. Thus the opportunity for thorough incorporation of amendments by tillage presents itself only once every 10 to 20 years. In South Africa, current recommendations for the lime and gypsum incorporated prior to the planting of a new crop are therefore tailored to accommodate the re-acidification which inevitably occurs during the long cropping cycle. Lime recommendations are calculated to reduce topsoil acid saturation levels to 20% (base saturation = 80%). Additional criteria used include minimum thresholds for topsoil Ca and Mg of 300 mg/L and 50 mg/L, respectively. The maximum recommendation for lime is 14 t/ha.

The importance of adequate reserves of Ca and Mg for crop and, in particular, root growth has repeatedly emerged in soil acidity studies. Kingston (2000) reports that the minimum soil threshold for Ca is 200 mg/kg. Brazilian studies suggest that the critical soil Ca level for maximum production is in the range 140 to 250 mg/L (Quaggio & van Raij, 2008). A critical soil Ca level of 300 mg/kg is applied in the Australian sugar industry (Schroeder *et al*., 2007).

In South Africa, gypsum requirements for addressing subsoil acidity problems are based on clay content and mean subsoil acid saturation levels. The maximum gypsum recommendation for soils with <15% clay is 3 t/ha, while on higher clay soils rates of up to 7 t/ha are recommended.

CONCLUSIONS

Sugarcane has a high demand for K. This macro-nutrient plays an essential role in numerous physiological processes in the crop, and adequate supplies of K are crucial for sustainable and profitable production. Estimates of crop removals vary enormously between sugar-growing areas of the world, as do recommendations for K. There is convincing evidence from Australia and South Africa that current K fertilization practices do not compensate for crop removals, and this could be a contributory factor to yield declines in these industries.

Management practices associated with the production of sugarcane, in particular the use of nitrogenous fertilizers and the removal of bases in harvested stalks, result in the acidification of the soils on which the crop is grown. Although sugarcane is tolerant of acid soil conditions, in many areas, severe top and subsoil acidity and associated deficiencies of Ca and Mg pose limitations to crop growth, and highly profitable responses to lime and gypsum applications have been widely reported. Evidence from long-term field trials suggests that relatively high lime and gypsum applications at planting greatly benefit production in advanced ratoons.

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Potassium requirements and soil acidity management for sugarcane

FSSA Conference

August 2012, Pretoria

Neil Miles

UNLOCKING THE POTENTIAL OF SUGARCANE

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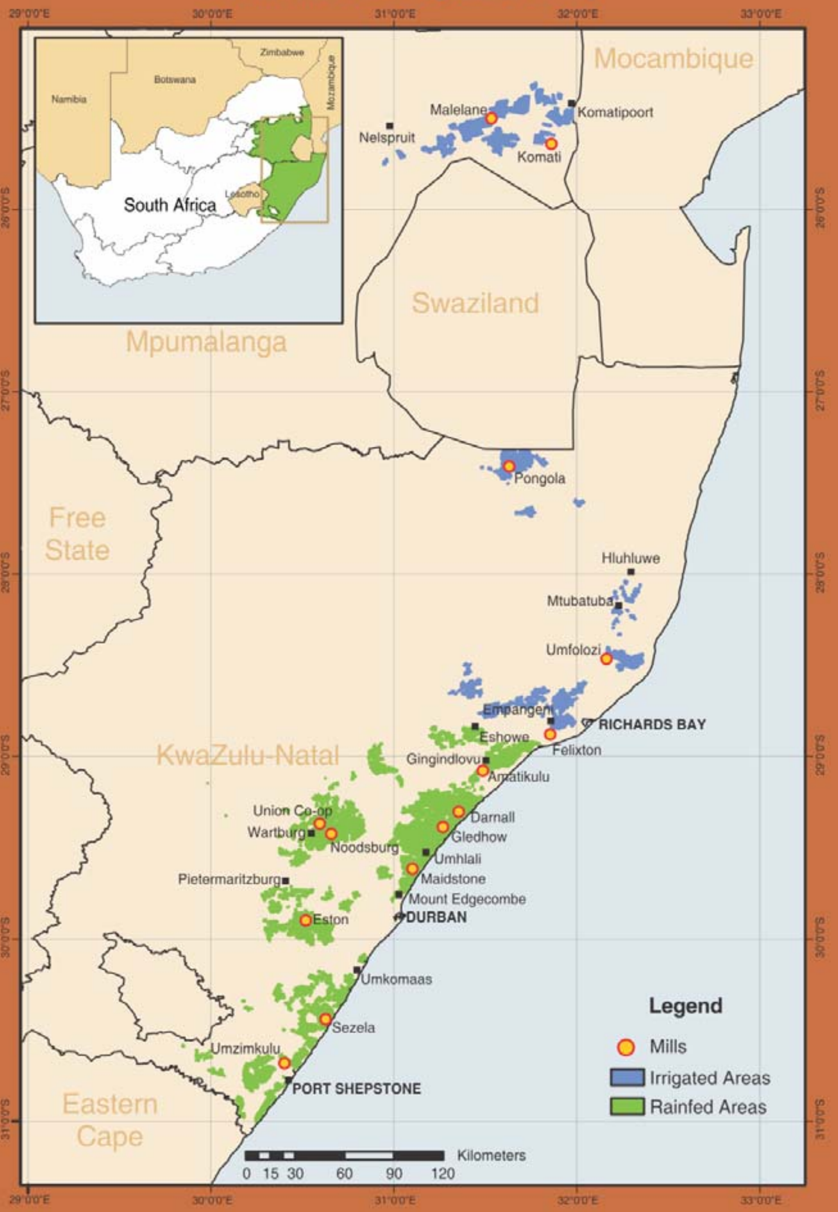
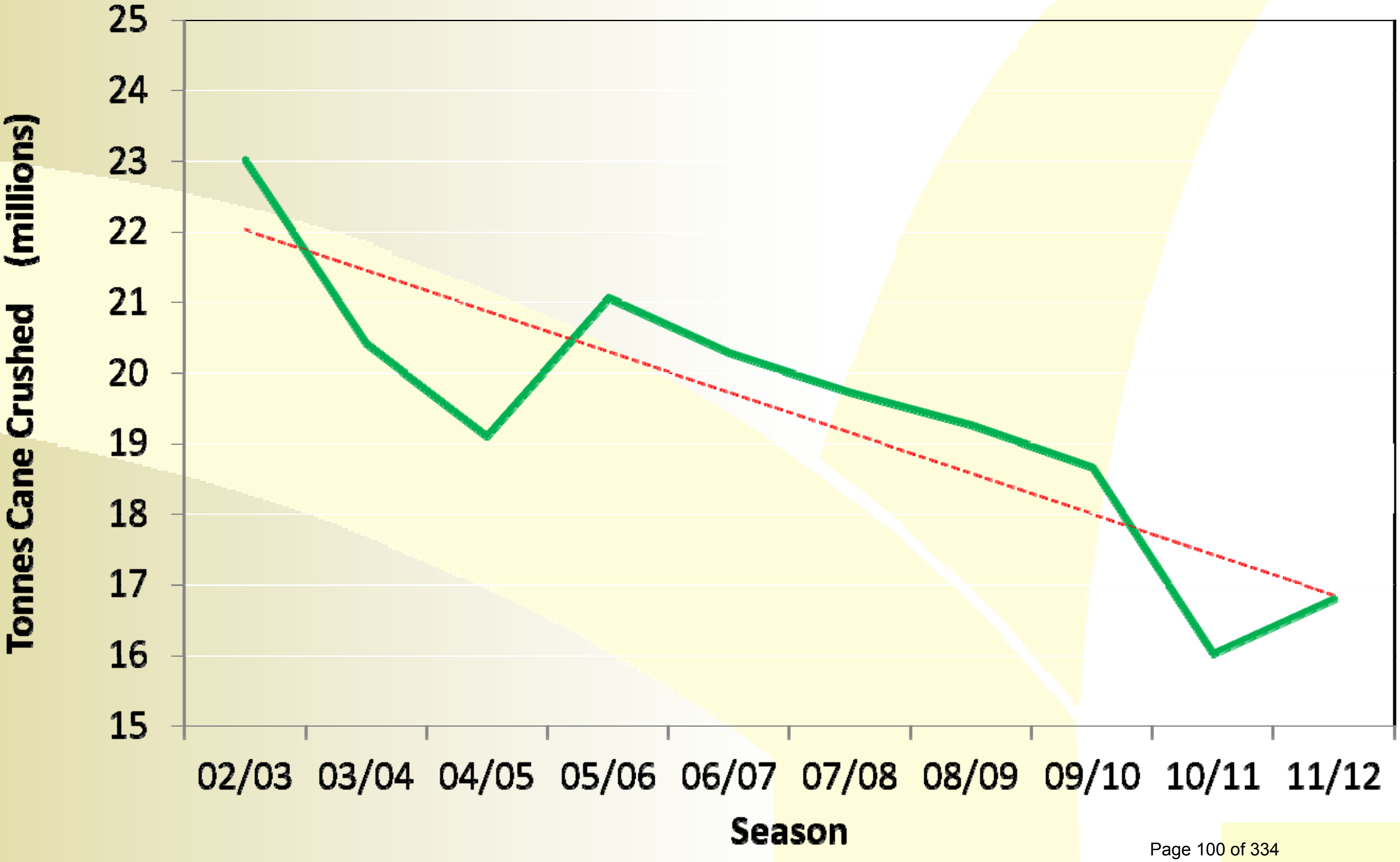
South African Sugar Industry



Trend in production in SA?

Crop Size (SA)


Tonnes Cane Crushed (millions)
25
24
23
22
21
20
19
18
17
16
15
02/03
03/04
04/05
05/06
06/07
07/08
08/09
09/10
10/11
11/12
Season

Factors thought to be implicated in yield plateau/decline:

- Crop nutrition
- In-field traffic (stool damage, compaction)
- Pests and diseases (Eldana, thrips, rust, nematodes….)
- Soil health

Profitability related to ratooning

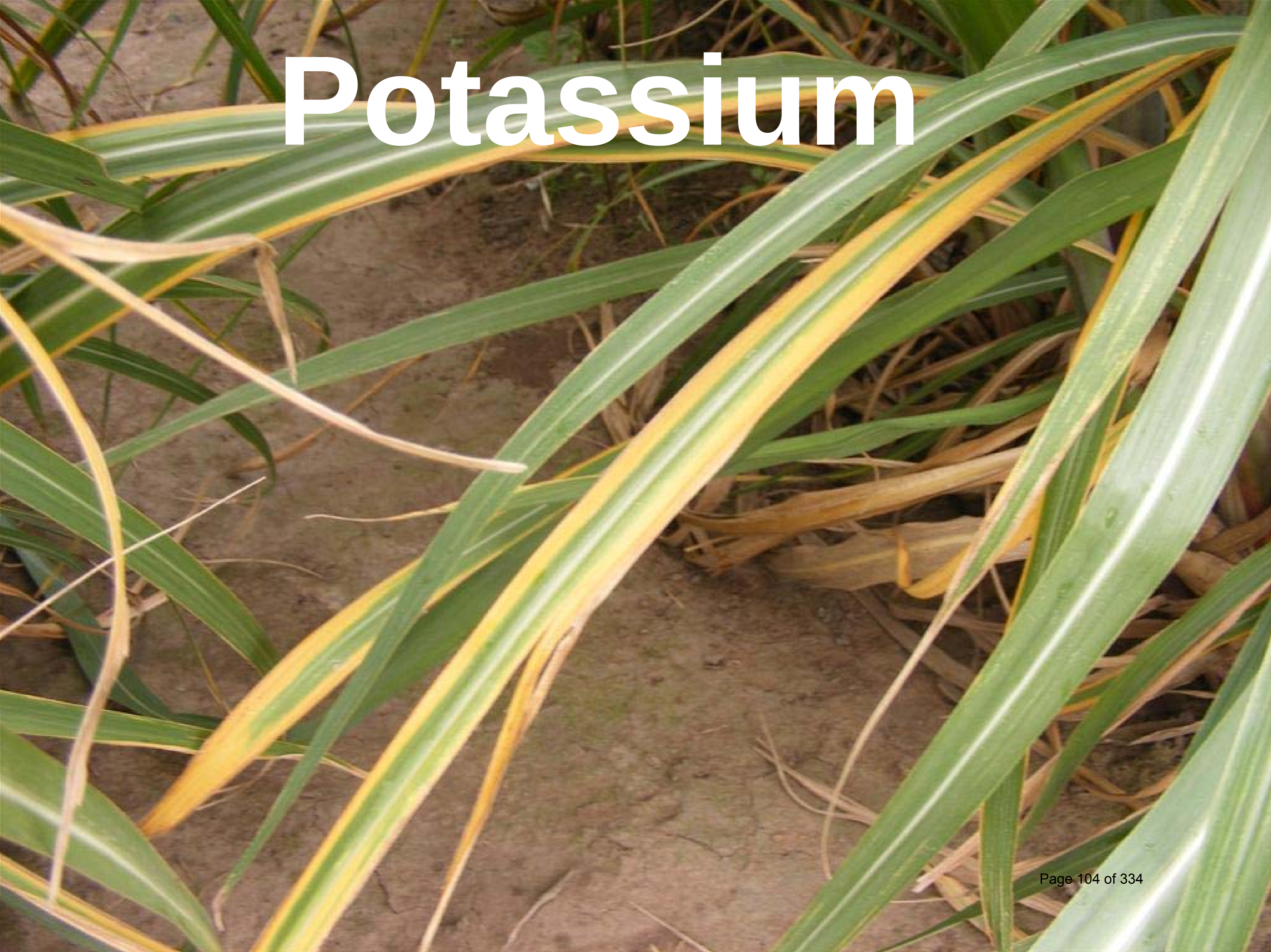
Operation	Dryland	Irrigated
Planting	R16 202	R16 202
Ratoon management	R5 100	R7 142

Interrogation of FAS soil and leaf test databases…

- Disturbingly low K levels in many soils
- Severe acidity problems in the coastal and inland areas of KZN
- Leaf N frequently below threshold
- Soil P levels generally adequate to excessive

…frequently higher P than K tests in topsoils!

Potassium

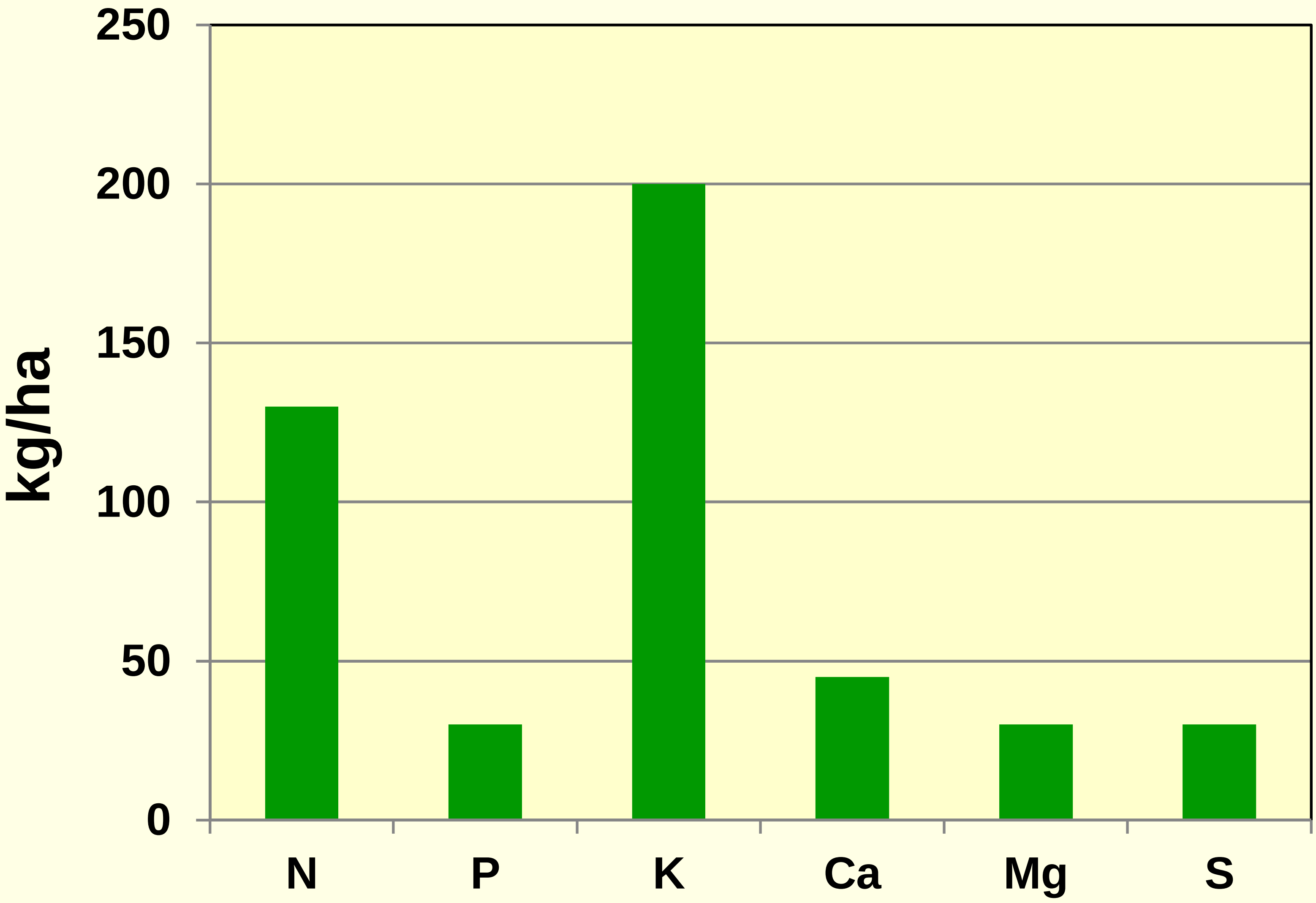


Critical importance of K in sugarcane production…

- Nutrient taken up in largest amounts
- Photosynthesis and sugar translocation
- Water use efficiency
- Lodging
- Cold tolerance
- Crop sucrose content???

Critical consideration:
K removals in harvested stalks?

Nutrient removals in a 100 t crop (approximate)



Potassium removals in stalks

Country	Stalk Yield (t)	Removal (kg K)	Reference
Australia	80	164	Wood & Schroeder, 2004
Brazil	100	53 - 256	Rosetto *et al*., 2008
Florida	103	343	Coale *et al*., 1993
India	100	280	Gopalasundaram *et al*., 2011
South Africa	100	150	Meyer, Jan, pers. comm.(2007)

Threshold K soil test values?

Threshold soil test K levels

Country	Soils	Critical K (ppm)	Reference
Australia	all	102 - 14	
Brazil			
South Africa	status	112 - 150	Meyer & Wood, 1985
South Africa	high base status	225	Meyer & Wood, 1985

Why the huge variation?

Diagnostic problems?

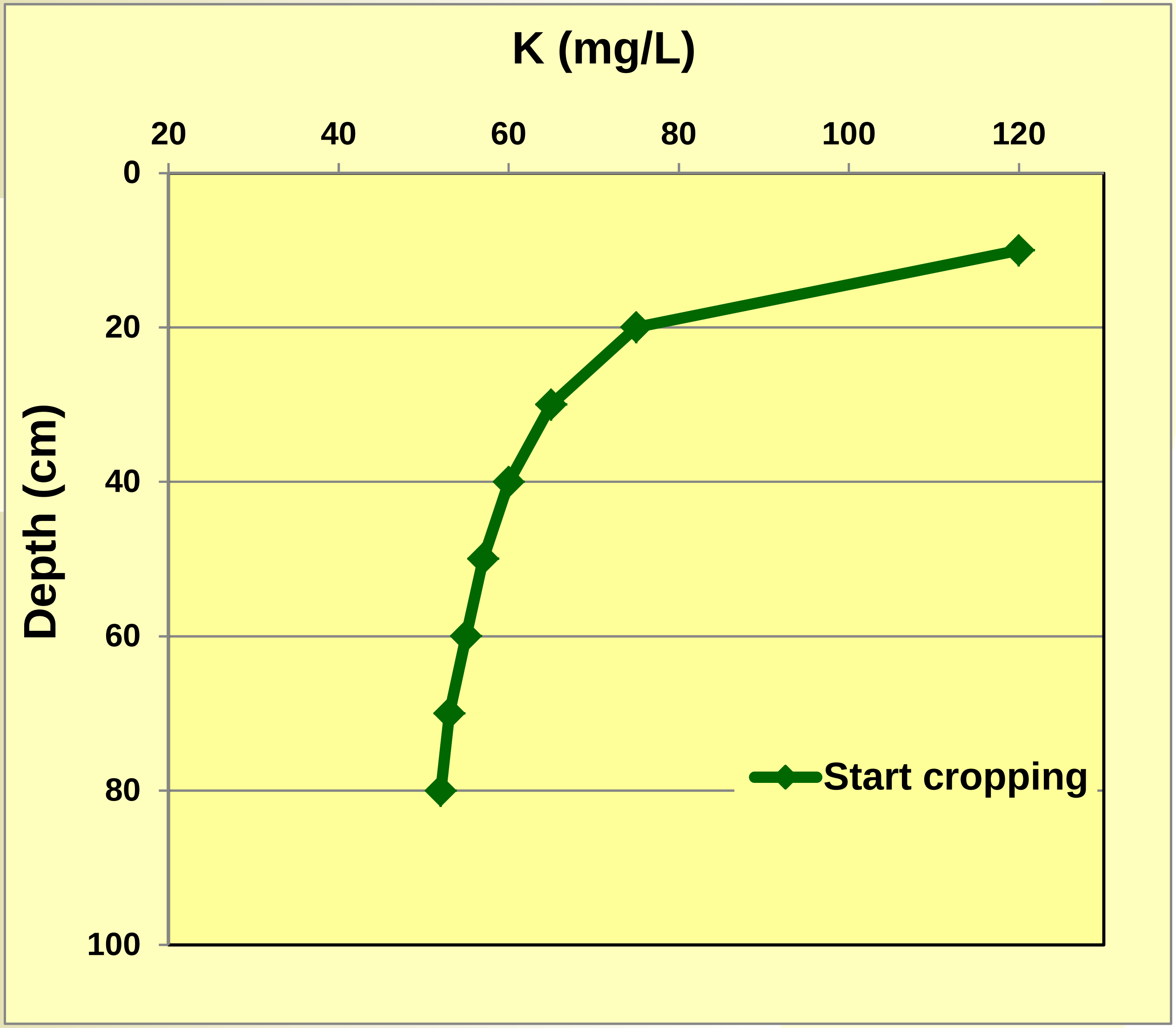

2,4 metros

Profile distributions of P and K in two sandy soils

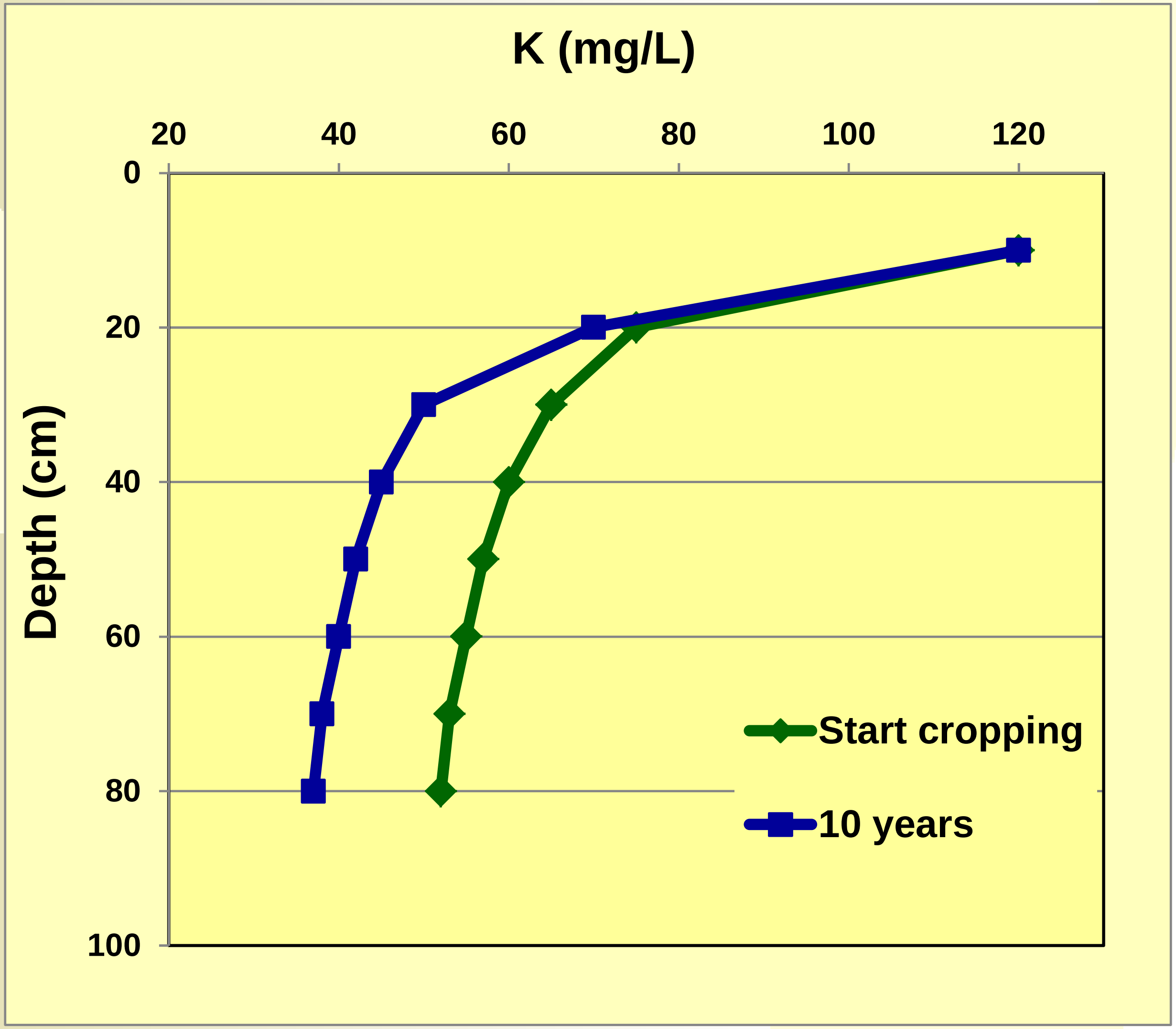
North Coast (15% clay)		
Depth (cm)	Truog P (mg/L)	Exch. K (mg/L)
0 – 20	19	31
20 – 40	13	23
40 – 60	15	14
60 - 80	13	10

Eston (8% clay)		
Depth (cm)	Truog P (mg/L)	Exch. K (mg/L)
0 – 20	63	45
20 – 40	45	25
40 – 60	33	15
60 - 80	12	14

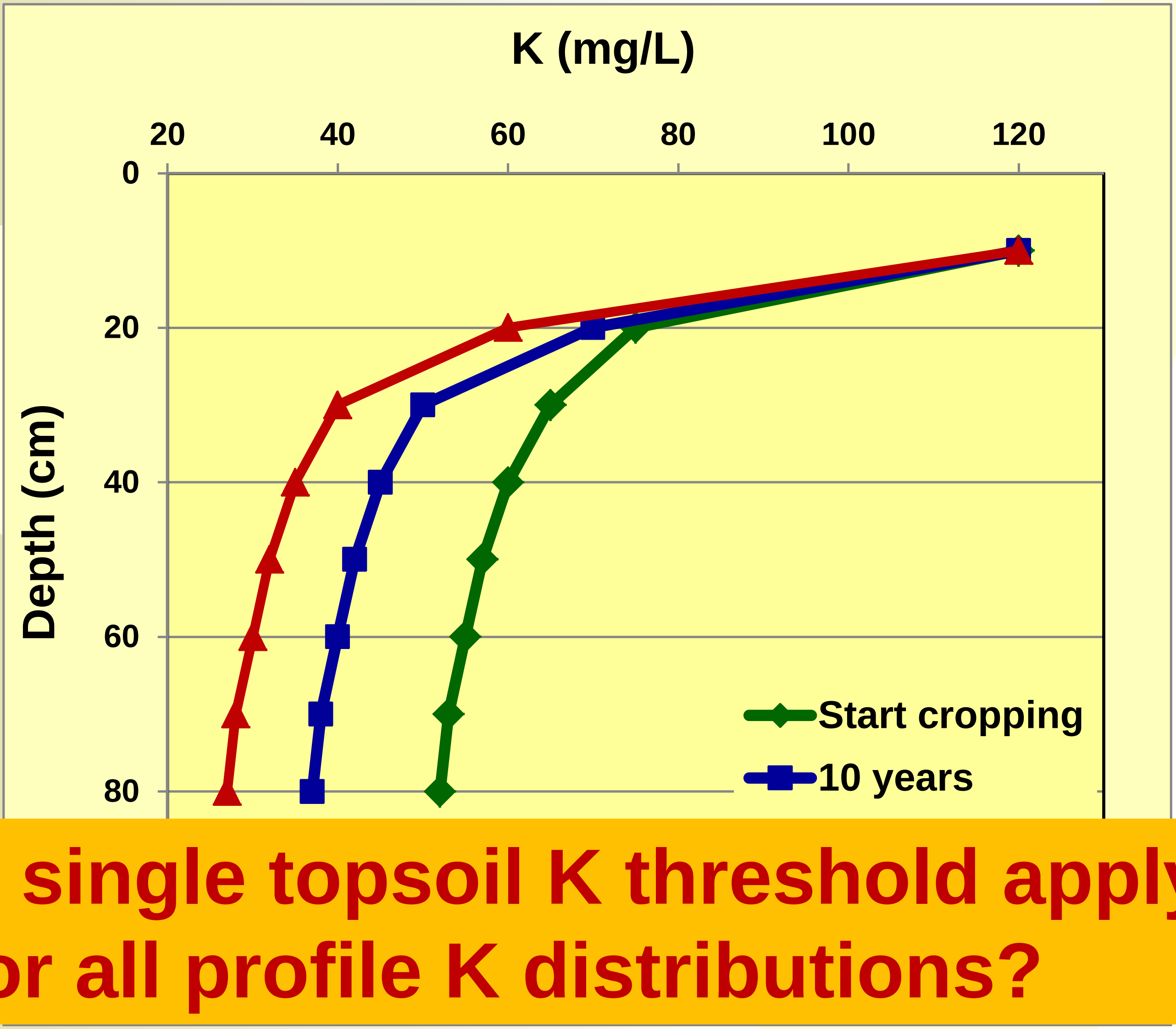
Suggested changes in profile K distribution with advances in cropping



Suggested changes in profile K distribution with advances in cropping



Suggested changes in profile K distribution with advances in cropping



Can a single topsoil K threshold apply for all profile K distributions?

Convincing evidence of K removals not being adequately addressed….

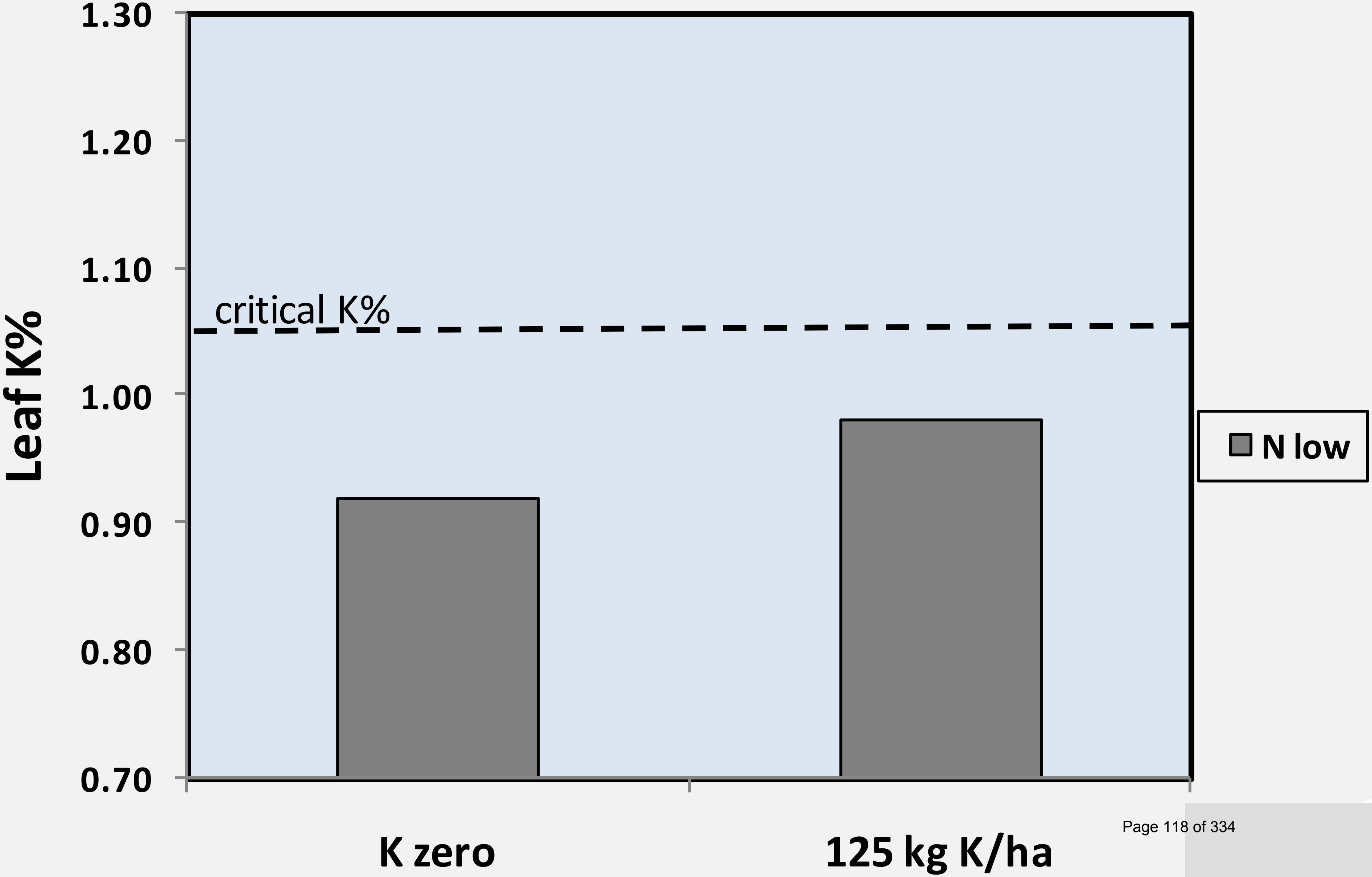
- **In Australia, on average 59% of removals applied as fertilizer (1.5 kg/t removed, 0.89 kg/t applied)**
- **In South Africa, low topsoil and extremely low subsoil K levels widespread**

Can leaf analysis be used to resolve the problem…?

Complication: major influence of N supply on K uptake

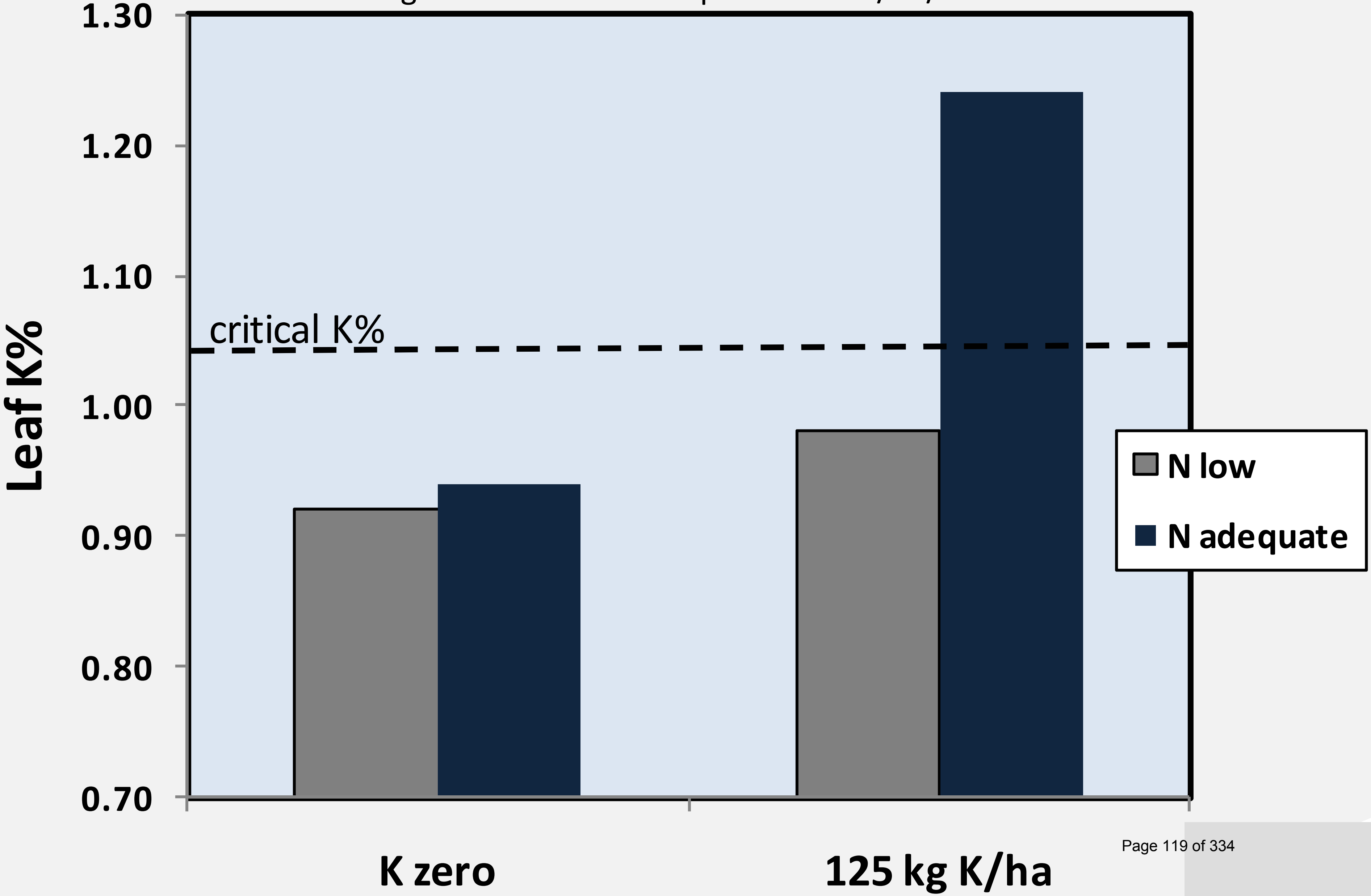
Sugarcane leaf K% in NxK trial at Umzinto

Agronomists Assoc. Report FT10NK/80/R6



Sugarcane leaf K% in NxK trial at Umzinto

Agronomists Assoc. Report FT10NK/80/R6

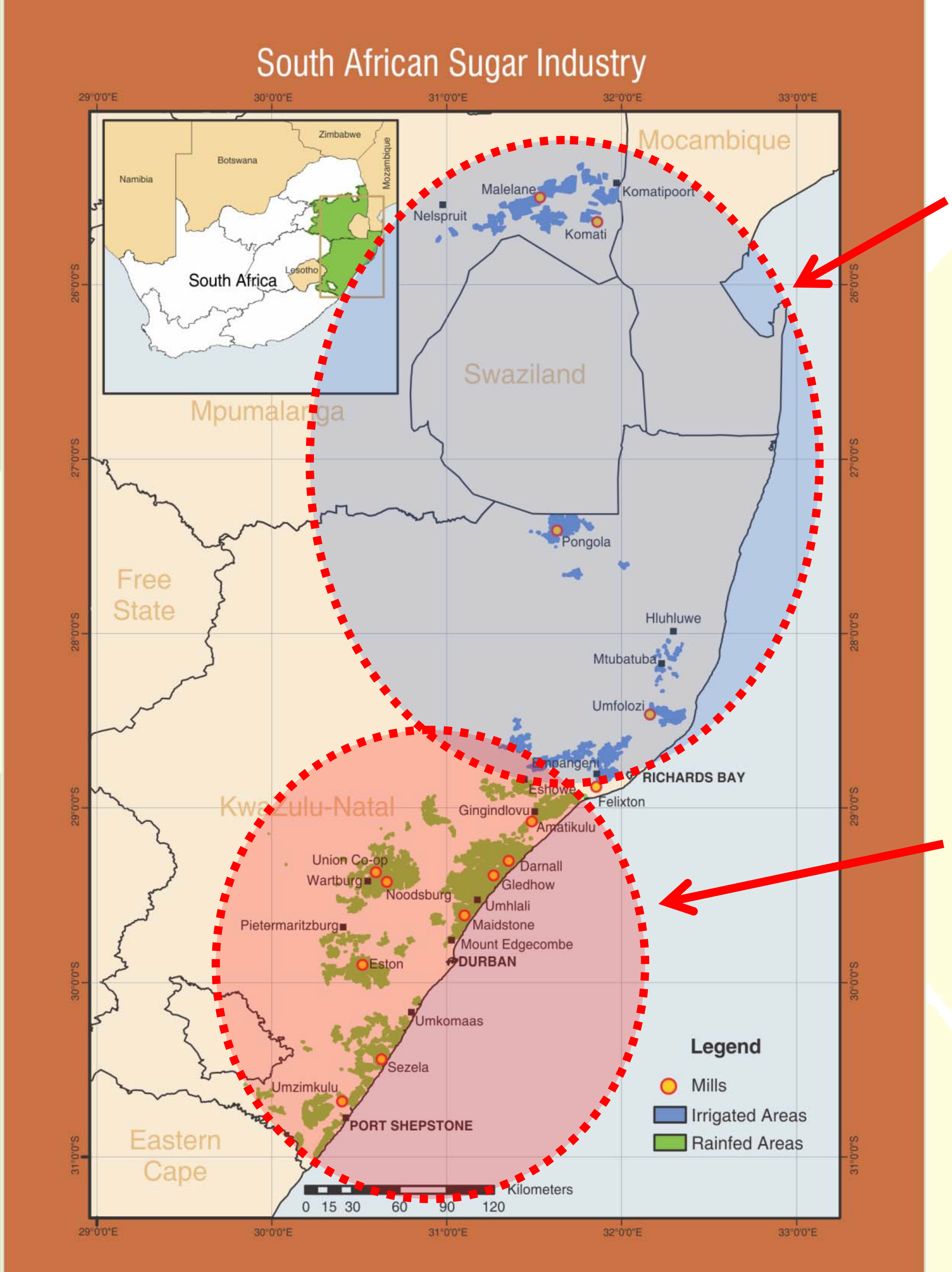


Current approach in SASRI's Fertiliser Advisory Service

K recommendations are related to:

1. Topsoil K test values
2. Yield targets (1.65 – 2.1 kg K/t cane)
3. Cropping system (burning or trashing)

Managing Soil Acidity

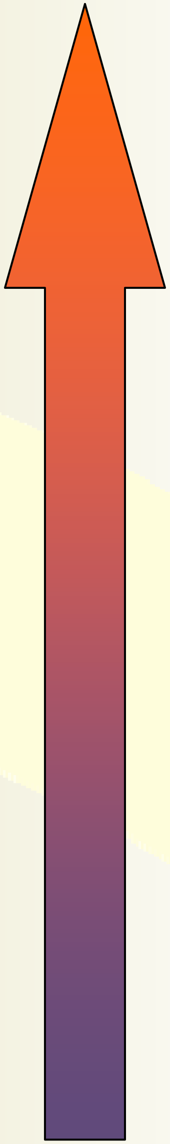


South African Sugar Industry

Irrigated, high pH and base status

Generally low pH and base status

Relative sensitivity to soil acidity of crop and vegetable species



highly
sensitive

moderately
sensitive

moderately
tolerant

highly
tolerant

carrot, cabbage, tomato

squash

sunflower / dry bean / cotton

sorghum

maize / lupin

soyabean

potato

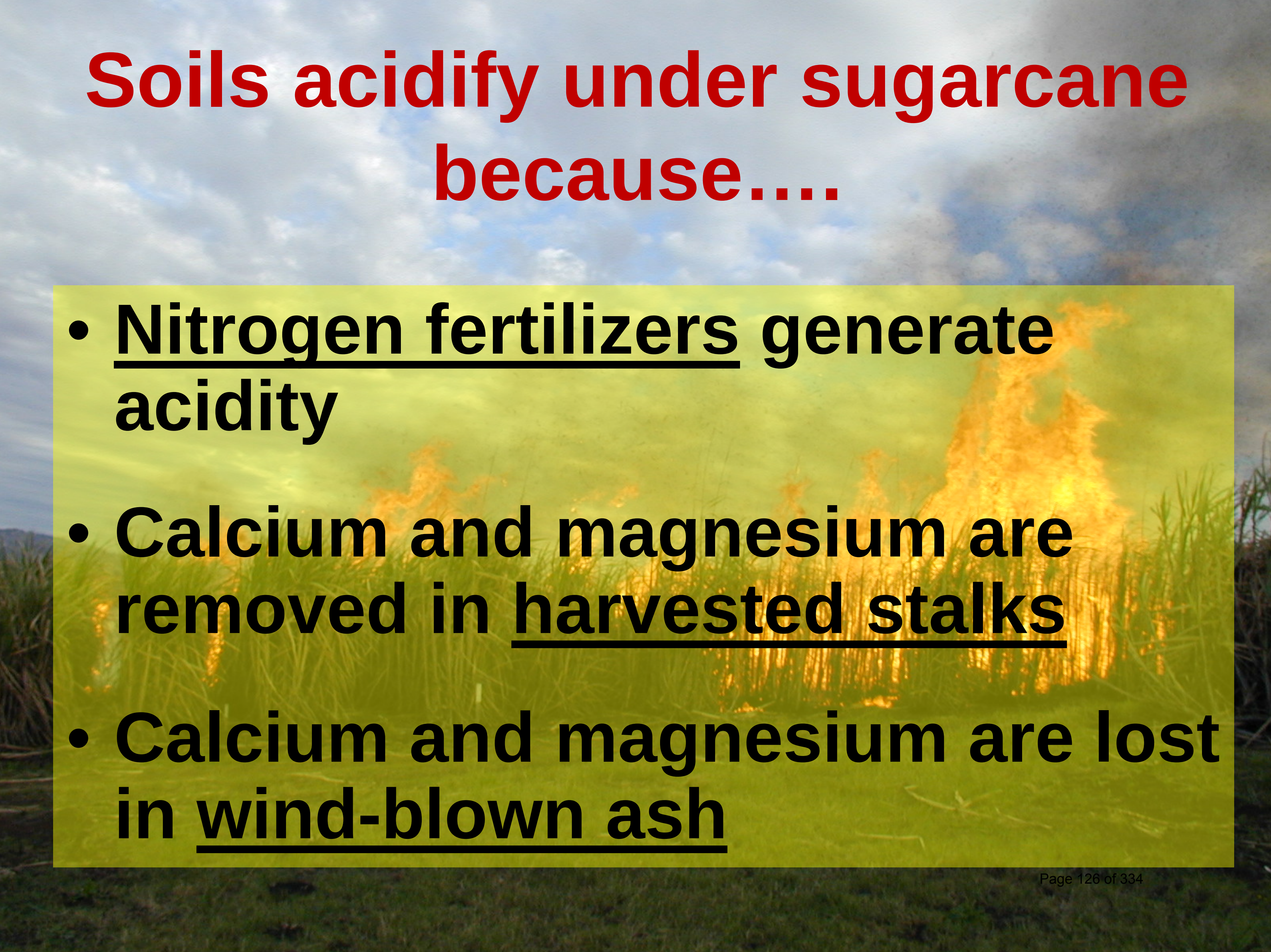
sweet potato

sugarcane, cow peas

CONCERNS

- **Widespread topsoil and subsoil acidity in coastal areas, Zululand and Midlands.**
- **Widespread nutrient deficiencies (Ca, Mg).**
- ***Re-acidification not adequately accommodated???***

Soils acidify under sugarcane because….



- Nitrogen fertilizers generate acidity
- Calcium and magnesium are removed in harvested stalks
- Calcium and magnesium are lost in wind-blown ash

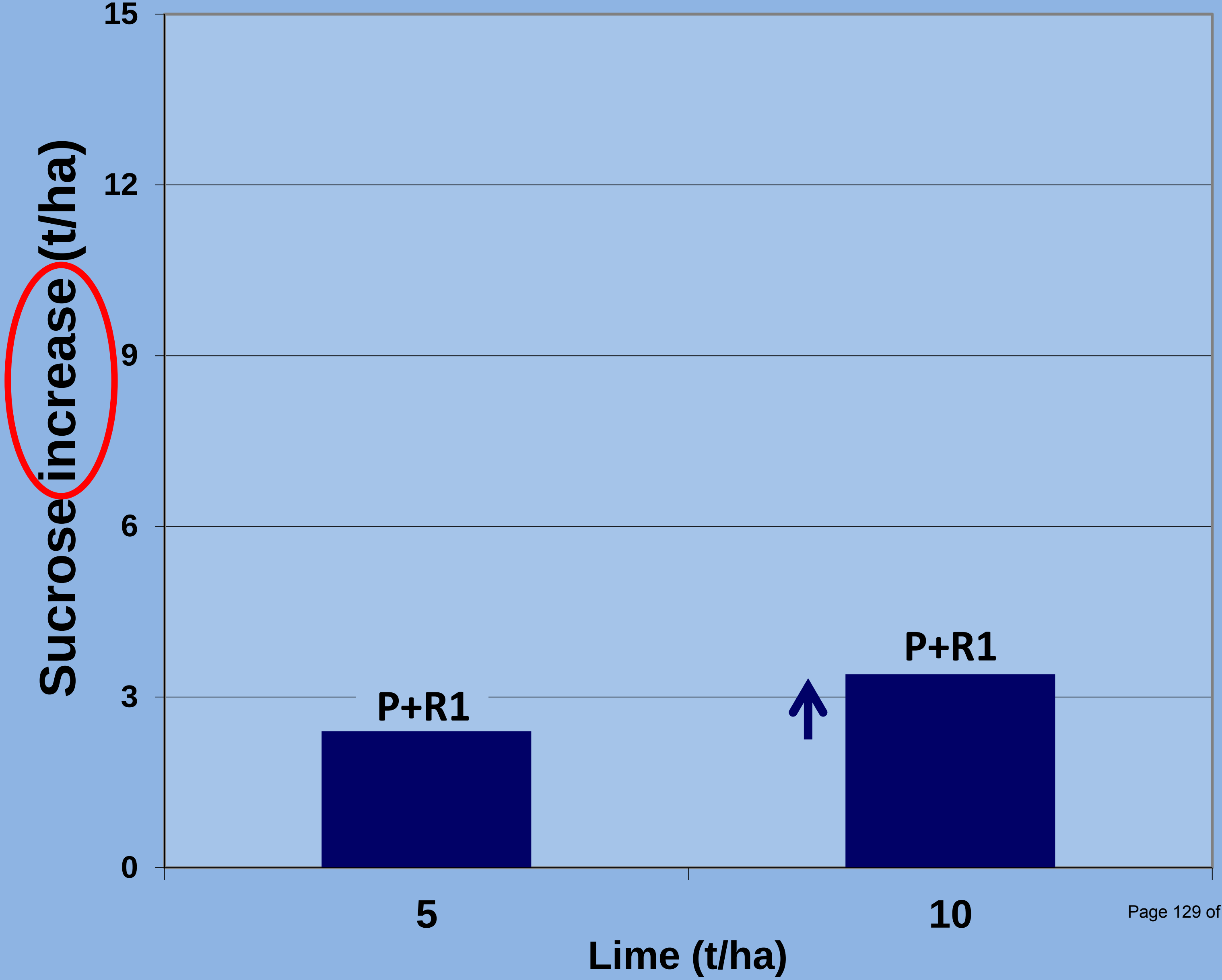
Sugarcane is successfully grown under <u>extremely acid soil conditions</u> in many countries, including South Africa, Australia and Brazil

Nevertheless, <u>highly profitable responses</u> to lime and gypsum are widely reported!

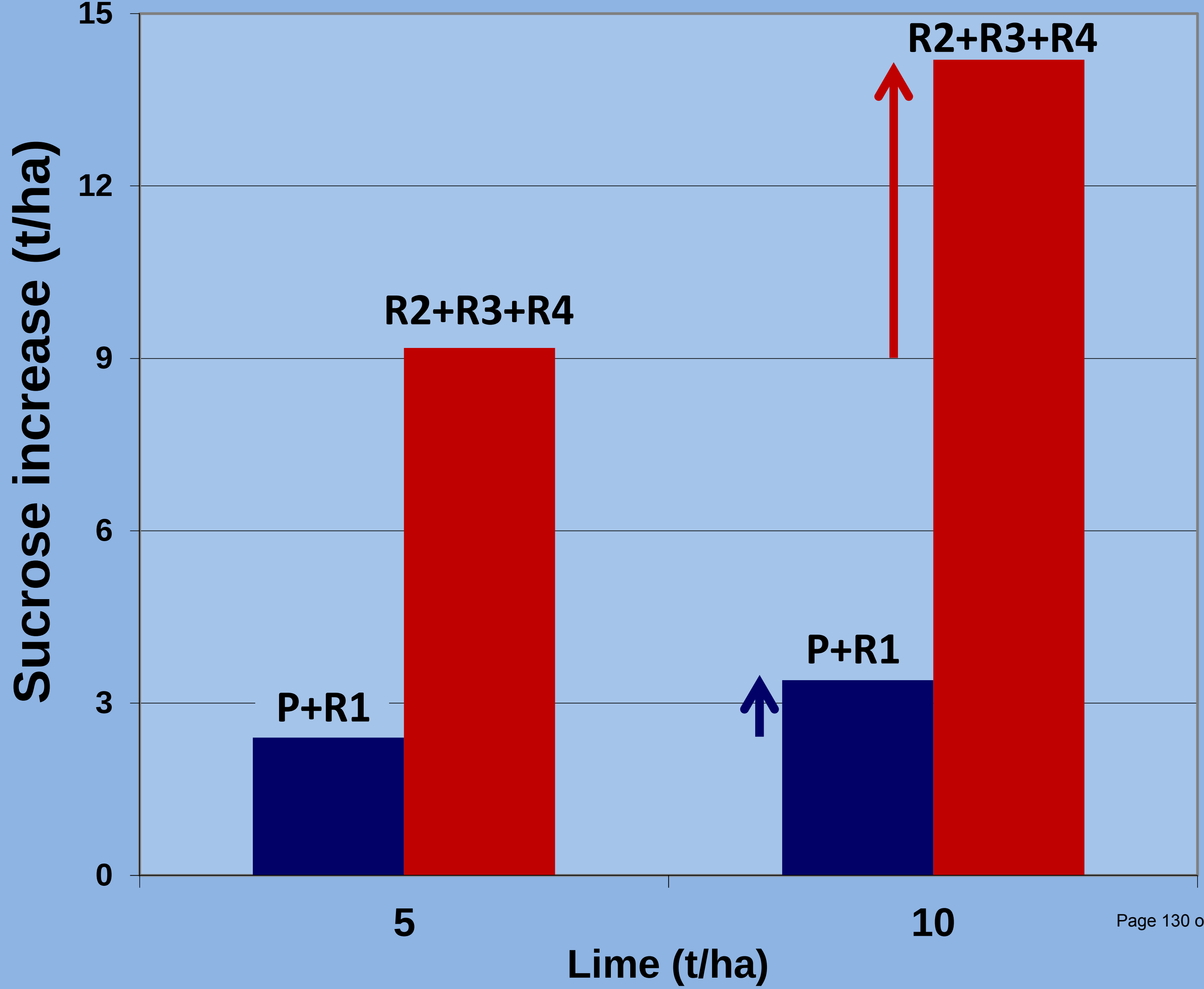
Sugarcane responses to lime and gypsum – literature reports

Country	Response %	Reference
Australia	**17 to 25**	Quinan & Wood, 1989
Brazil	**5 to 53**	Sumner, 2012
South Africa	**5 to 39**	Nixon *et al*., 2003
South Africa	**22 to 45**	Moberly, 1974

Response to lime of N16 at Dalton (Magwa soil)



Response to lime of N16 at Dalton (Magwa soil)



Profitability related to ratooning

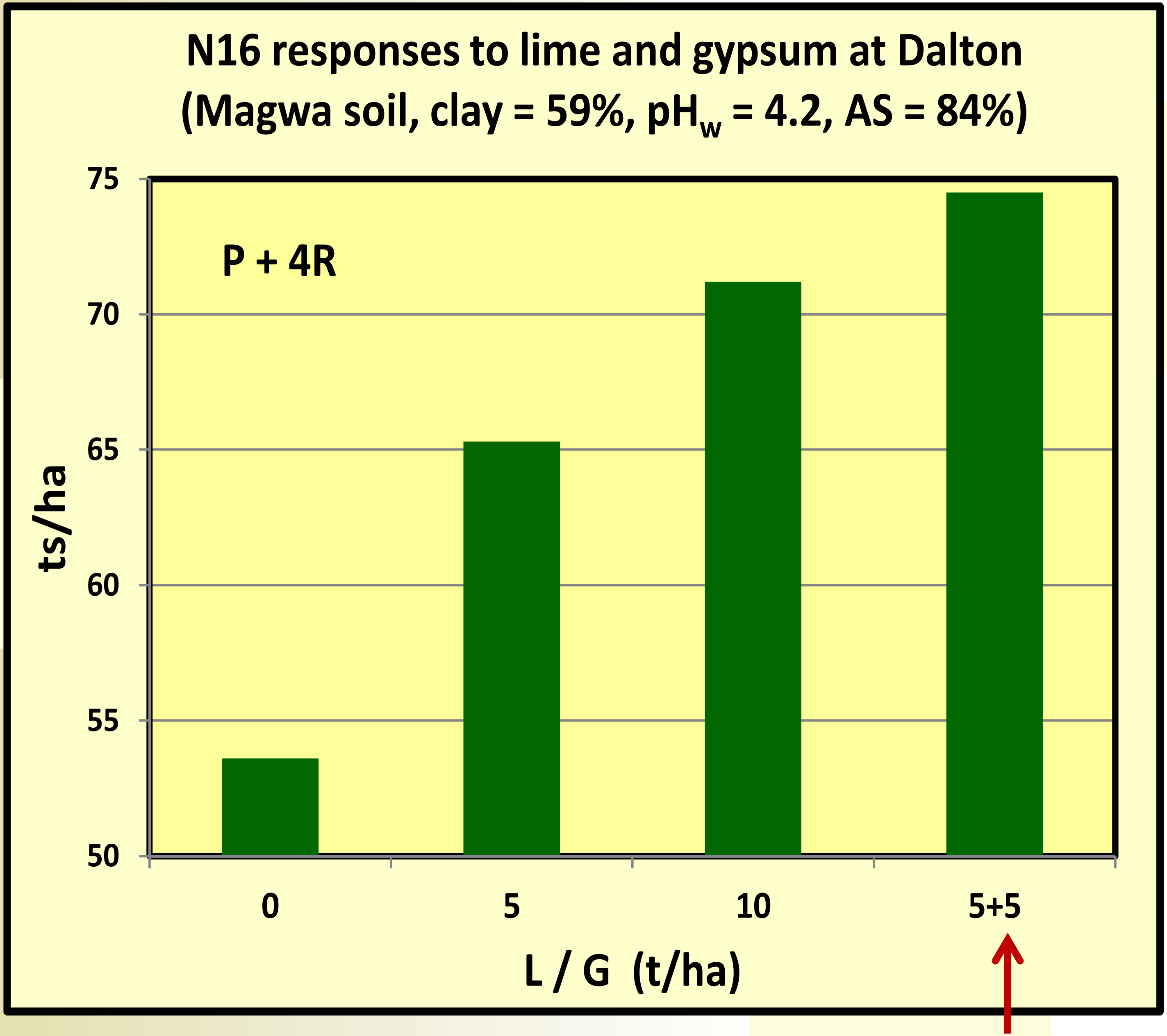
Operation	Dryland	Irrigated
Planting	R16 202	R16 202
Ratoon management	R5 100	R7 142

Longevity of responses…?

Long-term benefits of lime and gypsum applications often not appreciated……

Australia: Significant increases in sugarcane yields were still being recorded 18 years after a single application of 5 t/ha of lime, which resulted in approximately 366 t of additional cane relative to the unlimed treatment over the 18 year period!

(Noble and Hurney, 2000)



“Synergism between lime and gypsum” (Brazil)

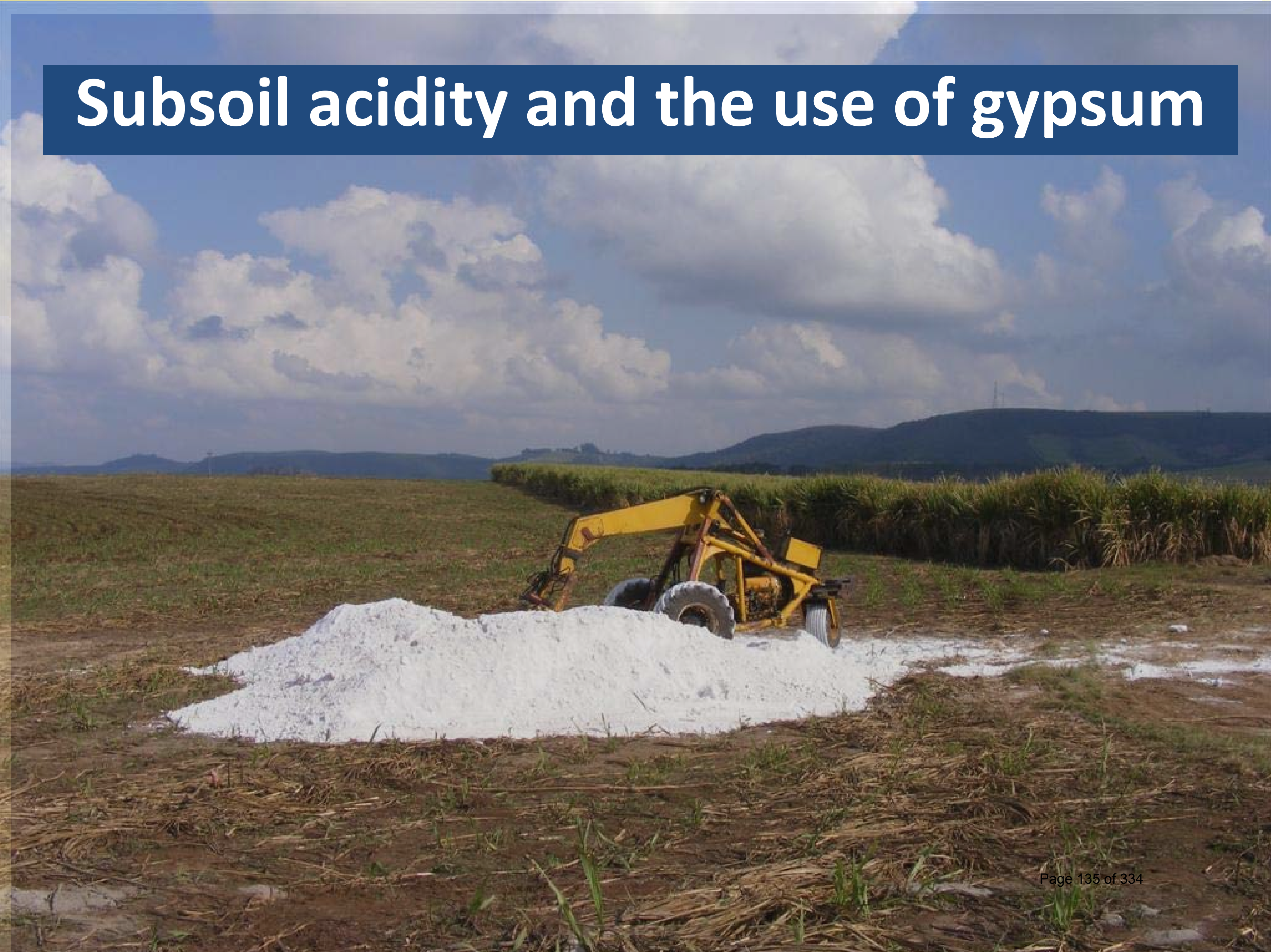
New criteria for managing soil acidity:

- Topsoil acid sat < 20% for all varieties

  (20% acid sat = ASI of ± 10%)

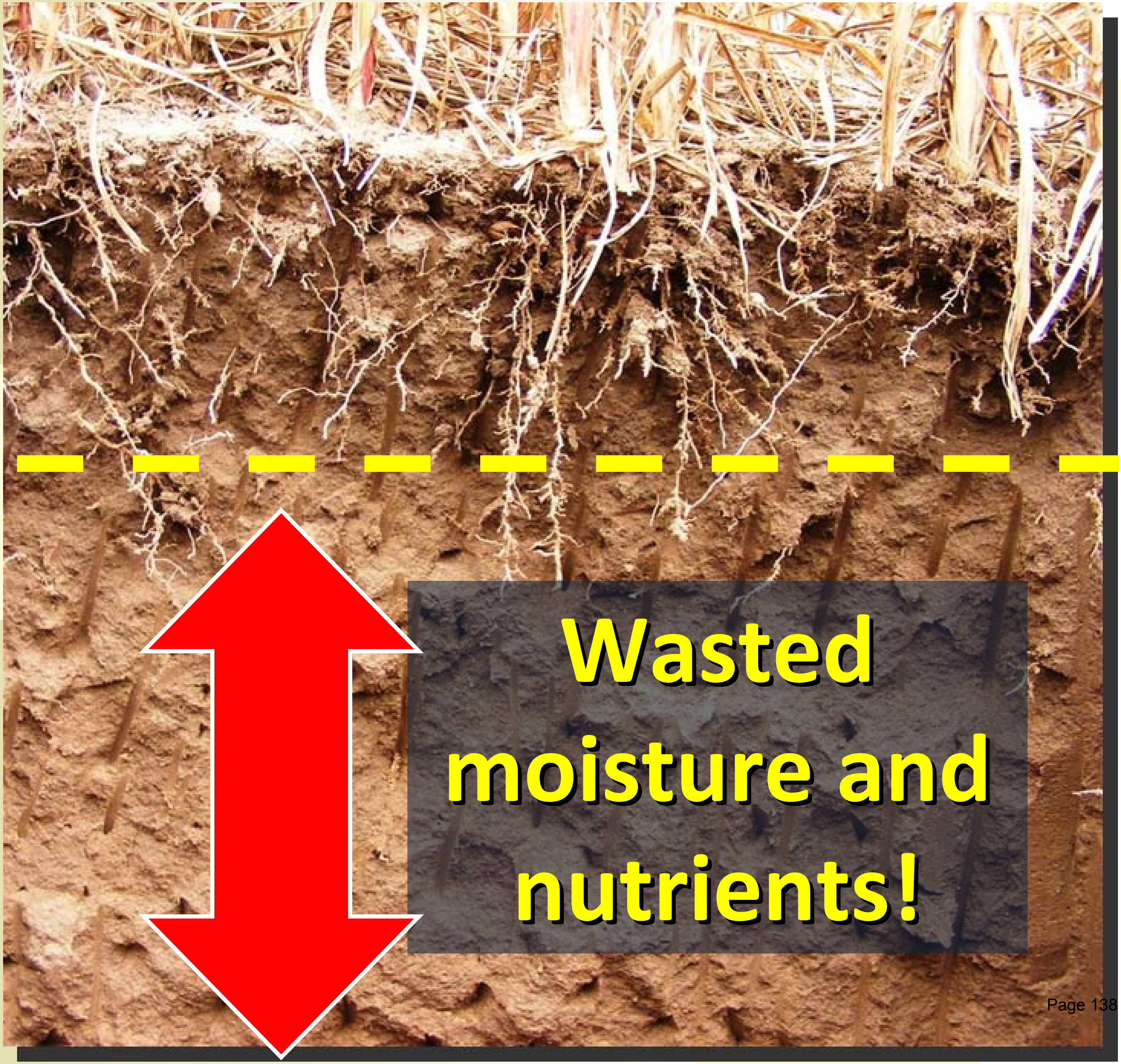
- >300 ppm Ca in topsoil
- > 50 ppm Mg
- Gypsum recommended to combat subsoil acidity

Subsoil acidity and the use of gypsum



Properties of a soil profile under sugarcane in the Stanger area (North Coast)

Depth (cm)	pH $CaCl_2$	Ca mg/L	Mg mg/L	Acid Sat %
0 – 20	3.73	104	20	66.7
20 – 40	3.65	69	12	81.7
40 – 60	3.71	51	10	86.4
60 - 80	3.84	68	8	78.6



Wasted moisture and nutrients!

Gypsum recommendations

- **Somewhat tentative – research necessary!**
- **Based on subsoil acid sat and texture.**
- **Maximum gypsum for plant crops on higher clay content soils is 7 t/ha.**
- **Maximum for ratoons is 3 t/ha.**

Results of new approach to soil acidity management….

- Heightened awareness of soil acidification problems in the sugar industry
- More intensive and regular soil sampling (including to depth)
- Massive increases in lime and gypsum usage
- Giving “legs” to the crop…..!

Thank You

EFFICACY AND APPLICATION OF BIOCHAR SOURCES – A REVIEW

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INTRODUCTION

Biochar is the latest buzz word in science and the number of research reports published on this topic over the last 10 years is astonishing! A cursory search for the term “biochar” over the internet yields a very large number of publications on the subject. Soil amendment with biochar is evaluated globally as a means to improve soil fertility and to mitigate climate change. However, the manufacturing and use of biochar is not new. About 2 500 years ago, farmers in the Amazon improved their soil’s ability to retain water and nutrients by tilling it with charcoal. In the process they darkened the colour of the soil substantially to depths of more than one metre. Portuguese settlers later dubbed this *terra preta*, or “black earth.” In these soils, the biochar acts as a soil conditioner, improving soil physical properties and nutrient use efficiency, thereby increasing plant growth. Today, 500 years after cessation of the practices that created these soils, the Terra Preta soils are highly valued for agricultural and horticultural use in the Amazon basin (Glaser *et al*., 2002).

WHAT IS BIOCHAR?

Black carbon, chars, charcoal and pyrogenic carbon are all names used in literature for a product produced through pyrolysis called biochar, a term coined by Peter Read around 2005 (Read, 2009). It is distinguished from charcoal by its use as a soil amendment (Lehmann and Joseph, 2009 referenced by Lehmann *et al*., 2011).

MANUFACTURING

Biochar is produced by heating organic material with little or no oxygen via a process called pyrolysis (Cheng *et al*., 2008; Novak *et al*., 2009; Krull & Griffiths, 2009; Inyang *et al*., 2010). When the pyrolysis temperature is increased the biochar yield decreases (Demirbas *et al*., 2006). Biochar produced at higher pyrolytic temperatures (500-700 °C) are well carbonised and exhibited a relatively high surface area (>300 m^2/g), little organic matter (<3%), and low oxygen content (≤10%). By contrast, the chars formed at low temperatures (300-400 °C) are only partially carbonized with a relatively low surface area (<200 m^2/g), high organic matter content (40-50%) and high oxygen content (>20%) (Chun *et al*., 2004). Another trend noticed is that biochar yield increases with increasing particle size of the feedstock (Demirbas *et al*., 2006).

The production of biochar via pyrolysis also yields bioenergy in the form of synthesis gas or ‘syngas’. Syngases consist of a variety of gases which in turn can be used to produce heat and power (Figure 1). Essentially, treating biomass through the pyrolysis process yield two products — biochar and biofuel (Krull & Griffiths, 2009) the latter of which can be split into biogas and bio-oil (Demirbas *et al*., 2006).

In short at higher temperatures more volatiles are driven off (more gas and tar is produced) which increases the carbon content and decrease the mass of the final product, biochar (Table 1).

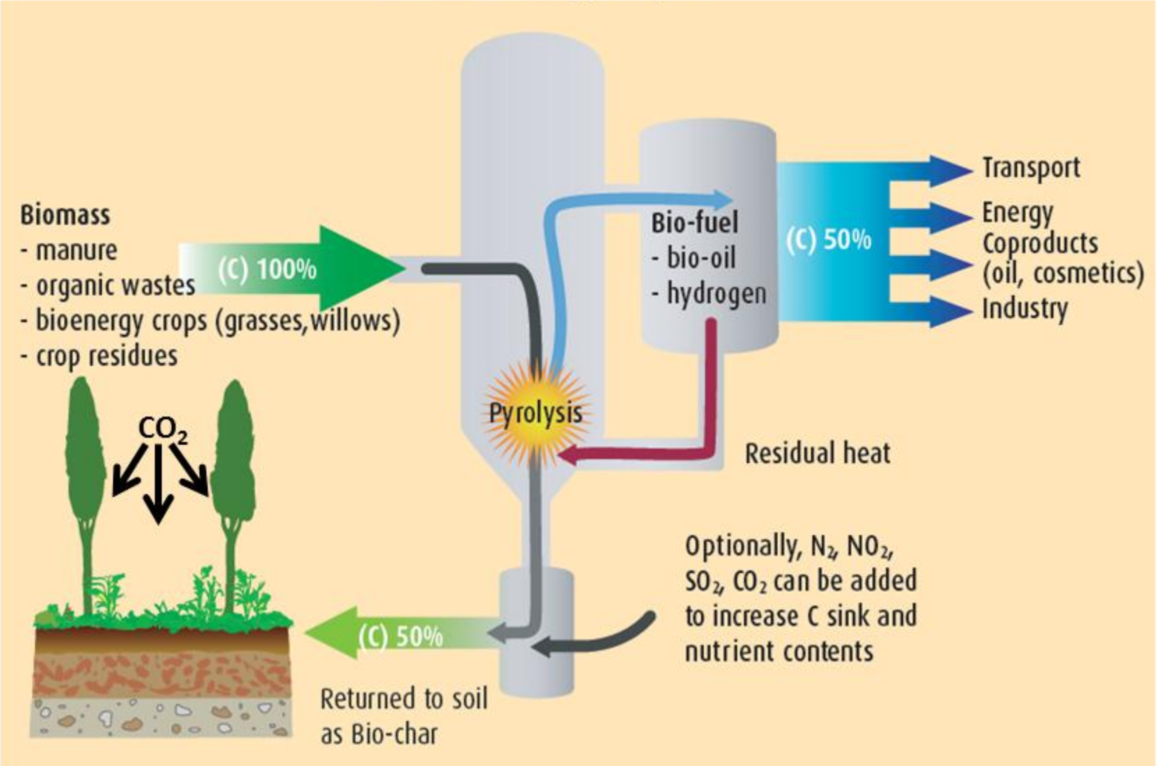

Figure 1. The combined process of biochar and bioenergy production, resulting in net carbon sequestration ('Carbon negative process') (Lehmann* et al.*, 2006).

Table 1. Effect of temperature on yield and composition of charcoal (FAO, 1987).

Carbonisation temperature	Chemical analysis of charcoal		Charcoal yield based on oven dry wood
°C	% of fixed charcoal	% volatile material	(0% moisture)
300	68	31	42
500	86	13	33
700	92	7	30

There are many different forms of biochar, determined by factors such as the nature of the source material, pyrolysis duration and temperature. The main effect of an increase of temperature is an increase in biochar surface area (Table 2) (Chun *et al*., 2004). However, the ability of biochar to absorb water, benzene and nitrobenzene seems to decrease with an increase in surface area (Chun *et al*., 2004). On the other hand, Krull and Griffiths (2009) found that biochar produced at 700 °C has a much greater adsorptive capacity and higher degree of micro-porosity than biochar produced at 400 °C. At temperatures in the order of 1000 °C (in the absence of oxygen) gasification of biochars takes place producing the so-called "activated carbon" (Lehmann *et al*., 2011; Suhas *et al*., 2007).

Finally, consideration should be given to the positioning of the biochar manufacturing plant. Ideally it should be close to the fields where it will be applied as transport costs could render biochar uneconomical (Figure 2) (Krull, 2009).

Table 2. The effect of pyrolysis temperature on biochar carbon (C) content, oxygen (O_2) content, surface area and absorption properties (adapted from Chun *et al*., 2004).

Pyrolysis temp (°C)	Surface area (m^2/g)	Elemental composition		Water uptake (mL/m^2)x10^{-4}	Ce/Cs = 0.1$^{\#}$		Ce/Cs = 0.3$^{\#}$	
		C (w%)	O_2 (w%)		*Benzene	*Nitrobenzene	*Benzene	*Nitrobenzene
300	116	69.2	26.6	13.0	4.14	8.02	6.55	11.55
400	189				3.39	5.34	4.66	6.98
500	309	83.4	10.1	4.1	2.52	3.11	3.01	3.69
600	438				2.90	3.45	3.31	3.90
700	363	88	6	4.1	3.11	3.58	3.61	4.05
AC**	776	87.6	7	3.5	2.85	3.53	3.56	4.16

* Volume absorbed per unit surface area (mL/m^2)x10^{-4}
** AC = commercially produced activated carbon
# Relative concentration

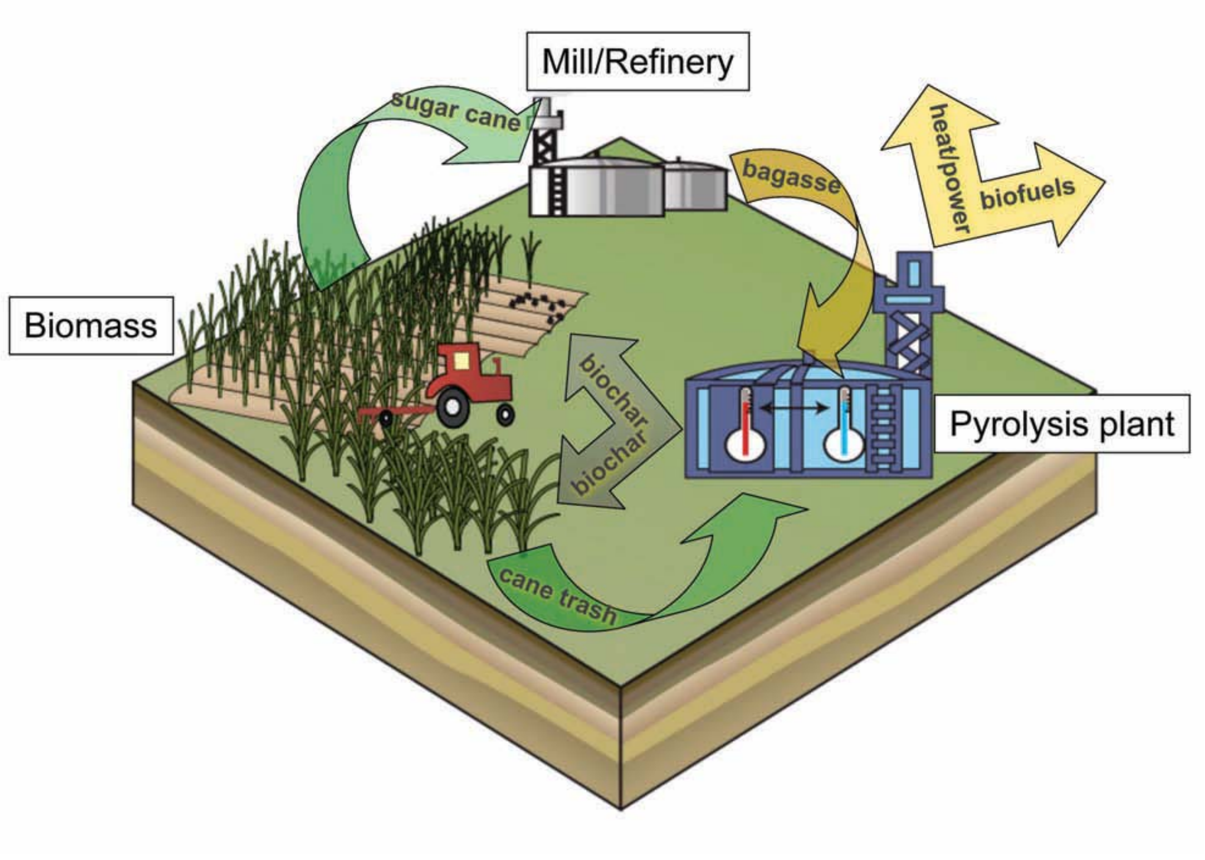

Figure 2. Illustration of the application of sugar cane trash and bagasse conversion to biochar. Note that the distance between field, refinery and pyrolysis plant should be kept to a minimum to avoid unnecessary fossil fuel emissions and to avoid expensive transport costs (Krull, 2009).

COMPOSITION

It is important to note that not all biochar is the same and that its properties also depend on the feedstock used. For instance, biochar made from manure will have a higher nutrient content than biochar made from wood cuttings. However, biochar from wood cuttings is likely to have a greater chemical stability, making it stable for longer (Krull and Griffiths, 2009).

Examples of differences in biochar composition and the effect it has on the composition of soils are given in Tables 4, 5 and 6. In comparison with solid fossil fuels, fresh biomass contains less carbon and more oxygen and has a low-heating value. Stricking in the composition of biochar is the relative high Si (10%), oxygen (1.98%) and C (83%) contents. All though low, it's content in K (0.41%), N (0.34%) and Ca (0.36%) are also useful (Table 5).

The value of biochar's salt load is reflected in the pH which is in general larger than 8 (Table 4) and serve as a reminder for users to apply biochar with caution and have their soils analysed annually for signs of alkalinisation. However, Jones *et al*. (2012) noticed that 3 years after biochar was applied, the alkalinity associated with the biochar had been fully neutralized and had lost most of its cations (K, Na, Ca).

SOURCES

Biochar can be manufactured from nearly any source of organic matter. Examples are sugarcane bagasse (Inyang *et al*., 2010), sugarcane trash (Krull, 2009), chicken manure (Hass *et al*., 2012), cattle manure (Cao *et al*., 2009), wheat residue (Chun *et al*., 2004), pine bark, almond shells, nut shells, apricot stones, cherry stones, and grape seeds (Demirbas *et al*., 2006), pecan shell (Novak *et al*., 2009), casein (Purevsuren *et al*., 2003), algal (Bird, 2012), Giant Silver Grass (Luo *et al*., 2011), switchgrass (Bailey *et al*., 2011), Perennial Ryegrass (de la Rosa & Knicker, 2001), apple wood chips (Li *et al*., 2011) and sewage (Harrabin, 2009). The complete list is of course much longer but in principle any organic matter can be used as a feedstock for the production of biochar.

CHARACTERISTICS AND BENEFITS

Plants absorb carbon as CO_2 from the atmosphere during photosynthesis. When the plant dies, the carbon-rich plant matter decomposes releasing carbon into the soil and back into the atmosphere, completing the cycle. However, instead of the plant matter decomposing it can be used as the feedstock for pyrolysis and thereby decreasing the turnaround time of the carbon cycle. Pyrolysis converts easily broken down organic matter into a highly stable form of carbon, which is mainly used as a soil additive to improve nutrient retention and carbon storage (Krull, 2009). There are several benefits associated with the production and usage of biochar and this is summarised in Table 3.

Both the nature of the precursors and the production process has a strong influence on the properties of the resulting biochar (Demirbas *et al*., 2006). For example, see Table 4 for the characteristics of biochar made commercially from hard wood species.

Table 3. Benefits associated with the use of biochar (Krull, 2009)

Biochar purpose	**Benefit**
Biochar used as a soil amendment can have beneficial effects for plant production as it may:	(a) reduce soil acidity, (b) increase or retain plant productivity with a lower amount of fertiliser use, and (c) more efficiently retain nutrients and avoid leaching from the soil profile.
Biochar and co-produced bioenergy from urban, agricultural and forestry biomass has the potential to help combat climate change by:	(a) displacing fossil fuel use, (b) sequestering C, (c) potentially decreasing N_2O and CH_4 emissions from soils, (d) avoiding emissions of CH_4 produced from landfill, (e) reducing energy requirements for soil tillage, (f) increasing C sequestration by plants through increased crop vigour, and (g) reducing emissions associated with the manufacture of fertilizer.
Biochar may enable soil and vegetation to adapt to climate change by:	(a) increasing water holding capacity of soils, and (b) increases soil pliability and increasing water infiltration.

Table 4. Characteristics of two commercial biochars manufactured from particles smaller and larger than 2 mm using two different pyrolysis processes (Jones *et al*., 2011).

		Bioregional biochar(1)		**Simcoa biochar**(2)
Parameter	**Unit**	**>2 mm**	**<2 mm**	**<2 mm**
pH_{water}		9.83	9.73	8.48
EC	(mS cm^{-1})	1133	1570	621
Bulk density	(g cm^{-3})	0.2	0.35	0.45
Specific surface area	(m^2 g^{-1})	ND	39	4
Moisture	(%)	3.5	6.4	11.6
Ash content	(%)	1.8	9.2	7.8
Total C	(%)	76	76	78
Total N	(%)	0.68	0.69	0.38
Size fraction	**(% of total)**			
7500 - 10000	µm	38.1	-	-
5000 - 7500	µm	38.8	-	-
2000 - 5000	µm	23.2	-	-
500 - 2000	µm	-	51.3	34
250 - 500	µm	-	14.8	16.6
125 - 252	µm	-	14.3	15.8
<125	µm	-	19.8	33.8
DOC	(mg C kg^{-1})	108	130	ND
TSN	(mg N kg^{-1})	1	0.6	ND

(1) Mechanically chipped trunks and large branches of Fraxinus excelsior L., Fagus sylvatica L. and Quercus robur L. (pyrolysed at 450 °C for 48 h)

(2) Eucalyptus marginatus Donn ex Sm. derived biochar (trunks and large branches pyrolysed at 600 °C for 24 h)

DOC = dissolved organic carbon; TSN = total soluble N; ND = Not determined.

Numerous studies have shown that many soil processes are affected by additions of biochar and that agronomic benefits of soils ameliorated with biochar include a number of soil chemical, physical and biological properties. Examples are exchange capacity and nutrient retention, nutrient availability, microbial composition and activity, denitrification, methane oxidation, carbon mineralization and nutrient transformations due to altered carbon sources, sorption of inorganic and organic compounds including enzymes, soil water retention, water infiltration properties, changes in pore architecture and soil structure (Glaser *et al*., 2002; Suhas *et al*., 2007; Krull & Griffiths, 2009; Lehmann *et al*., 2011).

Recycle period

- Due to its high chemical stability, high carbon content and its potential to reside in soil for decades, centuries, and even up to millennia, biochar has the potential to be a long-term carbon sink (Swift, 2001; Krull & Griffiths, 2009; Smith *et al*., 2010). However, recent research showed that the residence time could be less than 100 years (Hilscher *et al*., 2009). In comparison, typical turnover times of fresh soil organic matter is 6 to 20 years in surface horizons (Torn *et al*., 2005).

- Organic materials used as a source for biochar contain a fair amount of N in the fresh state. Rye grass charred for 4 minutes at 350 °C was shown to have mineralised 10% of its N after only 72 days and used for grass growth (De la Rosa & Knicker, 2011). The fast degradation of grass chars implies that such material may not be as recalcitrant during long-term humification as formerly thought, and that N from N-rich pyrogenic organic matter may have a future as slow release N-fertilizers (De la Rosa & Knicker, 2011).

Chemistry

- Novak *et al*. (2009) noticed that biochar has both a high surface area per unit mass and a high charge density. Fresh biochars can have net positive or net negative surface charge, but typically have initially low cation exchange capacities (CEC) compared to soil organic matter on a mass basis (Lehmann, 2007).
- Biochar effectively absorbs atrazine, simazine and heavy metals such as Pb(II), Cu(II), Zn(II), Cd(II), Hg(II), Cr(III) and Cr(VI) (Suhas *et al*., 2007; Cao *et al*., 2009; Jones *et al*., 2011).
- Given that different feedstock properties range from mineral poor woody materials to mineral-rich manures or crop residues, such as rice hulls, the resulting soil pH following the addition of biochar is highly variable and ranges from 4 to above 12, even for the same biomass type (Lehmann, 2007). Hass *et al*. (2012) have noticed that soil pH has increased from 4.8 to 6.6 following the addition of biochar. Typically, biochars with high mineral ash content have greater pH values than those with lower ash contents. For all feedstocks, pH generally increases with greater pyrolysis temperature (Lehmann *et al*., 2011).

Physical

- Biochar addition can reduce the overall tensile strength and bulk density of the soil (Lehmann *et al*., 2011).
- Biochar contains macro- and micropores (Downie *et al*., 2009), which can hold air or water, greatly reducing the bulk density of the biochar particle which typically lie between 0.09 and 0.5 g cm^{-3}.(Lehmann *et al*., 2011).

Microbial

- The chemical stability of a large fraction of a given biochar material means that microorganisms will not be able to readily utilise the C as an energy source or the N and possibly other nutrients contained in the C structure. However, depending on the type of biochar, a fraction may be readily leached and therefore mineralisable (Lehmann *et al*., 2009) and in some cases stimulate microbial activity and increase abundance (Steiner *et al*., 2008).

- In most studies, microbial biomass has been found to increase as a result of biochar additions, with significant changes in microbial community composition and enzyme activities that may explain biogeochemical effects of biochar on element cycles, plant pathogens, and crop growth (Lehmann *et al*., 2011). In spite of the larger microbial biomass the metabolic quotient (CO_2-C respired per unit microbial biomass C) and the absolute amount of carbon respired was noticed to be lower (Lehmann *et al*., 2011).
- Enzyme activities following biochar addition to soils are highly variable and these effects are likely associated with reactions between biochar and the target substrate (Bailey *et al*., 2011).
- Decreases in arbuscular mycorrhizal fungi have been observed after additions of biochar and a possible reason could stem from a reduced requirement for mycorrhizal symbiosis due to increased nutrient and water availability (Lehmann *et al*., 2011).
- It has been hypothesized that both bacteria and fungi are better protected against grazers or competitors by exploring biochar pore habitats. Visual investigations of both pore size distribution and size of the micro-organisms provide justification for this hypothesis (Thies & Rillig, 2009).
- Three years after a biochar application of up to 50 t/ha in the field, alkalinity associated with the biochar had been fully neutralised and biochar had lost most of its cations (K, Na, Ca), but had built up an associated microbial community (Jones *et al*., 2012).

Earthworms

- Earthworms seem to prefer biochar mixed in certain soils while in others the presence of biochar did not had a significant effect on their behaviour. Biochar produced from hardwood resulted in weight loss in earthworms (Lehmann *et al*., 2011).
- Earthworms do not benefit from adding dry biochar to soils, but if it is moistened to near field capacity, earthworms are not negatively affected (Li *et al*., 2011).

Roots

- Roots growing in soils ameliorated with biochar generally produced more root tips, biomass and length (Figure 3). No evidence exists so far for direct negative effects of biochars on plant roots (Lehmann *et al*., 2011).
- Skinner and Beattie (1916) noticed improved root growth following the incorporation of biochar and suggested the possible detoxification of the soil due to sorption of phytotoxic allelopathic compounds by biochar.

Figure 3. Abundance of roots in biochar
(http://images.iop.org/objects/erw/talkingpoint/3/6/2/ERWbiochar3_1006_09.jpg).

Crop growth

Evidence of crop response following biochar application is limited and the results are not conclusive.

- The larger growth of pepper plants following an application of biochar was explained by the positive effect that biochar has on *Trichoderma* numbers in the rhizophere (Graber *et al*., 2010).
- No studies have been published where shoot to root ratio increased while plant growth decreased, which would indicate a direct toxic effect of biochars on plant roots through the presence of organic or inorganic (heavy metals) compounds (Lehmann *et al*., 2011).
- Many of the short-term effects of biochar on plant growth and soil behaviour reported from laboratory studies were not observed in the field emphasizing the need for long term field trials to establish the effect of biochar on plant growth (Jones *et al*., 2012).

Case study

Novak *et al*. (2009) quantified the impact of pecan shell – based biochar (Table 5) on the fertility of Norfolk loamy sand. At pH_{water} 4.8, the Norfolk soil had 42% (2.4 $cmol_c$ exchangeable acidity kg^{-1} ÷ 5.7 $cmol_c$ CEC/kg x 100) of the total soil CEC sites occupied by $[Al(H_2O)_5]^{+2}$. Additions of 0.5% (10 t/ha) and 1% (20 t/ha) biochar to the Norfolk soil did not significantly modify the exchangeable acidity values, although soil pH values significantly increased by 0.7 units. With the addition of 2% (40 t/ha) biochar, the pH increased from 4.8 to 6.4 (Table 6), and exchangeable acidity was reduced by 38% (difference of 0.9 $cmol_c$/kg). Biochar was thus an effective liming agent, neutralising solution pH and reducing exchangeable acidity values. This was linked to the high K and Ca contents in pecan shell-based biohar. However, the pecan shell – based biochar had no effect on the CEC of the soil (Novak *et al*., 2009). On another hand, Lehmann *et al*. (2006) showed that biochar (black carbon) increased the CEC and specific surface area of Anthrosols (aged between 600 and 8700 years) in the Brazilian Amason.

Table 5. Fertility properties of pecan shell-based biochar and the untreated Norfolk loamy sand soil (Novak *et al*., 2009).

Macroelements (g kg^{-1})	Biochar	Norfolk soil
Al	0.22	5.10
C	834.2	16.80
Ca	3.64	0.49
Fe	0.07	2.91
H	10.30	-
K	4.15	0.38
N	3.41	1.26
O	19.80	-
Si	104.9	424.8
Microelements (mg kg^{-1})		
Cu	14	4.6
Cr	0.31	23
Mg	698	445
Mn	78	55
Na	218	951
Ni	0.5	2
P	263	185
S	95	2
Zn	7	43

Table 6. The effect of pecan shell-based biochar on soil fertility characteristics of a Norfolk loamy sand measured 67 days after it was added at a rate of 2% (40 t/ha) by weight (Novak *et al*., 2009).

Characteristic	Unit	0% Biochar	2% Biochar	Net change	Relative %
pH_{water}	-	4.8	6.4	1.6	33
CEC	$cmol_c\ kg^{-1}$	5.7	5.9	0.2	3.5
Exchangeable acidity	$cmol_c\ kg^{-1}$	2.4	1.5	-0.9	-38
C	$g\ kg^{-1}$	17.4	29.2	11.8	68
Ca	$mg\ kg^{-1}$	437	692	255	58
Cu	$mg\ kg^{-1}$	0.6	0.8	0.2	33
K	$mg\ kg^{-1}$	35	69	37	106
Mg	$mg\ kg^{-1}$	117	89	-28	-24
Mn	$mg\ kg^{-1}$	12	10	-2	-17
N	$g\ kg^{-1}$	1.24	1.21	-0.03	-2.4
Na	$mg\ kg^{-1}$	5	4	-1	-20
P	$mg\ kg^{-1}$	31	34	3	10
S	$mg\ kg^{-1}$	9	4	0.5	-56
Zn	$mg\ kg^{-1}$	13	10	0.3	-23

CARBON SEQUESTRATION

Biochar is regarded as a chemically and biologically very stable C pool and can persist in nature for long periods of time (Schmidt & Noack, 2000). Charring biomass into biochar therefore has been proposed as a way to divert C from a rapid biological C cycle into a slow geological C cycle (Kuhlbusch & Crutzen, 1995) and prompts investigations into actively managing biochar as a means to sequester atmospheric carbon dioxide (CO_2) in soils and to mitigate climate change (Lehmann, 2007).

Adding biochar to agricultural soils is receiving much attention as a way to improve soil quality and enhance crop yields, with the added benefit of gaining carbon credits by carbon sequestration and therefore reducing greenhouse gas emissions (Luo *et al*., 2011). Biochar production and its utilisation have the potential to result in a C negative greenhouse gas balance by converting CO_2 that was fixed by plants from the atmosphere into a highly stable form of C and have therefore additional mitigation benefits as listed above (Table 2). This net mitigation benefit is greater than the CO_2-equivalent in the biomass utilised to produce biochar (Krull, 2009). Additions of biochar in soils also have the potential to reduce the amount of methane and nitrous oxide released by decaying plant matter in the soil (Jones *et al*., 2012).

Biochar can either be used to produce energy (through further combustion in the presence of oxygen) or it can be added to the soil (sequestrated). If energy maximisation is the key goal, then biochar (charcoal) should be used for further energy generation (mainly heat), thus following the rapid biological carbon cycle. This process is carbon neutral. However, if emission reductions and climate change mitigation through carbon sequestration is the aim, then biochar should be added to the soil. This process is carbon negative. Consequently, the emission reductions by adding biochar to soil are much greater than the fossil fuel offsets when using the biochar as energy (Krull, 2009).

CONCERNS AND RISKS

Nearly all of the publications read in preparation of this article recognised that carbon sequestration as a tool to mitigate climate change is one of the major advantages of biochar. This subject was also covered in a report to the US government (Bracmort, 2009). Still, the practical problems to the adoption of this technology are feedstocks availability, biochar handling (that it will stay where it was applied and not pollute the environment – i.e. dust), and biochar system deployment (each industry will have its own requirements and plants will therefore differ inherently) (Bracmort, 2009).

Wind erosion of biochar dust during spreading in preparation for incorporation was identified as an inhalation risk for humans (Jones *et al*., 2012).

Incorporation of biochar can alter a soil's indigenous soil biota. Many of the negative effects of biochar on soil biota are associated with a mineralisable or labile fraction often quantified and described as the volatile matter, as well as salts such as Na or Cl. However, in the long term, these effects may be of lesser concern as labile organic matter is mineralised and salts are leached from the soil (Lehmann *et al*., 2011).

No negative aspects were noticed from the three year old trial run by Jones *et al*. (2012). This is potentially an important observation with regard to the formulation of legislation for an environmental risk assessment required for the use of biochar in agriculture.

To date, most biochar research have tended to focus on problem soils (e.g. with excessive soil acidity or salinity, severe nutrient imbalances, critically low soil organic matter, sandy) where the responses of biochar addition can often be dramatic. However, these soils are not representative of fertile agricultural areas where the likelihood of biochar application from a practical and economic perspective may be greatest (Jones *et al*., 2012).

APPLICATION

Biochar is being used mainly with focus on agriculture. Before it reaches the soil ultimately, it can be used for many purposes and in the process its value enhances (i.e. the extraction of biogas and bio-oil to be used as source of renewable energy).

Why do you need it? / Who needs it? / Where is it needed?

The largest responses in terms of improvement of soil properties are from sandy soils with low organic matter levels and therefore a low potential retain water and nutrients, to produce crops and to sustain production.

How much to apply?

One to 30 t/ha (Krull, 2009), not exceeding 50 t/ha Lehmann *et al.* (2006), although some apply up to 100 t/ha (Jones *et al*., 2011).

How often?

Clear guidelines regarding the frequency of application are lacking. It is however assumed that annual application of up to 30 t/ha should be acceptable. Due to the potential of biochar to increase the pH of soils, only recommended quantities should be applied while regular monitoring of the soil's properties are advised.

CONCLUSION

The use of biochar is an ancestral practice which appeared more than 2 500 years ago in the Amazon as a soil improver. It is therefore not a new product but merely one that was rediscovered as indicated by the large number of papers published over the last 10 years. Research on biochar is still in its infant stage and many questions are still unanswered. Examples of issues that need attention includes the development of reliable guidelines to estimate cost- and carbon-effective production processes, the optimum use of biochar and criteria to know how to make a good biochar (in terms of stability, agronomic benefit, and ability to control and contain contamination by pollutant). We do not know for certain what the effect of biochar is on soil chemical, physical and biological properties or how crops will respond, but in general it’s more beneficial than detrimental.

Early indications are that biochar has the potential to sequestrate significant amounts of carbon for at least a century, but only time will tell whether it will ever be adopted for this purpose. Pilot biochar research is probably in progress to provide short-term answers but we do not know the long-term effects and we cannot afford to wait for 10 years to find out. If biochar has the potential to sequestrate large amounts of carbon for a very long time and therefore to mitigate climate change, then we have to act now.

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Biochar Could Offset Up to 12% of Greenhouse Gases, Says Study | Inhabitat - Sustainable Design Innovation, Eco Architecture, Green Building.

Australia and New Zealand Biochar Researchers Network http://www.anzbiochar.org/index.html.

Various items in 2009 including an advertisement for the Asian Biochar congress and Biochar – a burning issue by Simon Shackley. http://environmentalresearchweb.org/cws/article/opinion/39442.

EFFICACY AND APPLICATION OF BIOCHAR SOURCES – A REVIEW

Rianto van Antwerpen & Damien Sabatier

FSSA Technical Symposium

22 August 2012

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Scope of this talk

- Definition
- Manufacturing:
  - can it be made from sawdust?
- What is it doing to the soil?
  - AWC
  - CEC
  - Nutrition
  - Micro-organisms
- Can it remove CO_2 from the atmosphere – sequestration?

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Introduction

- About 2 500 years ago, farmers in the Amazon improved their soil's with charcoal to depths > 1m. Portuguese settlers later named this *terra preta*, or "black earth."
- Soil amendment with biochar is evaluated globally as a means to improve soil fertility and to mitigate climate change.
- The number of research reports published on this topic over the last 10 years is astonishing! A cursory search for the term "biochar" yielded 683,000 results.

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Definition

- Biochar is produced via a process termed pyrolysis (pyro = heat; lysis = breaking down).
- High temperatures are applied to organic matter in an oxygen deprived environment.
- Thus, the organic matter is “cooked” .
- Other terms used in literature for the same product:
  - Black carbon
  - Chars
  - Charcoal
  - Pyrogenic carbon

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Biochar Feedstock

- Sugarcane bagasse
- Sugarcane trash
- Apricot stones
- Giant silver grass
- Perennial ryegrass
- Wheat residue
- Pine bark
- Cherry stones
- Switch grass
- Apple wood
- Chicken manure
- Almond shells
- Grape seeds
- Casein
- Sewage
- Cattle manure
- Nut shells
- Pecan shell
- Algae
- Maize residue

The complete list is undoubtedly much longer but in principle any organic matter can be used as a feedstock for the production of biochar.

http://hines.blogspot.com/2010/05/baja-robs-biochar-log-rocket-retort.html

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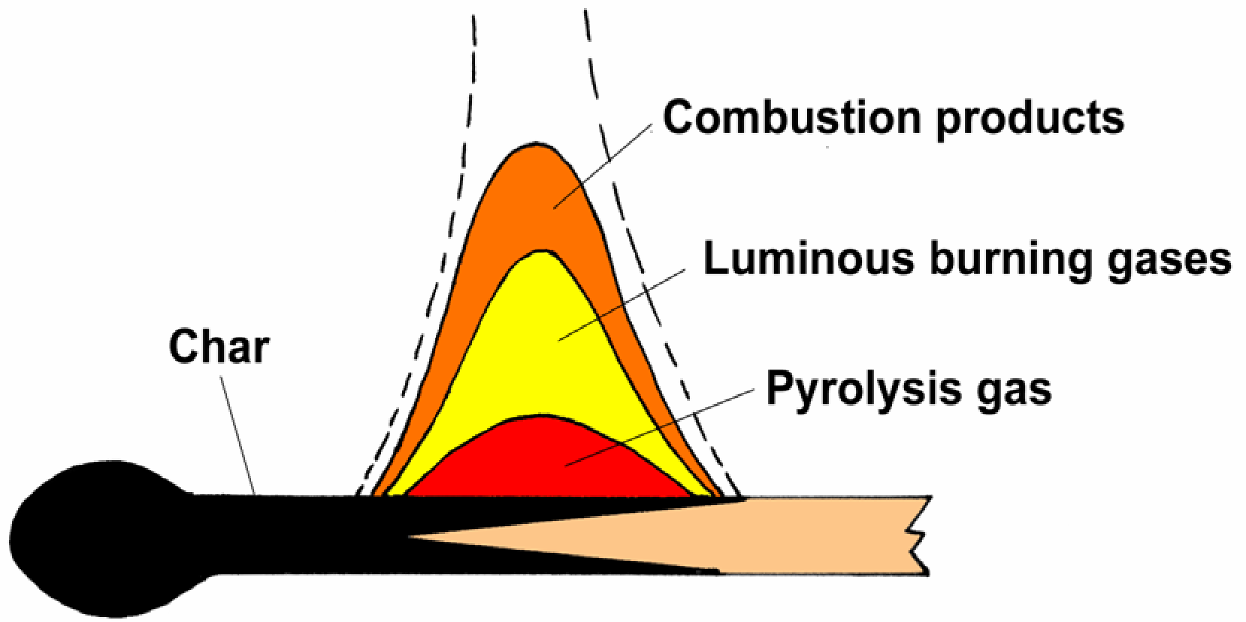
Products of Pyrolysis

- Biochar or Charcoal
- Bio-gas
- Bio-oil
- Heat



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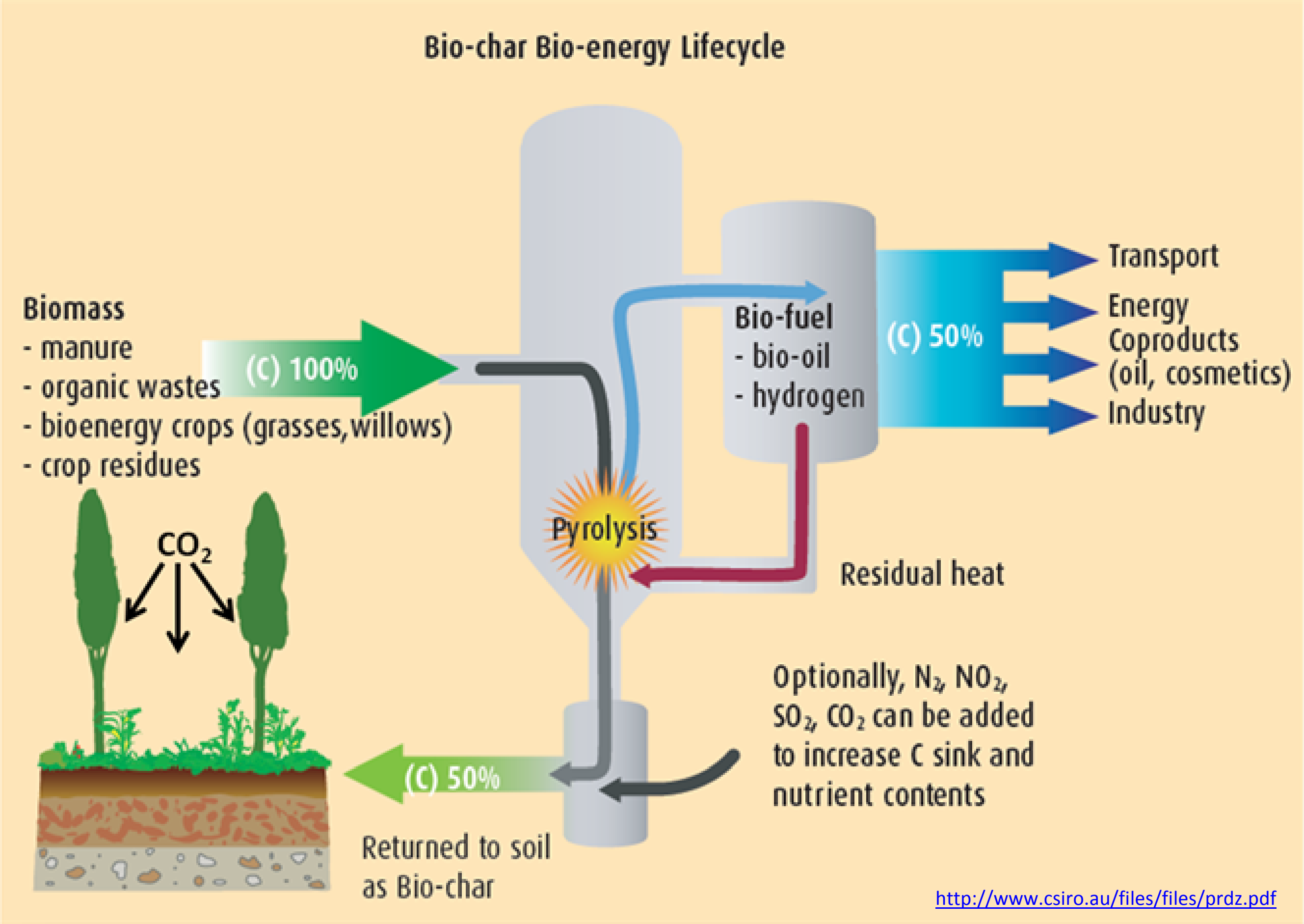
Manufacturing



http://www.csiro.au/files/files/prdz.pdf

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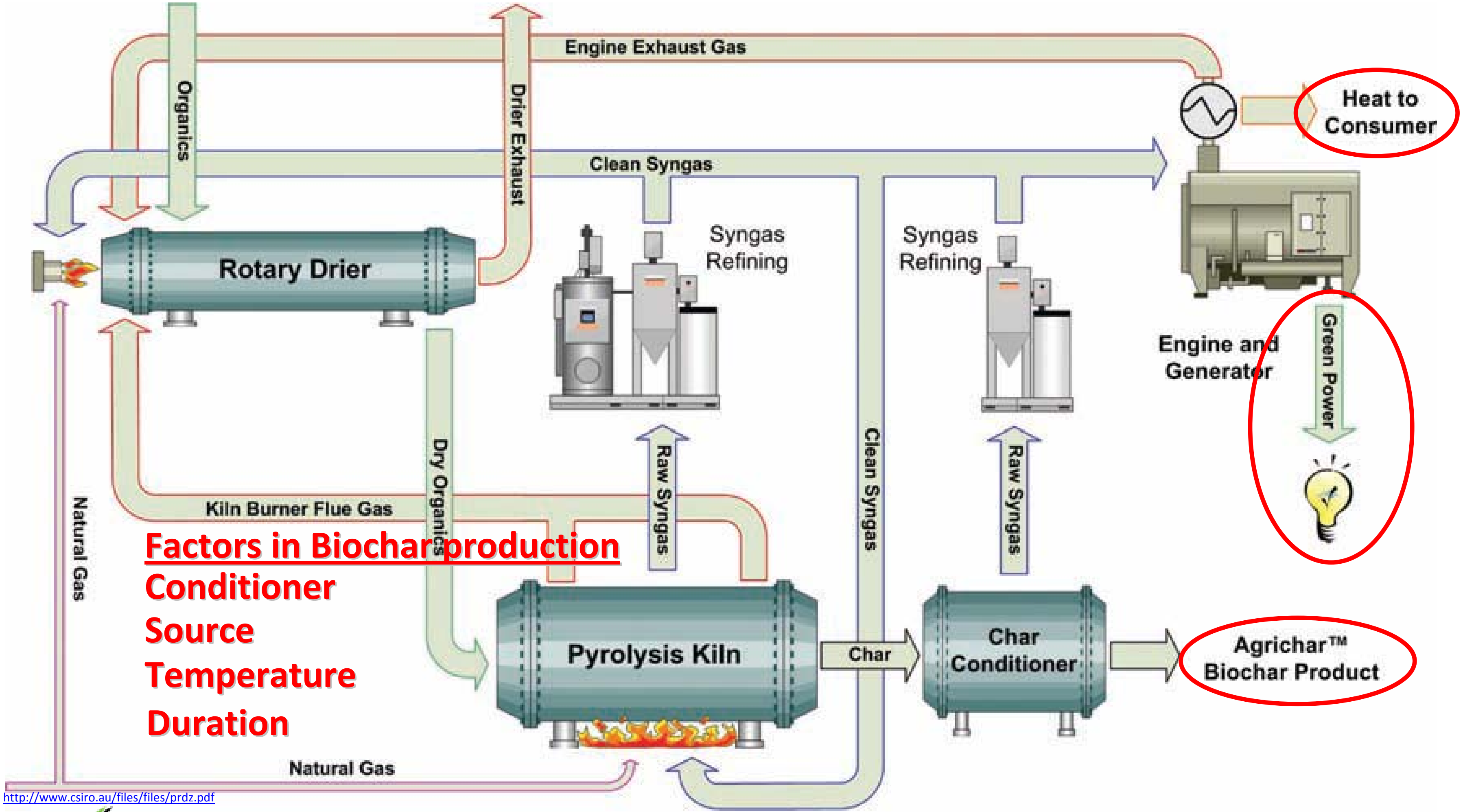
Example commercial operation



Factors in Biochar production

Conditioner

Source

Temperature

Duration

http://www.csiro.au/files/files/prdz.pdf

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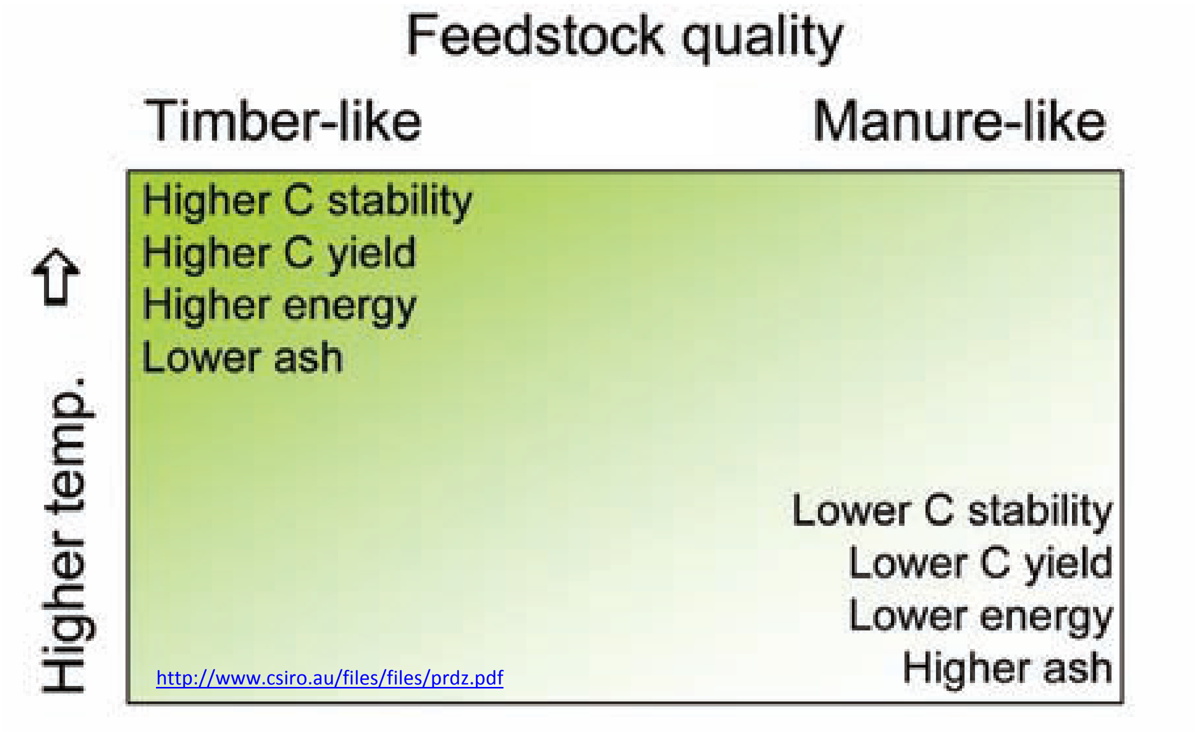
Effect of feedstock quality on properties of Biochar



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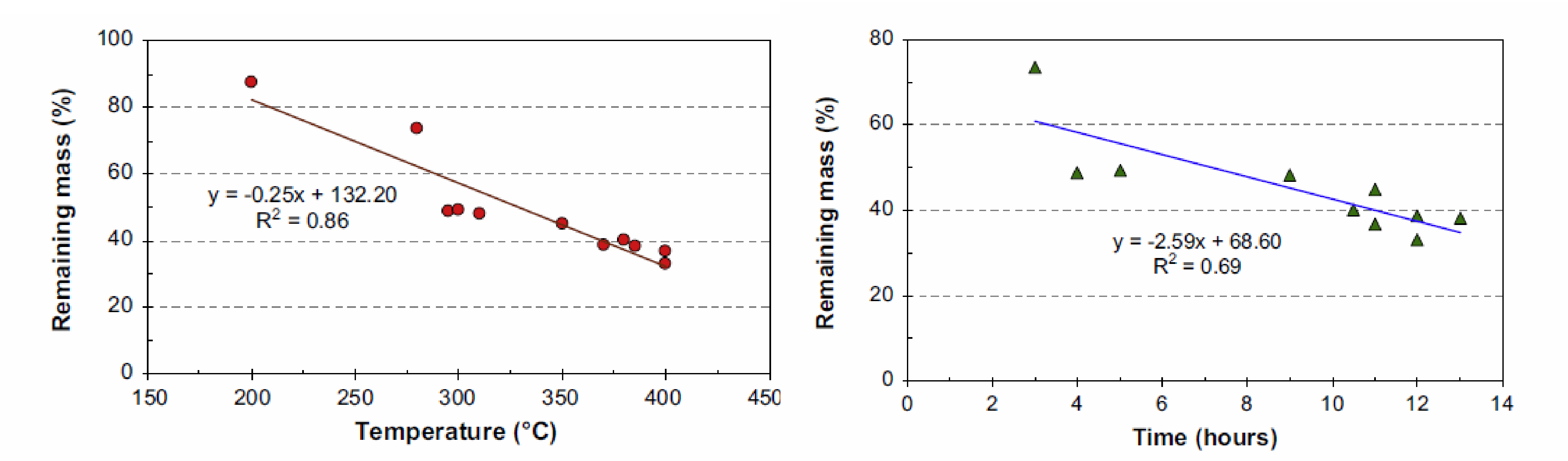
Effect of Temperature and Duration on Biochar Mass



Changes of charred mass of *Lolium perenne* (L) shoots as a function of charring temperature and duration.

Yakov Kuzyakov, Irina Subbotina, Haiqing Chen, Irina Bogomolova and Xingliang Xu (2009). Black carbon decomposition and incorporation into soil microbial biomass estimated by 14C labeling. *Soil Biology & Biochemistry* 41: 210–219. doi:10.1016/j.soilbio.2008.10.016

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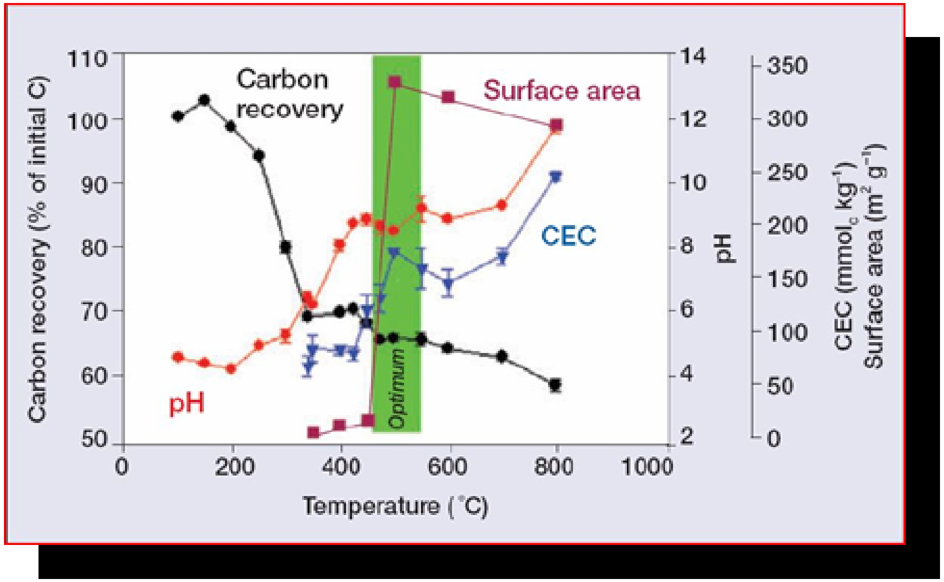
Effect of Temperature on Properties of Biochar



Property	Low temperature	High temperature
Temperature range (°C)	300 – 400	500-700
Surface area (m²/g)	< 200	> 300
Carbon (%)	> 40	< 30
Oxygen (%)	> 20	< 10

Chun Y, Sheng G, Chiou CT, and Xing B (2004). Compositions and sorptive properties of crop residue-derived chars. *Environ. Sci. Technol*. 38: 4649 - 4655.

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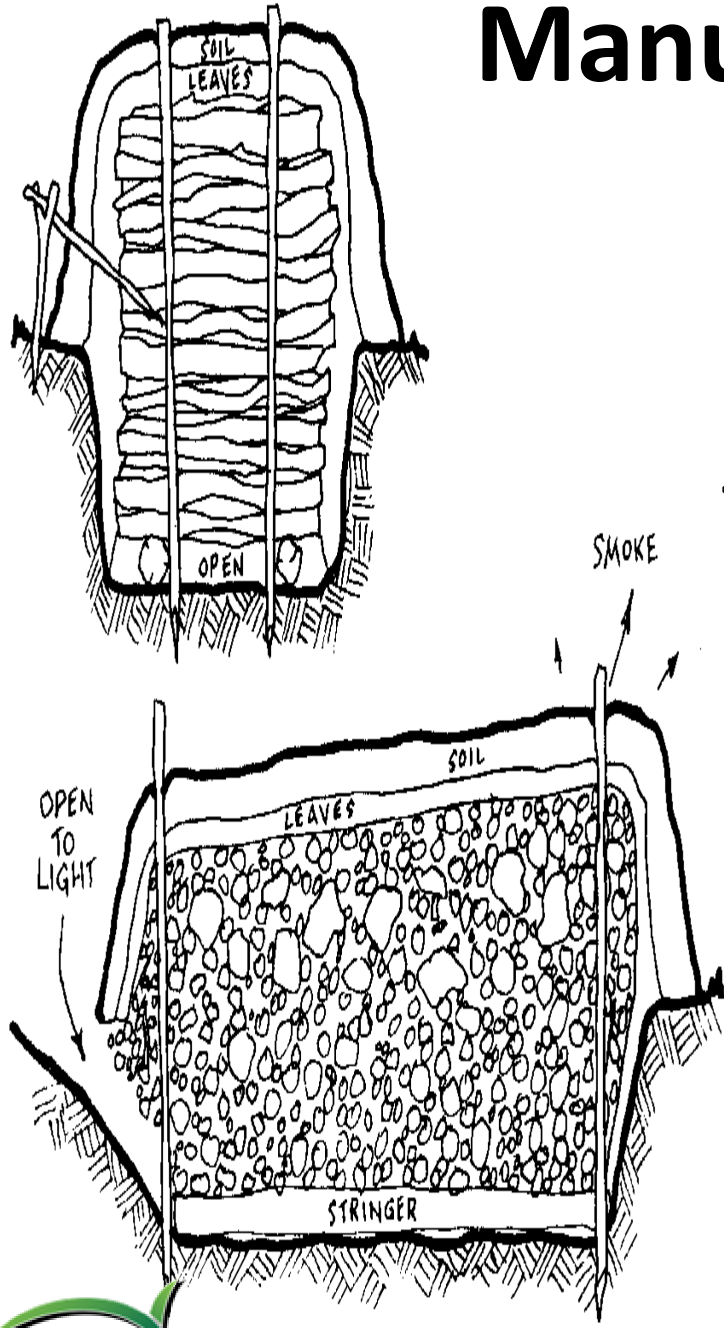
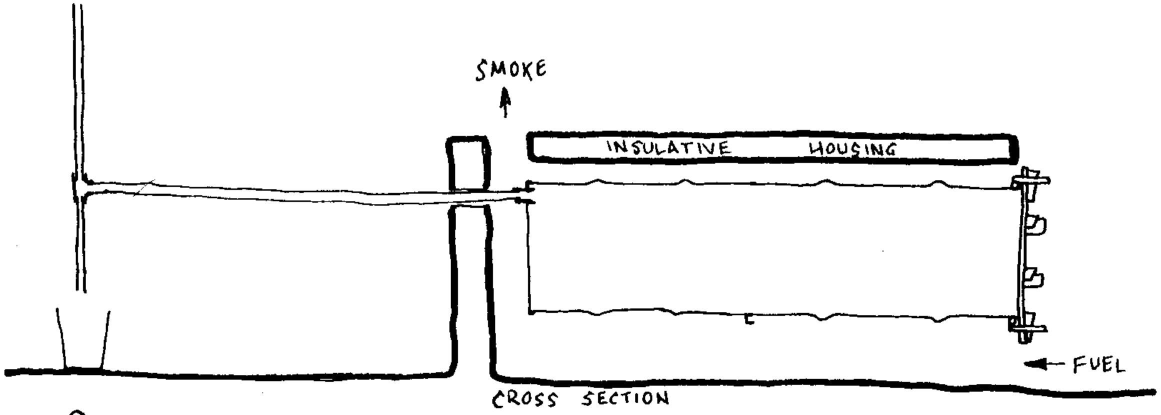
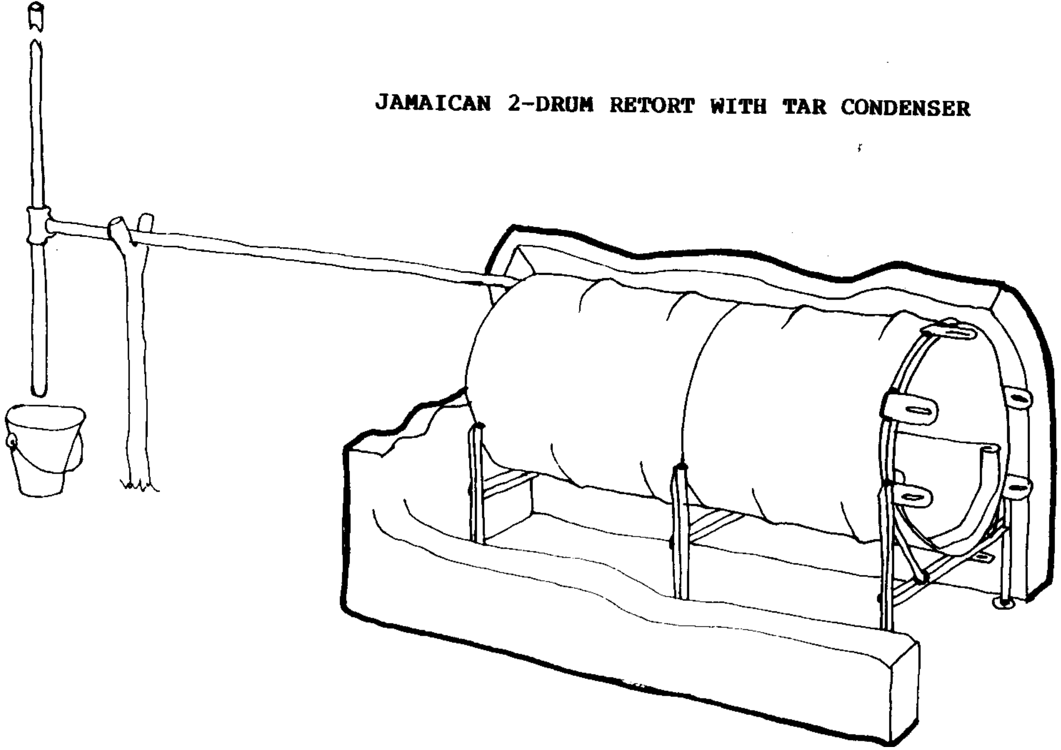
Manufacturing equipment





JAMAICAN 2-DRUM RETORT WITH TAR CONDENSER



http://www.cd3wd.com/cd3wd_40/vita/charcprd/en/charcprd.htm

Manufacturing equipment

Large capacity slow pyrolysis industrial system

Manufacturing equipment

Portable on-farm pyrolysis system

Biochar Companies and Equipment Manufacturers:

http://biochar.pbworks.com/w/page/9748038/BiocharManufacturers

- Carbon Diversion
- Eprida: Sustainable Solutions for Global Concerns
- Genesis Industries, licensee of Eprida technology
- BEST Pyrolysis, Inc. | Slow Pyrolysis - Biomass - Clean Energy - Renewable Energy
- Dynamotive Energy Systems | The Evolution of Energy
- Ensyn - Environmentally Friendly Energy and Chemicals
- Agri-Therm, developing bio oils from agricultural waste
- Advanced BioRefinery Inc.
- Technology Review: Turning Slash into Cash
- 3R Environmental Technologies Ltd. (Edward Someus)

  3R is the licensor and technology provider to
  - NviroClean Tech Ltd and
  - VERTUS Ltd.
- http://www.egenindustries.com/

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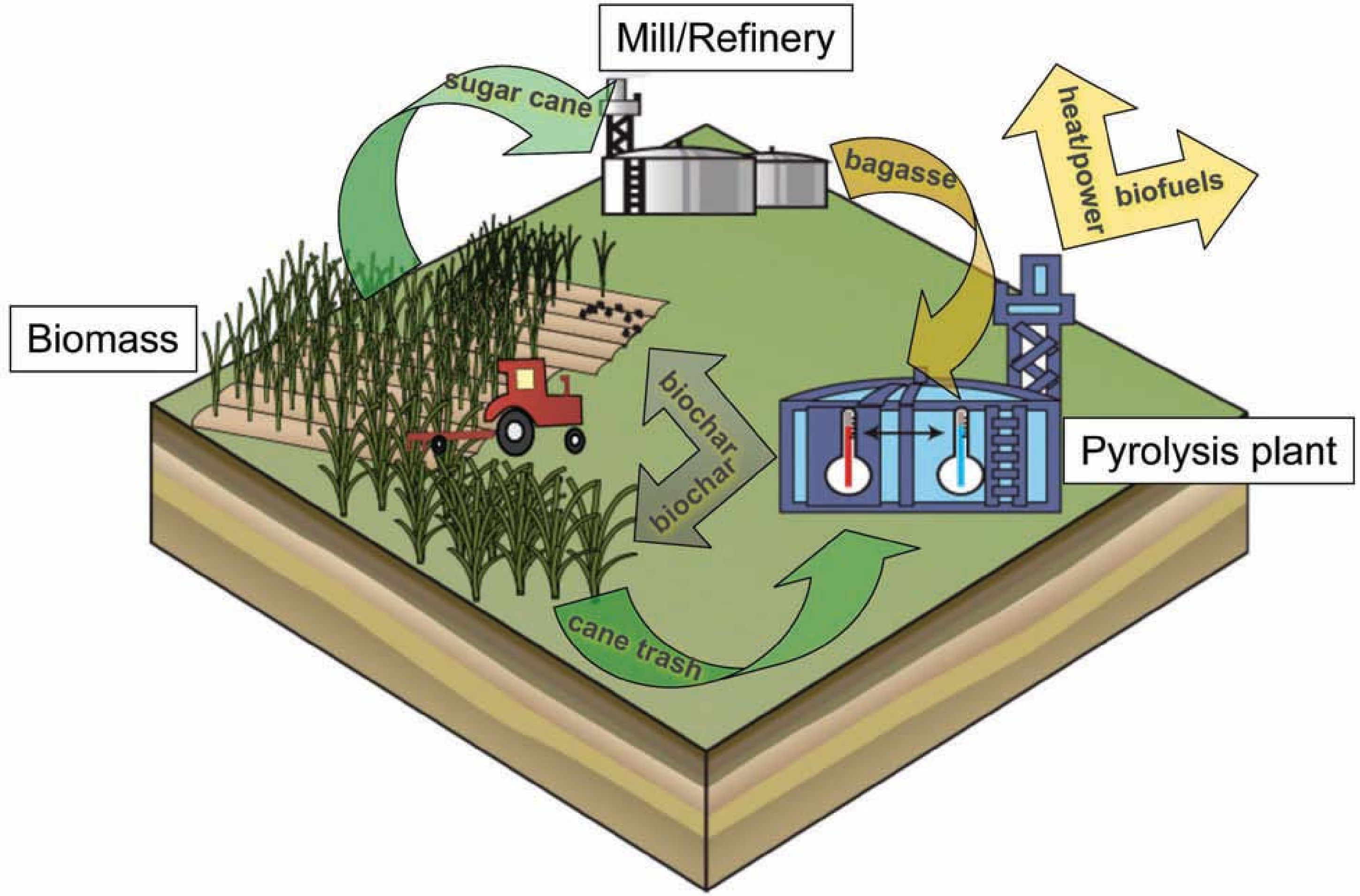
Illustration of the application of sugar cane trash and bagasse conversion to biochar. Note that the transport ways between field, refinery and pyrolysis plant should be kept to a minimum to avoid unnecessary fossil fuel emissions (Krull, 2009).



http://www.csiro.au/files/files/prdz.pdf

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Uses of Biochar

http://www.biochar.org/joomla/index.php?option=com_content&task=blogcategory

Biochar carbon sink Clean Development Mechanism (CDM) project in Indonesia

Ploughing biochar into the soil to store carbon

http://news.bbc.co.uk/2/hi/science/nature/7921619.stm

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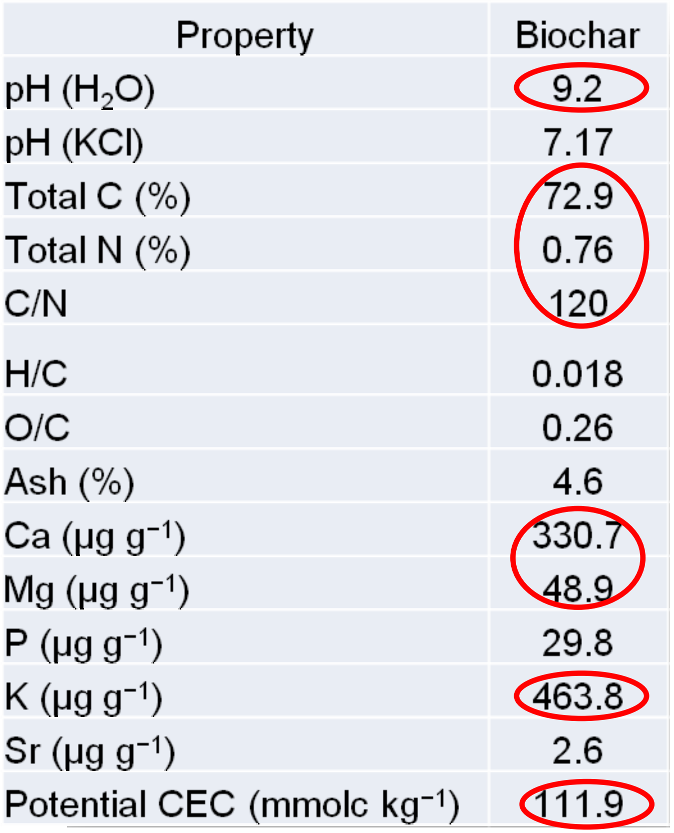
Properties of wood biochar made commercially for cooking



Property	Biochar
pH (H_2O)	9.2
pH (KCl)	7.17
Total C (%)	72.9
Total N (%)	0.76
C/N	120
H/C	0.018
O/C	0.26
Ash (%)	4.6
Ca ($\mu g\ g^{-1}$)	330.7
Mg ($\mu g\ g^{-1}$)	48.9
P ($\mu g\ g^{-1}$)	29.8
K ($\mu g\ g^{-1}$)	463.8
Sr ($\mu g\ g^{-1}$)	2.6
Potential CEC (mmolc kg^{-1})	111.9

Major *et al.* (2010). Maize yield and nutrition during 4 years after biochar application to a Colombian savanna oxisol. *Plant Soil* 333:117–128

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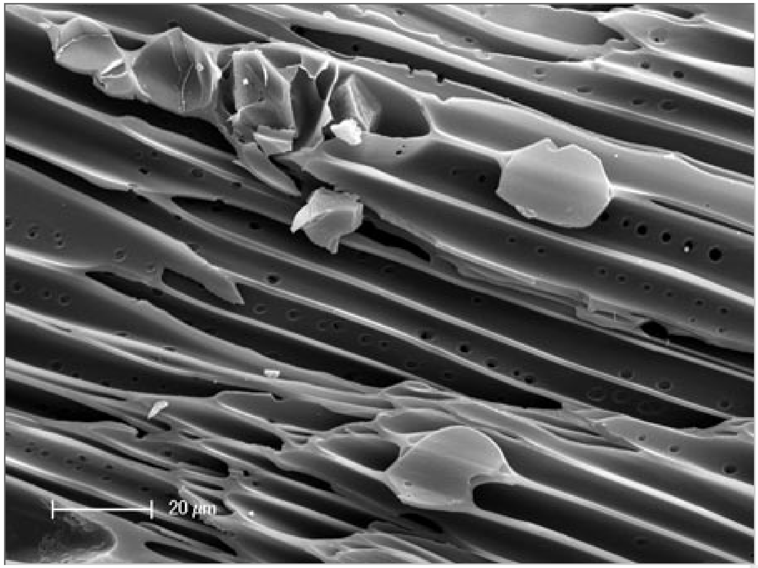
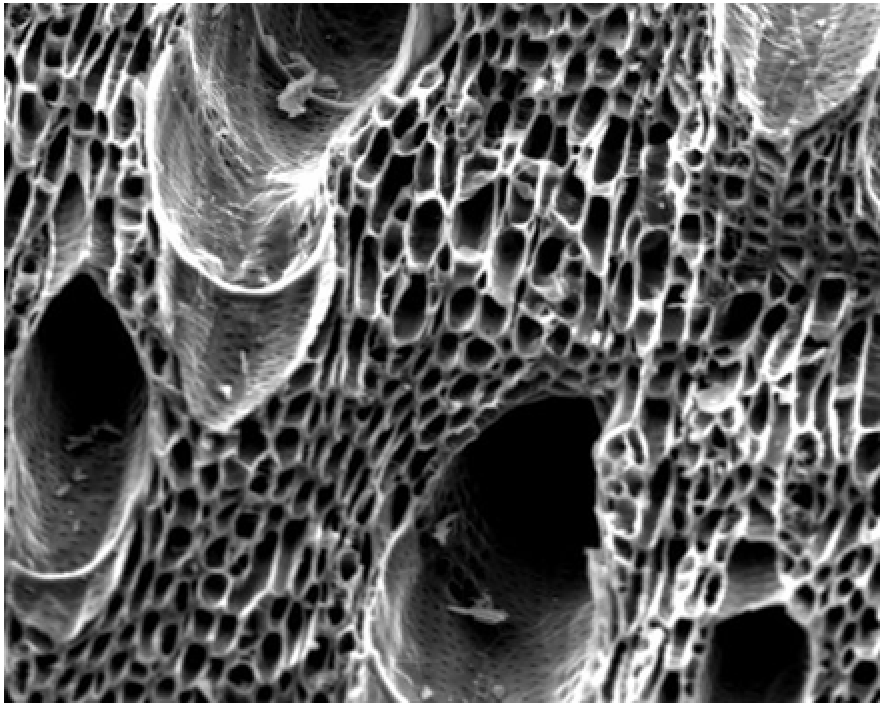
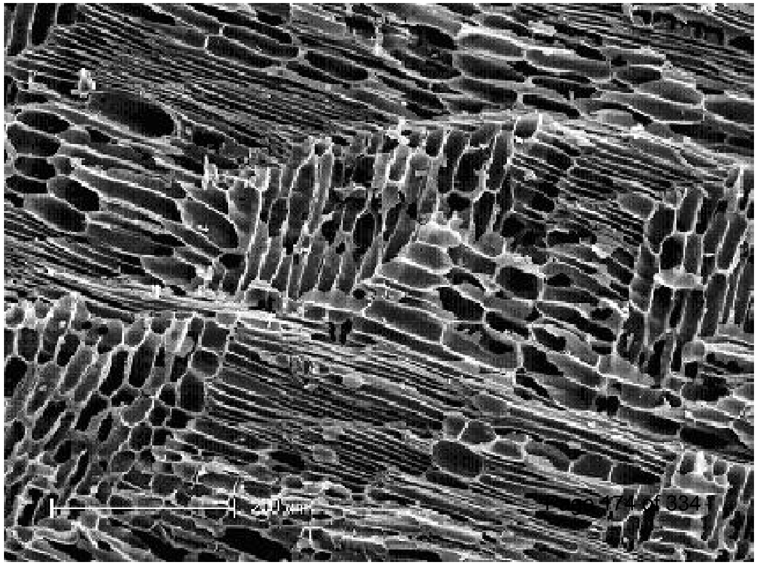
Properties of Biochar

Large surface area which is temperature dependant (i.e. 4 - 300m^2/g)





Biochar produced at 700 °C has a much greater adsorptive capacity and higher degree of micro-porosity than biochar produced at 400 °C.



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Properties of Biochar

- Has a high surface area.
- Has a high porosity.
- Very low bulk density (0.09 – 0.5 ton/m^3).
- Contains substantial amounts of energy.
- Stable form of carbon.
- pH ranges from 4 to 12.
- Has a high CEC.

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Concerns

- Biochar dust during production.
- Biochar dust during application.
- Incorporation of biochar can alter a soil’s indigenous soil biota.
- Can increase soil pH substantially at high application rates.
- Biochar is black and its application will change the albedo of the soil and reduce its ability to reflect light.

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Application

- Mostly beneficial to low potential soils (sandy, low OM).
- Up to 50 ton/ha.
- Annual application no more than 30 ton/ha.

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Soil benefits following additions of biochar

- Increased cation exchange capacity
- Suppressed methane emission
- Reduced nitrous oxide emission (estimate 50%)
- Reduced fertilizer requirement (estimate 10%)
- Reduced leaching of nutrients
- Stored carbon in a long term stable sink (sequestration)
- Reduces soil acidity: raises soil pH temporarily
- Reduces aluminum toxicity
- Increased soil aggregation due to increased fungal hyphae
- Improved soil water handling characteristics
- Increased soil levels of available Ca, Mg, P, and K
- Increased soil microbial respiration
- Increased soil microbial biomass
- Stimulated symbiotic nitrogen fixation in legumes
- Increased arbuscular mycorrhyzal fungi (?)
- Enhanced plant growth
- Mitigate climate change

http://biochar.pbworks.com/w/page/9748043/FrontPage

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Sequestration?

- Biochar is regarded as a chemically and biologically very stable.
- Biochar addition at 140MgCha^{-1} to 3000 Mha globally will result in a total of 400 Pg of carbon sequestration potential (Pg = g x 10^{15}).
- This is approximately 50 times the current anthropogenic carbon emissions of 7.8 PgCyr^{-1}.
- Charring biomass is a way to divert C from a rapid biological C cycle into a slow geological C cycle and to mitigate climate change.

http://www.orgprints.org/13268/1/Biochar_as_a_soil_amendment_-_a_review.pdf

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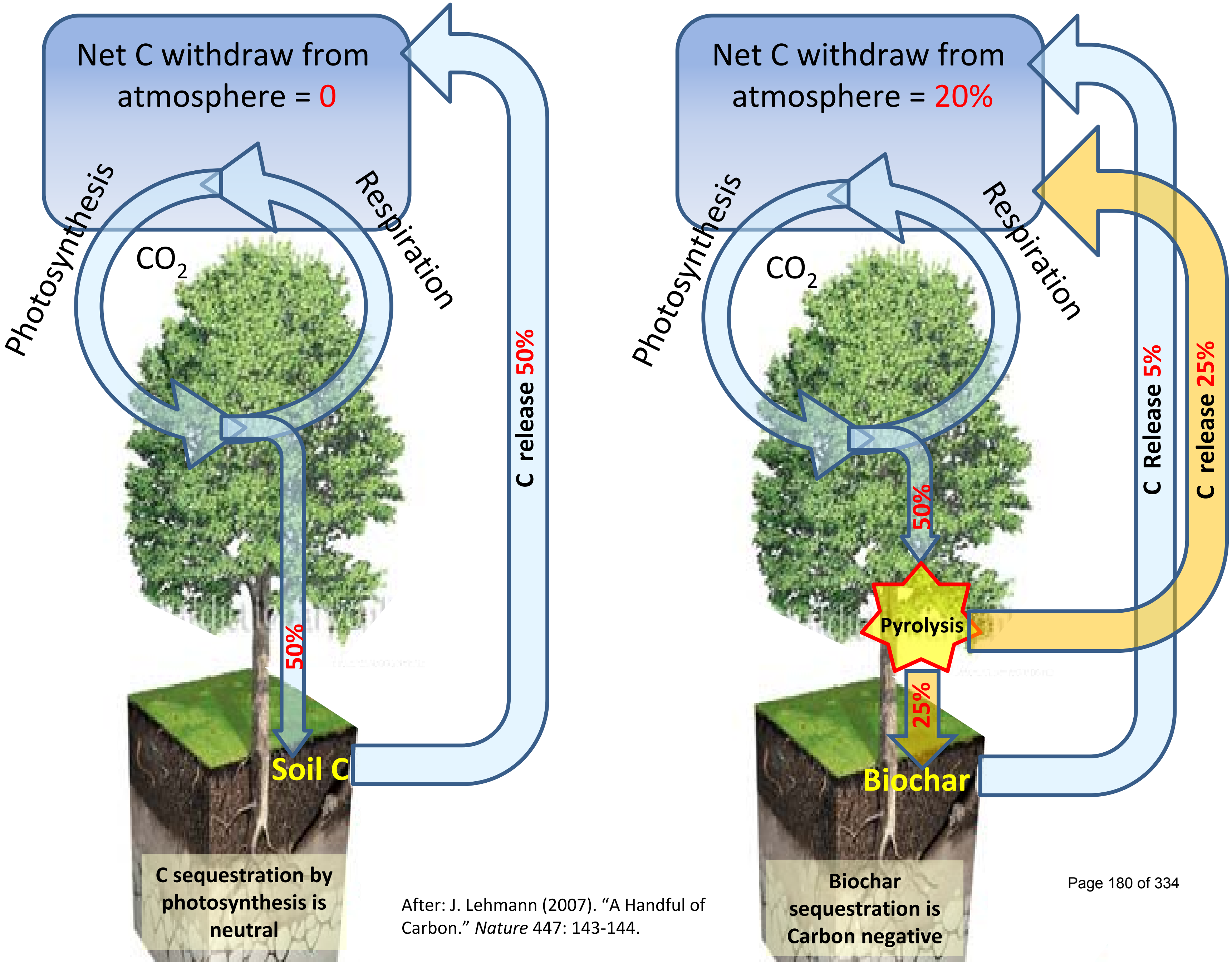
Carbon Cycle for Soil Carbon and Biochar



Net C withdraw from atmosphere = 0

CO$_2$

Photosynthesis

Respiration

C release 50%

50%

Soil C

C sequestration by photosynthesis is neutral

Net C withdraw from atmosphere = 20%

CO$_2$

Photosynthesis

Respiration

50%

Pyrolysis

25%

Biochar

C Release 5%

C release 25%

Biochar sequestration is Carbon negative

After: J. Lehmann (2007). “A Handful of Carbon.” *Nature* 447: 143-144.

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Benefits of Biochar

Author(s)	Study	Results
Oguntunde et al (2004)	Comparison of maize yields between disused charcoal production sites and adjacent fields. Kotokosu watershed, Ghana	Grain yield 91% higher and biomass yield 44% higher on charcoal site than control.
Kishimoto & Sugiura (1985)	Soybean on volcanic ash loam, Japan	0.5 $Mgha^{-1}$ char increased yield 151% 5 $Mgha^{-1}$ char decreased yield to 63% 15 $Mgha^{-1}$ char decreased yield to 29%
Kishimoto & Sugiura (1985)	Sugi trees on clay loam, Japan	0.5 $Mgha^{-1}$ wood charcoal increased biomass 249% 0.5 $Mgha^{-1}$ bark charcoal increased biomass 324% 0.5 $Mgha^{-1}$ activated charcoal increased biomass 244%
Chidumayo (1994)	Bauhinia trees on alfisol/ultisol	Charcoal increased biomass by 13% and height by 24%
Glaser et al (2002b)	Cowpea on xanthic ferralsol	67 $Mgha^{-1}$ char increased biomass 150% 135 $Mgha^{-1}$ char increased biomass 200%
Iswaran et al (1980)	Pea, India	0.5 $Mgha^{-1}$ char increased biomass 160%
Iswaran et al (1980)	Mung bean, India	0.5 $Mgha^{-1}$ char increased biomass 122%

Dominic Woolf (2008). Biochar as a soil amendment – a review, Page 20, Table 5
http://www.orgprints.org/13268/1/Biochar_as_a_soil_amendment_-_a_review.pdf

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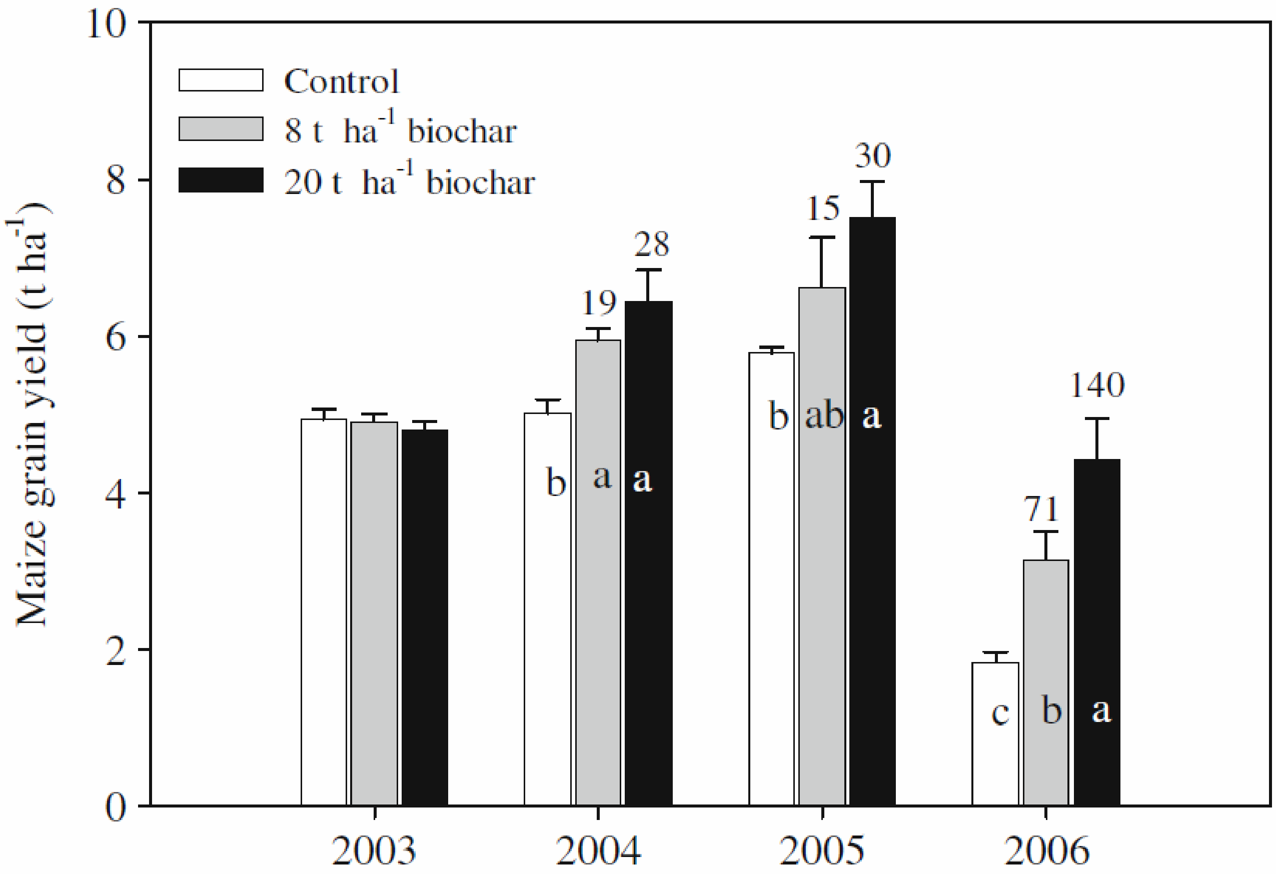
Maize grain yield on a Colombian savanna Oxisol amended with biochar



Major et al (2010). Maize yield and nutrition during 4 years after biochar application to a Colombian savanna oxisol. *Plant Soil* 333:117–128

Maize grown with and without Biochar

http://www.biochar.info/biochar.biochar.info.cfml

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Potential to increase yield

© 2012

Conclusions

- Although we don’t yet fully understand how crops will react following the addition of biochar, it’s reasonable to except that most crops will respond favourably.
- We don’t need to wait 10 years to adopt this technology. It was used 2500 years ago to improve the quality of poor soils – and those soils are still highly valued.
- Should we have a toolbox full of technologies to choose from to mitigate climate change, Biochar as a near permanent storage ability of C should be in that box.

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GRANULAR ENHANCEMENT AND SOIL HEALTH: WHAT DOES THE PREMIUM REALLY COST?

Andre Cilliers
Biofix: Product Manager,
Lake International Technologies (Pty) Ltd

Fertilizer coatings are receiving increased attention recently and various materials and coating agents are being used to enhance or add value to granular fertilizers. With the onset of precision farming and the ever-increasing pursuit of higher crop yields, farmers, scientists and fertilizer manufacturers are looking for new ways to differentiate themselves from competitors and to aid farmers in increasing yields and quality of crops. Regular NPK fertilizers have been highly effective in increasing yields, as have pesticides, new varieties/cultivars and lately even GM crops. However, a new era is dawning where farmers are looking towards additional soil amendments which will improve soil health, yields and quality. In the fertilizer industry, value is being added to NPK blends by adding trace elements, natural soil enhancers and even microbes.

LAN coated with iron oxide.

These coatings come at an extra cost to the farmer which has to be recovered from the crop in the form of yield or quality increases. In some cases farmers consider a dust-free granular fertilizer as being worth the additional charge, and consequently many blenders coat their blends to curb dust only. Coating products that are used to curb dust only are often waste stream products which are in many cases effective at suppressing dust. Other coating products add value to fertilizers by decreasing nitrogen volatilisation or attaching value-adding powders to granules. Most products used to attach powders are oil based. However, over time oils migrate into granules, and the powders attached to the surface of the granules detach, and the valuable powders are lost or create a safety hazard.

The principal of attaching powders to each granule means that whatever is being added to the fertilizer blend will be evenly distributed throughout the farmers' field, making the product more available to the plant. The most effective way of attaching large amounts of powder to granules (up to 4%) is by using Biofix. Biofix is a natural product made from components which are of vegetable origin. The product is an emulsion, which polymerises on the surface of fertilizer granules, and does not migrate into granules. Powders are therefore effectively bound and not released, even over months of handling and storage. Biofix is capable of attaching-up to 8 kg of powders for every kilogram of Biofix applied to a fertilizer blend, depending on the quality (dustiness) of the raw materials, and also at a minimum of 3.5 kg per metric ton of fertilizer. This is the minimum Biofix required to coat the entire surface area of 1 metric ton of fertilizer. One thing that needs to be seriously considered when doing any coating is that nitrogen fertilizers and organics together pose an explosive risk. There is legislation and best practice procedures that should be followed when adding any organics to nitrogen fertilizers.

The coating and powder attachment procedure. Raw materials are mixed, powder is added, Biofix is sprayed into the blender, and coated fertilizer emerges from the blender.

In the coating process, the application and even coverage of a coating agent is of the utmost importance. All granules have to be coated so that the maximum area for attachment is provided. If coating levels are too low, only a portion of the fertilizer granules will be covered with coating, and therefore a smaller area will be available for attachment. Through extensive studies and calculations, it has been found that 3.5 kg of Biofix will effectively coat 1 metric ton of fertilizer. For effective coating, batch blending systems tend to be more effective at coating than continuous systems. A coating is achieved into a granule in two ways: direct spray “hits” and rub-off between granules. In the case of batch systems, rub-off is better than in a continuous system. However, in some continuous systems excellent coating can be achieved. An example of a highly effective continuous system is a coating cylinder, which feeds fertilizer into one end of a coating cylinder which is angled, and the fertilizer is coated while tumbling through towards the exit of the cylinder.

Poor uneven coating. **Good even coating.**

Batch systems include paddle blenders, ribbon blenders and drum mixers. In a batch system the blend is “held” for a certain length of time and mixed. This is the window period for coating. During the mixing process, Biofix is applied to the blend as the granules are mixed. The fertilizer is coated by direct contact of the spray with the granules, and then by rub-off between granules. Powders, including dust, adhere to the coated granules and are effectively attached. The shape of raw material granules is also of utmost importance for optimal rub-off. Round regular-shaped granules have a better rub-off, while “chips” such as KCl and some forms of ammonium sulphate do not rub off very well. However, such granules are highly effective at trapping dust in the creases of the uneven granule surface.

Trace elements coated with Biofix to a NPK blend. Note the white powder in the creases of the KCl granule.

The spray of a coating agent is just as important as the blender into which it is being sprayed. Biofix is a viscous liquid, and research and experience has shown us that an air-atomising nozzle works best for the application of such liquids. The alternative is a hydraulic nozzle, where the spray pattern is determined by the pressure behind the liquid. In the case of air-atomisers however, the spray pattern is determined by the air pressure which is fed to the nozzles, and not by the pressure behind the liquid. For this reason air-atomisers are chosen above hydraulic nozzles, which also tend to block more easily than air-atomisers do, because of the smaller spray orifice.

Ideal spray nozzle for application onto granular fertilizer in a blender

Fertilizer coating is therefore not a simple procedure, and the correct equipment and coating agent should be used, if coating is to be performed effectively. At a premium of 0.78% of the fertilizer price per ton, Biofix enhanced fertilizer is the best way to produce a premium range of fertilizer for any fertilizer company.

If you're serious about plant nutrition & soil health

Granular Enhancement and Soil Health: What does the Premium really cost?

Andre Cilliers

BIOFIX®
Intelligent Agriculture

Lake International Technologies

What do the experts say?

- Shoji and Gandeza (1992) say that the ideal fertilizer should have a minimum of the following three characteristics:
  - A **single application** should supply enough nutrient throughout the entire growing season to meet the plant demand for optimum growth;
  - A **maximum percentage recovery** to achieve the largest return for the cost of the input;
  - **Minimum detrimental effects** on the soil, water and atmospheric environment.

- Biofix® provides a method of adding value to granular fertilizers using an environmentally friendly emulsion coating and customized equipment.

What is BIOFIX®

- **Completely natural** binding agent for granular fertilizers;
- **Biodegradable** in the soil;
- Used to **attach/add** value to granular fertilizers and blends;
- **Particle size**: preferably **150 microns** or less;
- Attachment of any **Value Adding** powders;
- **Nutrition** for **beneficial soil microbes. NON** Toxic to beneficial organisms.

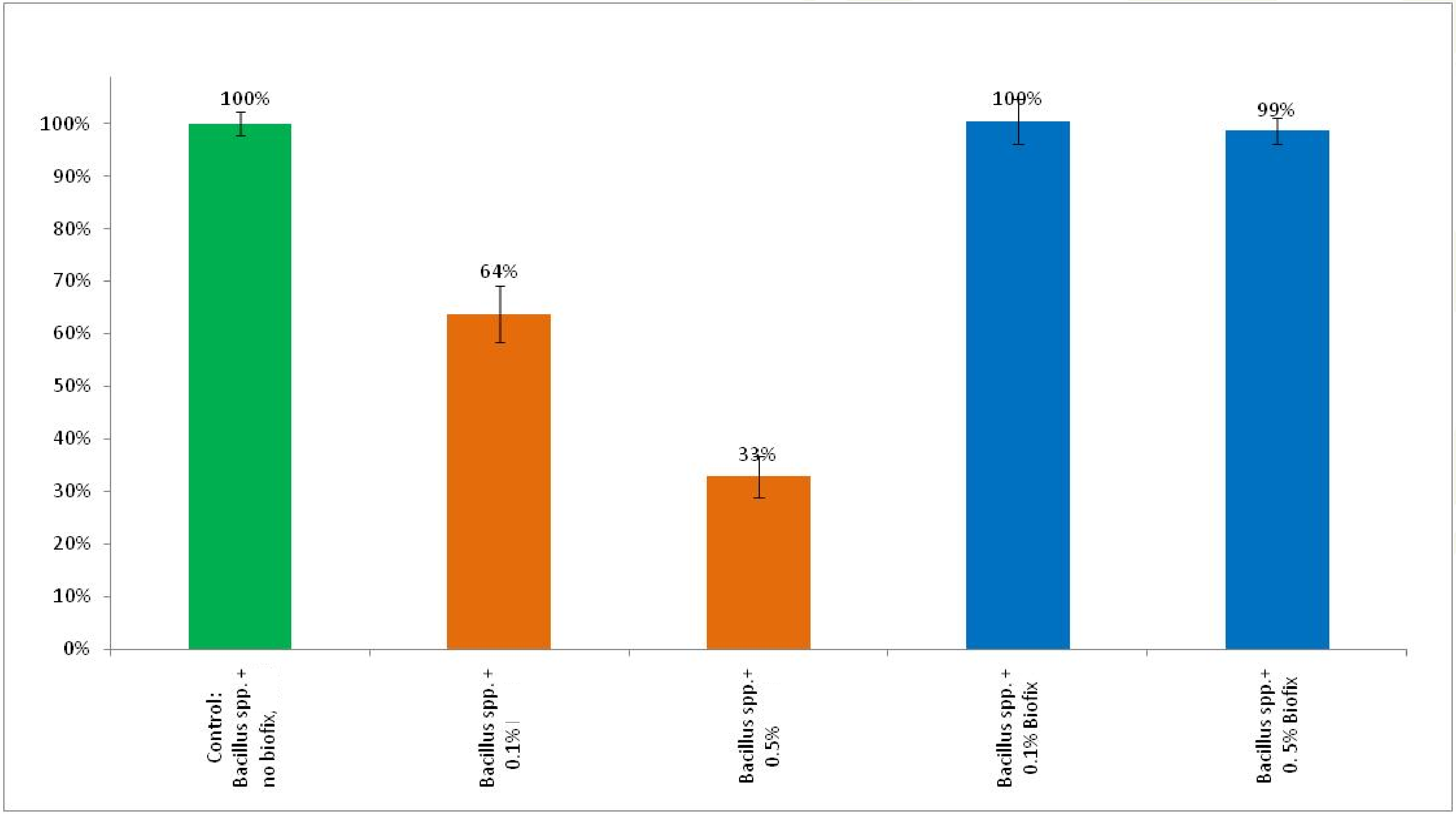
!

One thing that needs to be seriously considered when doing any coating is that nitrogen fertilizers and organics together pose an explosive risk. There is legislation and best practice procedures that should be followed when adding any organics to nitrogen fertilizers.

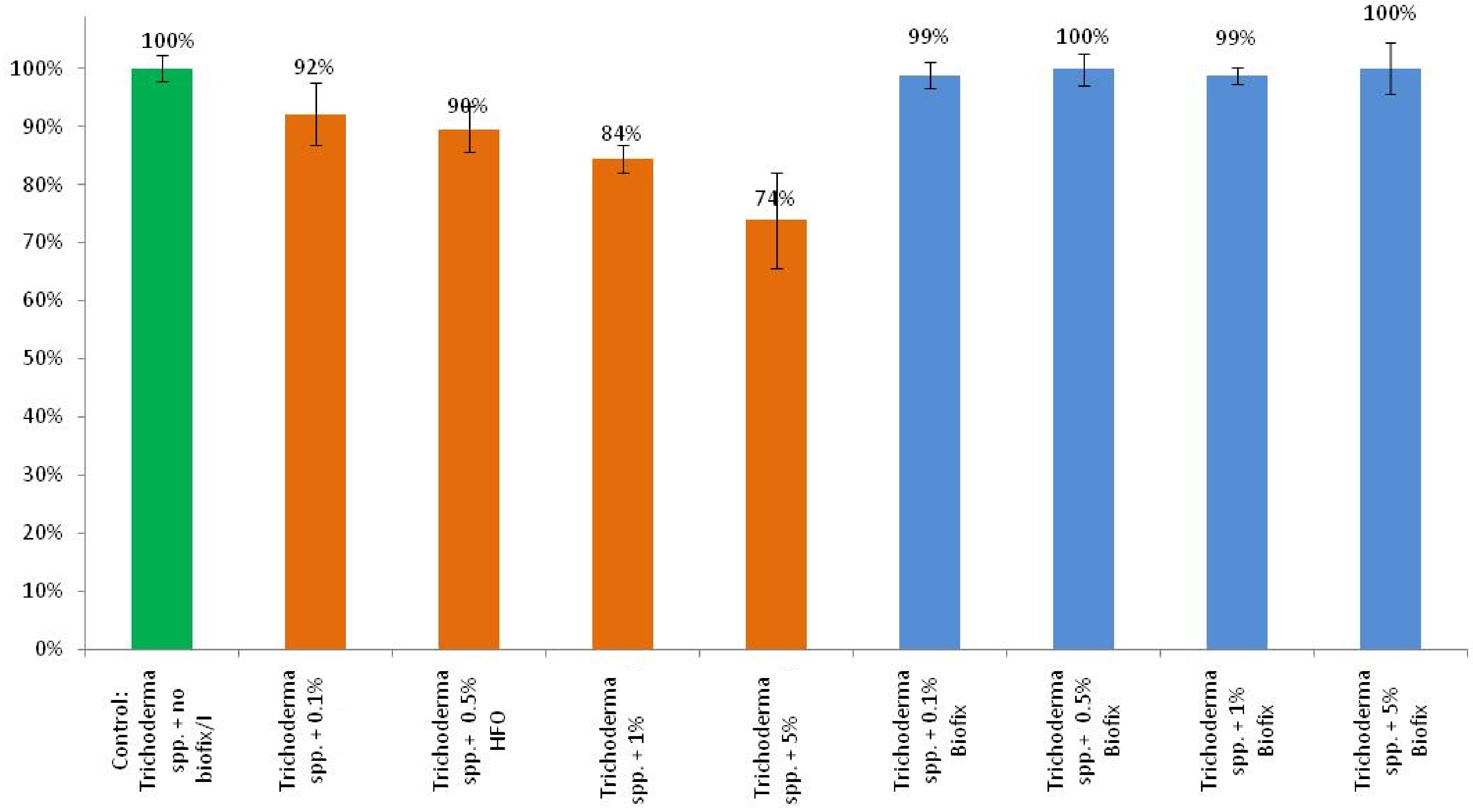
What does BIOFIX® CO$T?

- “Other” coating agents at 3 kg per ton: Premium 0.42%
- Biofix at 3kg per ton: Premium 0.78%
- Difference/Saving 0.36%, in Rand terms R18 per ton
- At what cost are we saving this?

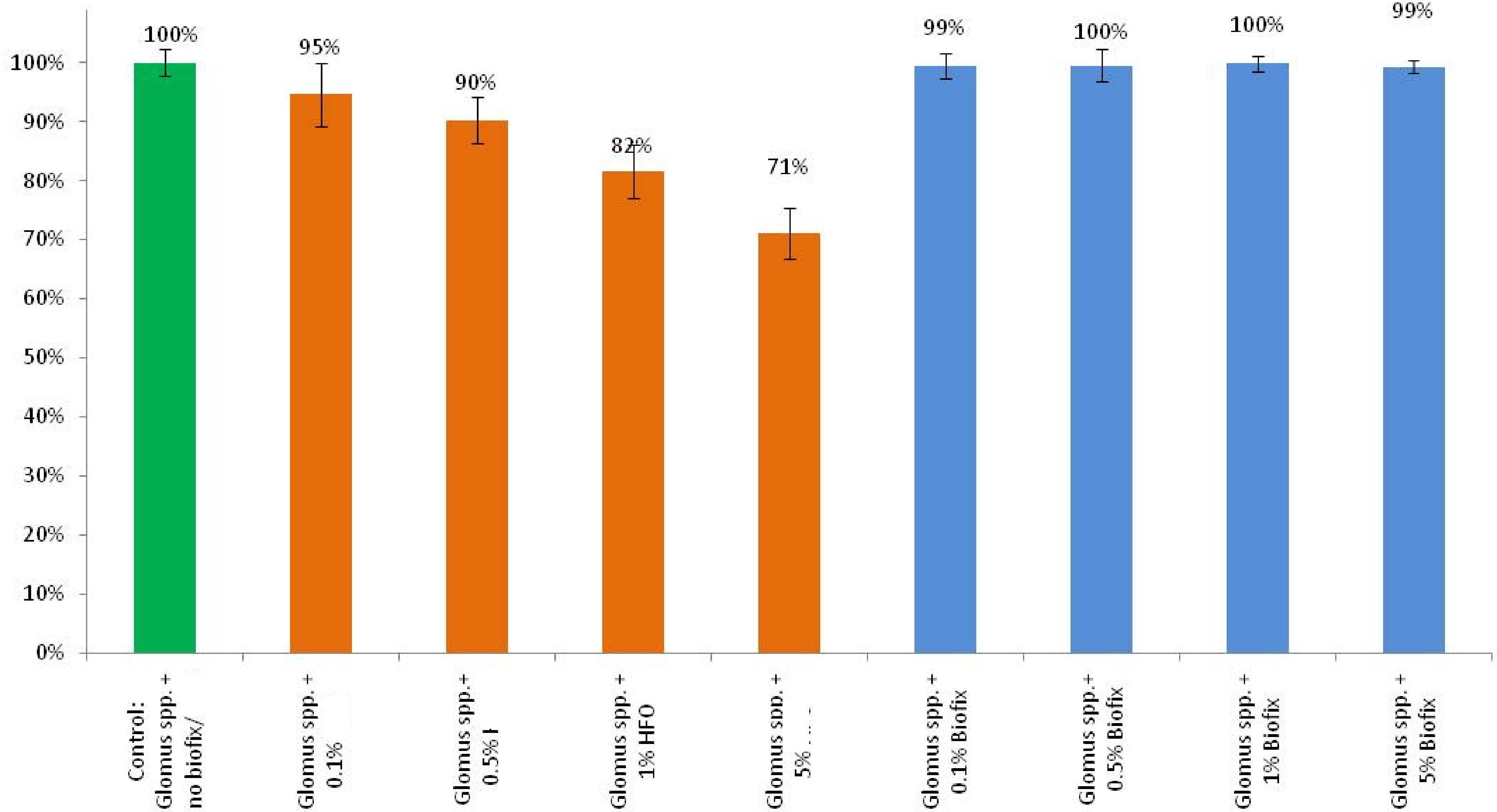
% Survival of Bacillus spp. after contact with XXX and Biofix.



% Survival of Trichoderma spp. after contact with XXX and Biofix



% Survival of arbuscular mycorrhizal spp. after contact with XXX and Biofix



Effect of Various Granular Enhancement Agents on the survival of Soil Microbes after 10 minutes

Soygro bio-fertilizers Soygro bio-fertilizers Soygro bio-fertilizers Soygro bio-fertilizers

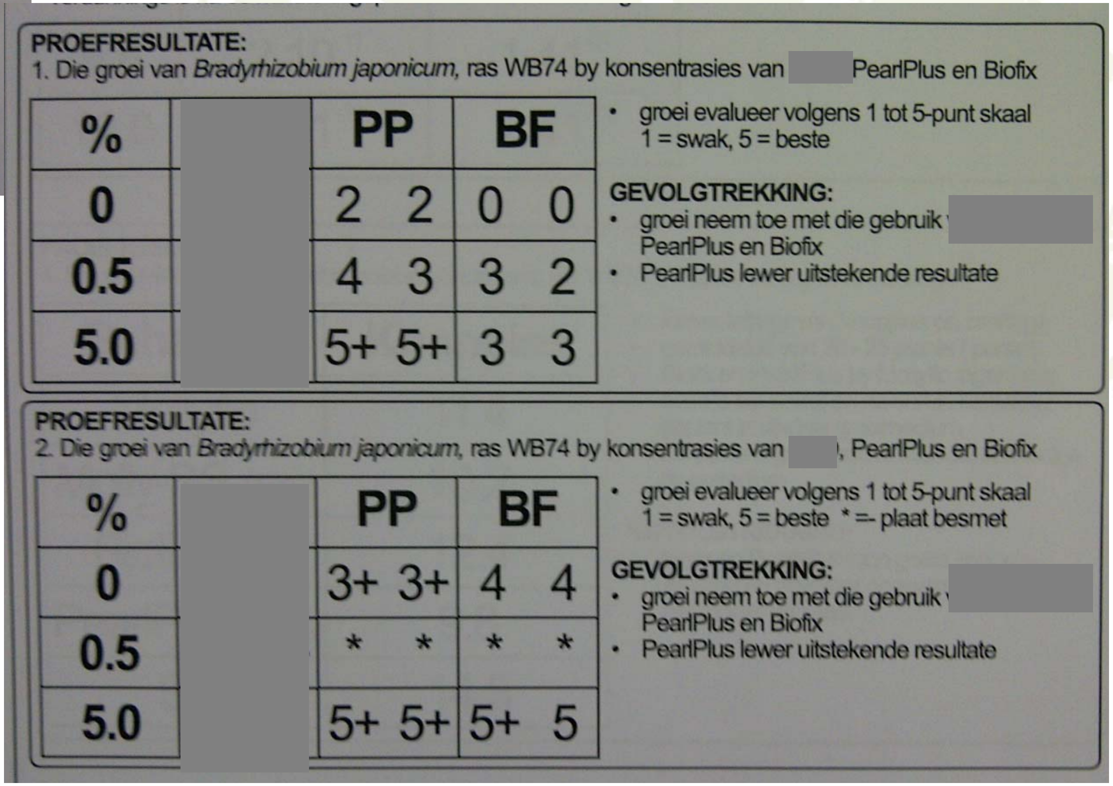
Soygro (Edms) Bpk

Reg no: 98/05788/07

Ber

AANDAG: André Cilliers
Lake International Technologies
Sel: 082 499 6515
E-pos: Andre.Cilliers@lake.co.za

INSAKE: **Biofix / PearlPlus /** [redacted]



PROEFRESULTATE:
1. Die groei van *Bradyrhizobium japonicum*, ras WB74 by konsentrasies van [redacted] PearlPlus en Biofix

%	[redacted]	PP		BF	
0	[redacted]	2	2	0	0
0.5	[redacted]	4	3	3	2
5.0	[redacted]	5+	5+	3	3

- groei evalueer volgens 1 tot 5-punt skaal
  1 = swak, 5 = beste

GEVOLGTREKKING:
- groei neem toe met die gebruik v[redacted] PearlPlus en Biofix
- PearlPlus lewer uitstekende resultate

PROEFRESULTATE:
2. Die groei van *Bradyrhizobium japonicum*, ras WB74 by konsentrasies van [redacted], PearlPlus en Biofix

%	[redacted]	PP		BF	
0	[redacted]	3+	3+	4	4
0.5	[redacted]	*	*	*	*
5.0	[redacted]	5+	5+	5+	5

- groei evalueer volgens 1 tot 5-punt skaal
  1 = swak, 5 = beste * =- plaat besmet

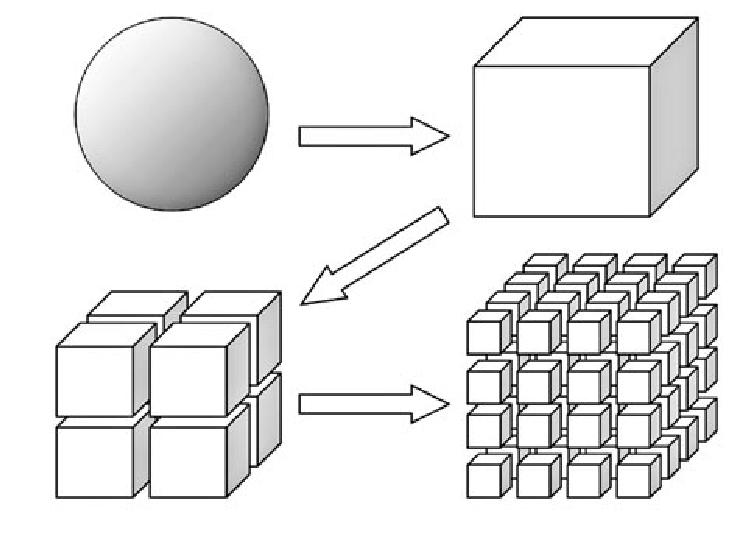
GEVOLGTREKKING:
- groei neem toe met die gebruik v[redacted] PearlPlus en Biofix
- PearlPlus lewer uitstekende resultate

Other differences between Enhancement Agents

- Oil based agents do not set, and attached powders are released over time;
- Many other products are waste-stream products;
- No technical and mechanical back-up team.

It is Very Important to do the Application Correctly

- Raw Materials should be of Good Quality;
- Surface area of dust is massive!!!!

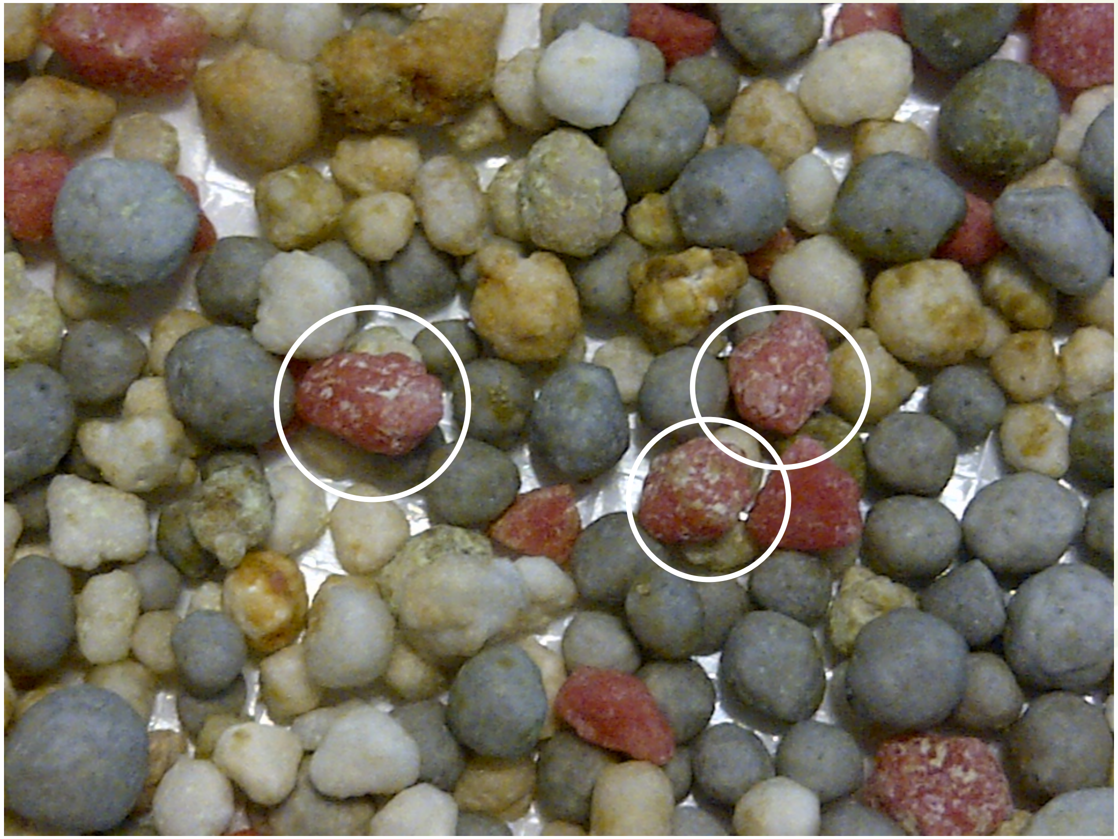


- For effective attachment of powders, blend components have to be as dust-free as possible.
- Coverage is achieved by direct spray hit, as well as rub-off between granules.
- Ideal placement between crevices of granules.

✗

✓

Effective trace element attachment to a NPK blend.

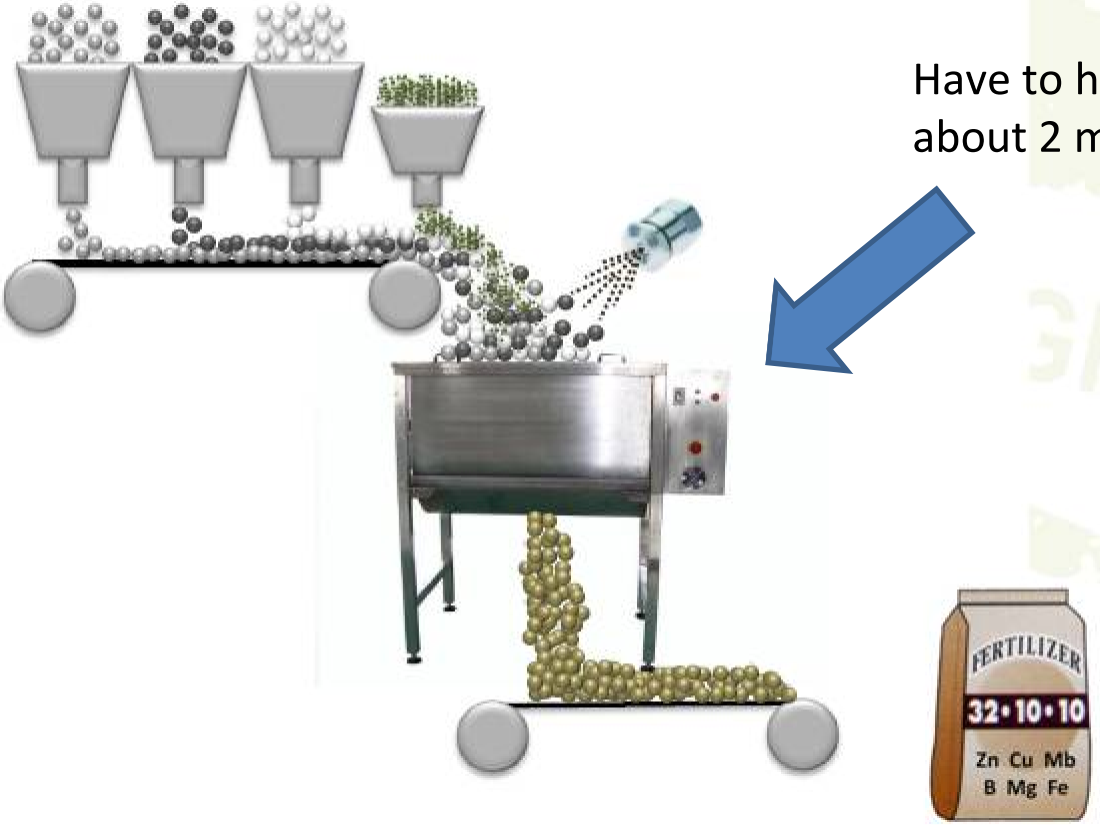


Effective trace element attachment to a NPK blend.

What are Nozzles and what are not?

30.09.2011 13:40

The Ideal Coating Procedure



Have to hold the fertilizer for about 2 minutes in a batch

Lake's Coating Plant, Natalspruit
Ribbon Blender

Double Axle Paddle Blender

Batch Systems:

Cement Mixer Drum Blender

Batch Systems:

Which Nozzles are best for Application?

Air Atomizing Nozzles are best in most Applications

Hydraulic nozzles – pressure determines spray pattern.

Continuous Systems

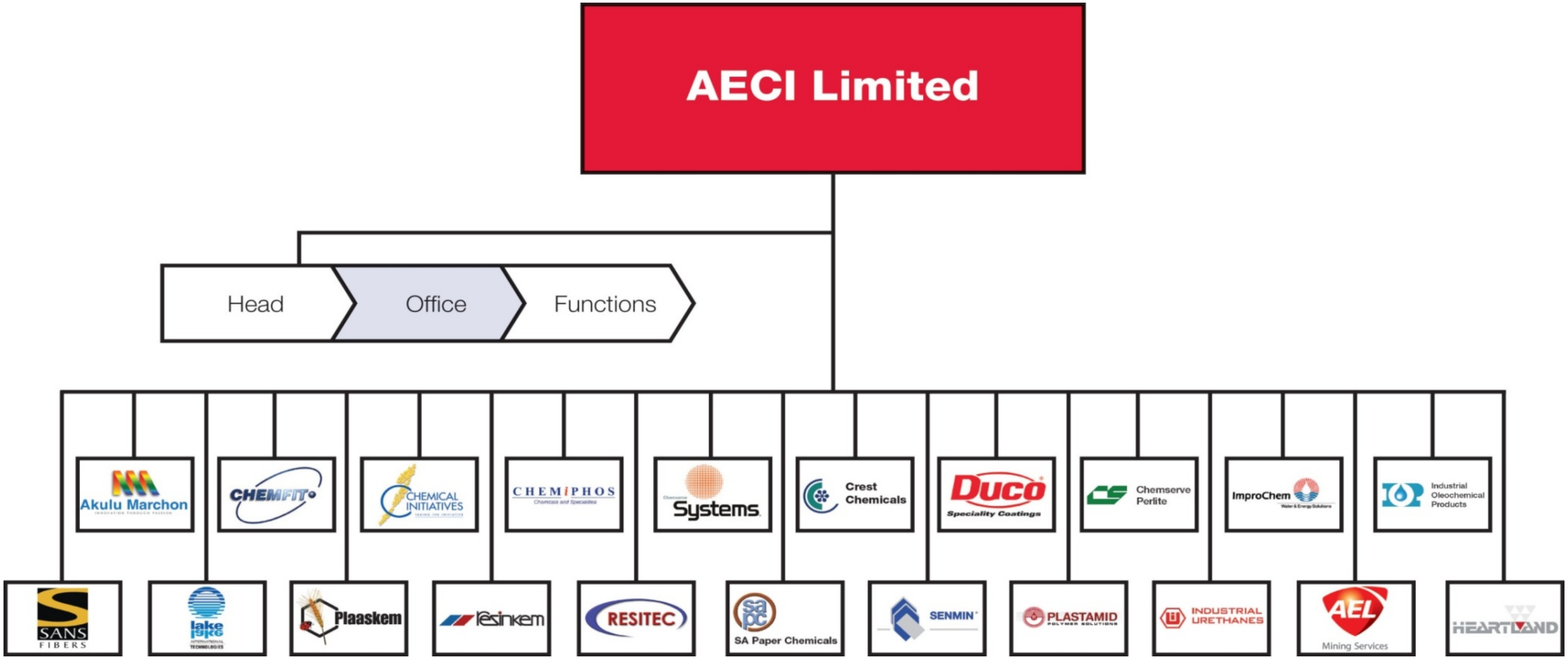
Cement Mixer: Batch Blender

Continuous System: Belt Coating

Batch System: Blender

Continuous system: no Biofix

Continuous system: Biofix added



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Head Office Functions

Manufacturing – Umbogintwini, Durban

Thank you…


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Na
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If you're serious about plant nutrition & soil health
BIOFIX®
Intelligent Agriculture
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Intelligent Agriculture

CROP NUTRIENT SULPHUR: SUPPLY AND DEMAND

Lawrence Jansen van Rensburg
Ecologika, a division of Chemical Initiatives (Pty) Ltd

BACKGROUND

Agriculture can be considered as the conversion of dispersed resources into concentrated forms of energy and nutrients, through the production of crops for human and animal consumption or conversion into downstream derivatives such as biofuels. Crops are bred to deliver specific results in terms of yield and disease resistance, given climatic and soil conditions. In order to deliver these results, specific, and high nutrient, inputs are required which are typically supplied through the application of mineral fertilizers. To do this cost effectively, the farmer needs to understand the crops' requirements and ensure the efficient delivery of these inputs to the growing crop.

Sulphur, like nitrogen, is an essential element in the growth of all living things. Its application has largely been taken for granted as adequate levels were inadvertently supplied to growing crops through fertilizers such as single super phosphate or through industrial emissions. This scenario has changed in many parts of the world and sulphur deficiencies have increasingly been identified as the limiting factor in crop yields and crop quality [1]. The main reasons for this situation include: the move to high analysis fertilizers to deliver the crop's NPK requirements cost effectively; increasing crop yields; reduction in sulphur-based pesticide usage; and a reduction in industrial emissions - which effectively provided free sulphur units. Left unchanged, these factors have the potential to limit yields and impact on the nutritional value or disease resistance of crops.

Sulphur is a building block of proteins, enzymes and vitamins and is a key ingredient in the formation of chlorophyll and for fixing nitrogen in legumes [2]. Sulphur deficiencies can manifest as stunted growth, yield reductions and reduced crop quality. The presence of adequate levels of sulphur can however enhance the uptake of other nutrients and improve the nitrogen utilisation efficiency [3]. This paper addresses the key role that sulphur plays in plant physiology and its potential impact on human health through the production of amino acids such as cysteine and methionine. It will also address how sulphur demand is met through atmospheric deposition, soil organic conversion and applied nutrients.

PART 1: SULPHUR DEMAND BY CROPS

IMPORTANCE OF PROTEIN FORMATION

Plants are the primary converters of sunlight and supply the bulk of utilisable energy, vitamins, minerals, proteins and essential fatty acids for human and animal health. It is estimated that plants provide as much as 65% of the per capita supply of protein globally [4]. In particular, cereal grains provide a substantial portion of the world's food protein followed by food legumes. The exact make-up of the dietary protein balance is very dependent upon socio-economic conditions, but highlights the importance of growing healthy crops as efficiently as possible to meet global nutritional food demand.

The basic components of living cells are proteins, made up of amino acid building blocks. Plants synthesise these amino acids from the primary elements, carbon, oxygen, hydrogen and nitrogen obtained from the air and soil via metabolic pathways, facilitated by photosynthesis. Each protein has a specific function, such as a structural function, a metabolic function (enzymes), a transport function and a defence function against disease [5].

Methionine and cysteine are the two most important sulphur-based amino acids out of 20 amino acids involved in the formation of proteins. The formation of these sulphur amino acids is dependent upon the availability of sulphur to the growing crop.

Methionine is the initiating amino acid in the synthesis of almost every eukaryotic protein, while cysteine plays an important role in protein structure, protein reactivity and in protein-folding pathways [6].

SULPHUR AND PLANT PHYSIOLOGY

Plants typically take up sulphur in the form of a sulphate ion (SO_4^{2-}). Small quantities can be absorbed through the leaves in the form of H_2S or SO_2, as these molecules are small enough to pass through the stomata - but high levels can be toxic to the plant.

The sulphate ion is absorbed from the soil solution into the roots and vasculature system, from where specific trans-membrane transporters move it into root cells or leaf tissues for assimilation or storage in vacuoles [7].

The sulphate anion is relatively inert and requires activation before it plays a role in cellular metabolism. This activation is achieved through the reaction with ATP, a by-product of photosynthesis, to form adenosine 5'-phosphosulfate (APS). APS is the starting point of sulphate assimilation in plants.

This assimilation can proceed via two routes, namely the sulphatation process in the cytosol or the reduction pathway in the plastids [7].

Sulphatation pathway

In the sulphatation pathway, APS is phosphorylated to 3'-phosphoadenosine-5'phosphosulphate (PAPS) through the activity of APS-kinase (APSK) as shown in Figure 1 below. PAPS serves as the precursor for multiple downstream metabolites including flavanols, choline, betains, extracellular polysaccharides and glucosinolates [7]. The exact role that many of these substrates play is unclear, but increasing evidence suggests that the sulphatation pathway may serve to regulate enzyme activity [8], while glucosinolates act as a defence mechanism against herbivore attack by releasing toxic cyanide [9].

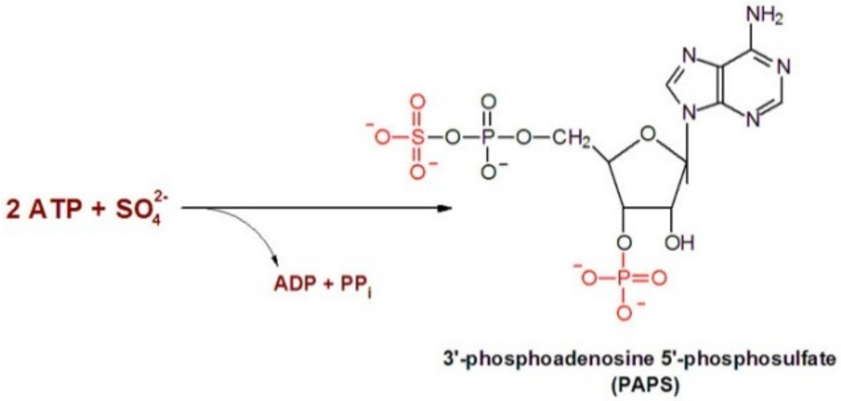

Figure 1. Phosphorylation of APS to produce PAPS

Reduction pathway and cysteine formation

In the reductive pathway, the sulphur in the sulphate moiety in APS is stepwise reduced from the 6+ oxidation state to the sulphide 2- oxidation state to form the amino acid cysteine [8]. Cysteine is the precursor for all downstream compounds containing fully reduced sulphur [7].

The transport of the sulphate anion into the cell and its subsequent reduction to sulphide is an energy intensive process for the plant harnessing the reducing power of photosynthesis requiring a total of 11 electrons and ATP [7, 8]. The full reduction process occurs in the chloroplast of the leaf as all intermediates of the process are found there whilst the presence of cysteine in the mitochondria and cytosol also implies that certain steps of the assimilation process also take place in these organelles [7].

Cysteine thus serves as the intermediary between sulphate assimilation and downstream metabolisation in plants. Optimal crop yields and quality can only be obtained under conditions of optimal sulphate provision together with all other nutrients [7].

Methionine biosynthesis

One such downstream derivative of cysteine is the S-containing amino acid methionine. As with cysteine, methionine serves both as a primary plant cell metabolite and also as a building block for protein synthesis.

Methionine is synthesised by a complex process involving three pathways, namely (i) the C- amino backbone provided by aspartate, (ii) the sulphur moiety supplied by cysteine and (iii) methylation of the thiol group by folates [10].

Methionine is classified as an essential amino acid, meaning that it is not formed in the human body, but is absorbed through the intake of food.

Methionine's importance lies in its role as the precursor for S-adenosyl methionine (SAM), a versatile methylating agent. Figure 2 shows the central role of SAM in the metabolism of methionine to form important vitamins, pectins, carboxylic acid, phytosterols, lignins, flavonoids, hydroxycinnamic acids and downstream products such as biotin, lipoic acid, cysteine and the hormone ethylene which regulates developmental stages in higher plants [6, 10]. Methionine thus plays a central role in regulating essential cellular processes such as cell division, synthesis of cell walls, synthesis of chlorophyll and membrane synthesis [11].

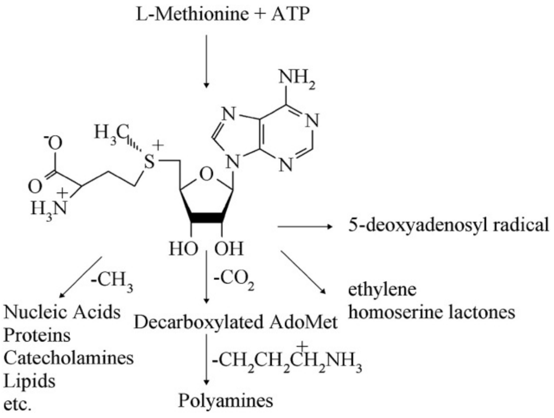

Figure 2.Metabolic versatility of S-adenosylmethionine
(Source: Brosnan J. T. *et al*., J. Nutr., June 2006, vol.136 no. 6, 1636S – 1640S)

SULPHUR'S ROLE IN ENHANCING NITROGEN EFFICIENCY

Nitrogen and sulphur are symbiotic in that both are needed in the synthesis of amino acids and further in the role that sulphur plays in the activation of the enzyme nitrate reductase, which is necessary for the conversion of nitrate into amino acids in plants [12]. High levels of nitrate which can accumulate when sulphur is deficient can impede the formation of seeds in crops such as canola and also be toxic to animals foraging on sulphur deficient silage. Having adequate levels of sulphur, have been shown to improve nitrogen uptake in crops and minimise potential for nitrate leaching into groundwater [13].

SULPHUR’S ROLE IN PHOTOSYNTHESIS

Sulphur is a component in the synthesis of ferredoxin which is responsible for electron transfer in the first phase of photosynthesis. Ferredoxins are small proteins containing iron and sulphur atoms organized as iron-sulphur clusters with the formula Fe_2S_2. These biological "capacitors" can accept or discharge electrons, the effect being change in the oxidation states (+2 or +3) of the iron atoms. In this way, ferredoxin acts as electron transfer agents in biological redox reactions. In chloroplasts, ferredoxins function as electron carriers in the photosynthetic electron transport chain and as electron donors to various cellular proteins, such as glutamate synthase, nitrate reductase and sulphite reductase [14].

Without adequate sulphur, chlorophyll is not stable and plants suffer from chlorosis or lack of chlorophyll. Like calcium, sulphur is a structural component in plants and is therefore not mobile within plant tissues. For this reason a continuous supply of sulphur is needed throughout the growing season of the crop.

SULPHUR REQUIREMENTS IN CROPS

Different crops require different amounts of sulphur depending on seed production, protein and oil content, crop yield, crop removal practises and therefore respond differently to sulphur nutrition. High protein crops such as legumes have a higher sulphur requirement compared to cereal crops while forage crops also have a high sulphur requirement as most of the biomass is removed at harvest [15].

As a rule of thumb, most crops require as much sulphur as they do phosphorus and typically 9 to 15% of the nitrogen uptake. For crops in the crucifer family, such as canola, this can increase to as much as one third of the nitrogen uptake [16]. Sulphur concentrations in plants typically range from 0.1 to 0.3% but can reach levels up to 2% in certain crop leaves and increases in the order Gramineae < Leguminosae < Cruciferae [17].

A sulphur content of less than 0.2% is generally considered suboptimal in cereal plants [17]. Sulphur content is generally high in protein rich crops such as legumes, crucifers, and Brassica. Oil producing plants store the sulphur in organic sulphur form rather than sulphate sulphur form.

Table 1. Typical sulphur requirements and removal by crop type

	Sulphur requirement for crop growth (kg S/tonne grain produced)	**Sulphur removal in grain (kg S/ tonne grain produced)**
Cereals	5	2
Pulses	8	3
Canola	20	10

Broadacre crops with high sulphur requirements will typically require sulphur application at a rate of between 25 to 40 kg of sulphur per hectare, whereas crops with medium sulphur requirements will require between 15 to 35 kg of sulphur per hectare [18].

Crops which are sulphur deficient typically show stunted or spindly growth, general yellowing of younger leaves and reduced seed set.

The extensive work conducted by the Sulphur Institute has characterised sulphur deficiency symptoms for most major crops [16]. In maize, deficiencies manifest as yellowing between the veins along the entire length of the leaves especially in the younger, upper leaves. In latter stages, reddening at the base of the stem and along the leaf margins may occur. For canola, cupped leaves and a reddening on the underside of the leaf and stem is a sign of sulphur deficiency. Flowers abort prematurely resulting in poor pod formation. Reduced oil content is also observed when sulphur is deficient – a trend noticeable in all oilseed crops.

PART 2: SULPHUR SUPPLY

Having established the key role that sulphur plays in many plant functions and the crops requirements, attention is now focused on the typical delivery systems for supplying sulphur to crops, including atmospheric deposition, soil organic matter and applied fertilizers. S emissions from sea spray caused by the decomposition of phytoplankton (the “smell of the sea”) is not included in this analysis as the majority of it is re-deposited back into the oceans. On land, the typical sulphur cycle involving the route for sulphate availability in the rhizosphere is shown in Figure 3 below.

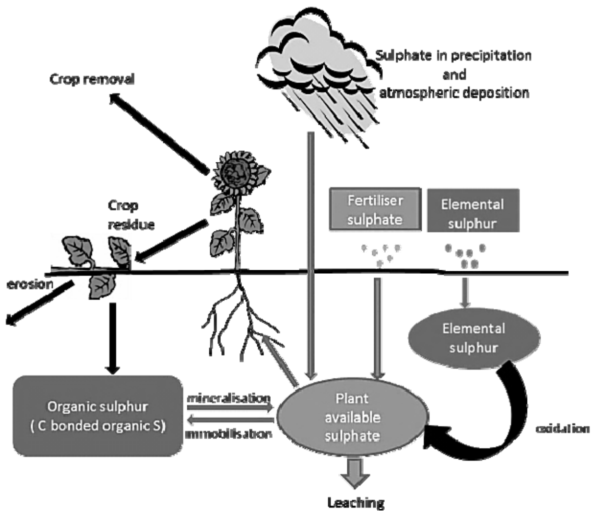

Figure 3. Illustration of the Sulphur Cycle

ATMOSPHERIC DEPOSITION

Atmospheric sulphur deposition in the form of SO_2 and SO_4^{2-} particulates, given the generic name SO_x, along with several nitrogen species given the generic name NO_x are the fugitive emissions from a host of anthropogenic activities. These include power generation, fuel production and refining, pulp and paper production, metallurgical processes, domestic and vehicular emissions. According to Scorgie *et al.* [19], the industrial sector accounts for 96.8% of these fugitive emissions and in South Africa, this is largely concentrated in the Highveld region.

These industrial activities result in the creation of SO_2 containing emissions which are vented to atmosphere via stacks, where the SO_2 can either be dispersed in dry form or react with atmospheric moisture and form sulphurous acid or acid rain or even ammonium sulphate upon reaction with NO_x species. The atmospheric deposition of SO_x species comprises an important source of sulphur nutrition for growing crops and hence requires quantification.

Globally, and locally, efforts are being made through tightening legislation (and incentives) to reduce emissions at point sources such as power utilities and industrial entities. In certain parts of the industrialised world, these measures were so successful that farmers started noticing sulphur deficiency symptoms in crops in the 1980’s [20].

South Africa’s position as an industrial giant in the Southern Hemisphere and on the continent and its reliance on burning coal for electricity production warrants closer analysis. In recent years, two important atmospheric modelling studies have been undertaken to determine the extent and effects of atmospheric deposition of sulphur and nitrogen species [19, 21]. An overview of the literature available on this topic reveals the following approximate picture of the total SO_2 emission inventories per annum in South Africa's main industrial centres [19, 21, 22, 23, 24, 25, 26,]. The Governments' State of the Air Report for 2005 [27], estimates that total SO_2 emissions amount to 2,153,917 tons per annum, roughly accounted for as follows:

Figure 4. Schematic of SO_2 emissions per annum over South Africa's industrial areas

The implication of this atmospheric fallout to the farmer is shown in the modelling analysis of Scorgie *et al*. [19] for the Highveld region. Ground level monitors within the fallout area and modelling studies, taking into account seasonal wind directions and rainfall patterns over the period 2000/1 (representing an average rainfall period) and 2006/7 (representing a low rainfall period), showed that sulphur deposition rates as high as 35 kg/ha/annum can be expected in areas adjacent to point sources and dissipating in concentric circles further away to around 1 to 5 kg/ha/annum. The extent of the high concentration plume is thus dependent upon rainfall patterns and dispersion by prevailing winds.

We can therefore assume that a portion of the required sulphur for crop nutrition is delivered "free of charge" to farmers in a confined locality adjacent to industrial hubs. For the bulk of farmers, however, this free sulphur requires further supplementation to cater for the requirements of the growing crop.

SOIL ORGANIC MATTER

Organic matter in soil is important as it imparts physical chemical and biological properties to the soil. Physically, it promotes aggregation of soil particles which in turn promotes water penetration and retention. Chemically, it increases the cation exchange capacity, soil buffer capacity and nutrient supply, whilst biologically it promotes microbial life and diversity [28]. Changes in land use patterns in South Africa, and in particular crop production, have contributed to the depletion of soil organic matter with a resultant loss of nitrogen and sulphur reserves.

Du Preez *et al*. [28] report that these changes have coincided with changes in the composition of amino sugars, amino acids and lignin and a decline in water stable aggregates needed for the prevention of soil erosion. As a result, lower nitrogen and sulphur reserves have been reported in South African soils and management thereof should form an integral part of farming practices.

Inorganic sulphate sulphur is important for crop nutrition and is the species assimilated by the plant roots. However, this is typically only a small percentage of the total sulphur available in the soil.

Eriksen [29] estimates that more than 95% of soil sulphur is organically bonded and, whilst not immediately available, may play a role in meeting some of the demand of the growing crop through the process of mineralization whereby this organic sulphur is processed by soil microbes into plant available sulphate sulphur. Organic sulphur in soils comprises of plant, animal and microbial residues in various stages of decomposition.

The process of mineralization is proposed to occur via two different pathways namely biological and biochemical [30]. In the biological pathway, sulphate-sulphur is released as a by-product from the microbial processing of organic carbon to produce energy and carbon dioxide. Alternatively, biochemical processing is the release of sulphate from the sulphate-ester reserves in the soil through hydrolysis through the activity of sulphatase enzymes.
The other side of the microbial process is where available sulphate is immobilised and transformed into non-available organic sulphur [31, 32]. As microbial biomass builds up in the soil, this can serve to tie up considerable amounts of sulphate into forms unavailable for immediate crop requirements.

According to Eriksen [29] several papers have shown that mineralization only constitutes approximately 0.5 to 3% per year of the soil available organic sulphur. Stated differently, for every 1% of organic matter available in the soil, approximately 3.8 kg/ha/annum of sulphur is mineralised and available for crop uptake [32].

Minimising crop removal practices and the application of animal manures or composts play an important role in rebuilding soil organic carbon levels.

With 58% of South African soils reported to contain less than 0.5% organic carbon and only 4% containing more than 2%, [28] the availability of sulphur for crop nutrition from soil organic carbon is too low to meet the needs of the growing crop and requires further supplementation in the form of inorganic fertilizers – both sulphate and elemental sulphur based.

INORGANIC SULPHATE-SULPHUR FERTILIZERS

The final balancing of sulphur nutrition, having taken into account the potential quantities from atmospheric deposition and soil organic mineralization, is the addition of sulphur based fertilizers.

Sulphate-sulphur based fertilizers are available in combination with other nutrients, typically nitrogen or potassium. The sulphate is readily soluble and thus is immediately available for uptake by the growing crop. Examples of sulphur containing fertilizers are shown in Table 2 below.

Table 2. Compositions of some sulphate-sulphur and elemental-sulphur based fertilizers

Product	N	P	K	S
Sulphate based				
Ammonium sulphate	21			24
Gypsum				13 – 18
Single Super Phosphate				12
Potassium sulphate			49	18 - 20
Zinc sulphate				18
Elemental S based				
Sulphur bentonite				90

The concentration of inorganic sulphate retained in the soil can vary throughout the growing season due to variations in atmospheric fallout, the application of fertilizers, organic decomposition, plant uptake, leaching and microbial activity. This sulphate can be present in the soil solution or attached to soil colloids. Harward and Reisenauer [33] argued that the concentration of sulphate present in the soil is dependent upon pH, the presence of other ions in the soil solution and the nature of soil colloids.

Sulphate is absorbed by the hydrous oxides of iron and aluminium and by the edges of clay particles through a combination of electrostatic and chemisorption processes. Therefore the larger the clay particles surface area and concentration of the iron and aluminium, the higher the concentration of sulphate present [33, 34].

Curtin and Syers [35], and Appel [36] proposed that where the soil pH is below the point of zero charge (PZC), the charge of the colloid is positive due to the hydration of the metal oxides and thus the sulphate ion is attracted to the colloid. Conversely, where soil pH is higher than the point of zero charge, as is typical in most agricultural soils, the sulphate ion is poorly attracted to the colloids and hence is typically found in the soil solution, making it vulnerable to leaching.

Lastly, the capacity for sulphate adsorption is strongly influenced by the presence of other anions. Tisdale [37] gives this order as follows: hydroxyl > phosphate > sulphate > nitrate > chloride. Hence the addition of high levels of phosphates to the soil has been shown to result in increased sulphate leaching [38, 39]. We briefly examine a few of the more common inorganic fertilizers containing sulphate-sulphur.

Ammonium sulphate is widely used as a source of nitrogen in the fertilization programmes of many cereal growers, with the added benefit of the sulphate component. Improvements in the granulation process of ammonium sulphate have contributed to its growing application in blends and ease of handling due to its low hydroscopicity and chemical stability. The acid forming reaction of ammonium sulphate in the soil can also have a beneficial effect when dealing with high pH soils [40].

When applied for its nitrogen value, ammonium sulphate has the potential to deliver more sulphur than is required by the crop. Due to its solubility, the sulphate component may be leached from the soil or immobilised as the growing season progresses, and result in sulphur deficiencies at the key stage of grain filling [41]. Owing to the lack of mobility of sulphur within the plant tissue, the net result could be a sulphur shortage during grain filling.

Gypsum, or calcium sulphate, is widely used as a calcium and sulphur bearing material for nutrition and soil reclamation. The presence of calcium ions assists with the flocculation of soil particles to improve soil structure, aeration and water penetration.

Gypsum is also used for treatment of sodic soils, where the calcium ion is able to replace the sodium ion attached to the soil colloid, making it leachable through the formation of sodium sulphate.

Since gypsum is a neutral salt it has no effect on soil acidity within the range pH (H_2O) 4.5 to 8.4 [42]. For soils with a pH (H_2O) below 4.5, the aluminium ions dominate the soil pH chemistry and the application of gypsum can be effective to replace aluminium ions with calcium ions and restore pH levels to the region of 4.5. In strongly alkaline soils with pH greater than 8, the presence of sodium in the form of sodium carbonate dominates pH chemistry and gypsum can work in much the same manner as for treatment of sodic soils to restore pH to the region of 8. For these reasons gypsum cannot be considered an effective liming (to increase pH) or acidifying (to lower pH) agent [42] within the optimal crop growing pH range.

When looking at gypsum as a source of nutrient sulphur, its poor solubility at 2.5 g/l is its main drawback when compared to other soluble sulphur sources such as ammonium sulphate. Problems associated with the handling and application of gypsum in a fine powder form (to increase the surface area and enhance the solubility) should also not be underestimated.

Single super phosphate has largely been the phosphate fertilizer of choice around the world, containing between 8-10% P, 10-14% S and 18-21% Ca. The trend to higher analysis fertilizers such as concentrated or triple super phosphates, containing between 19-23% P, and often < 1% S, in order to minimise logistics costs has had the unintended consequence of contributing to the growing shortfall of sulphur nutrition around the world.

Potassium sulphate is widely used in higher value crops as a source of potassium and typically contains between 18-20% S. Its high solubility makes for ease of application (both liquid and solid forms) and mobility into the soil solution for uptake by the crop or leaching below the root zone.
Micronutrients sulphates such as zinc, copper, iron and manganese can also supply a valuable portion of the crop’s sulphur requirements when applied as a sulphate. The low levels of micronutrients typically required may not provide adequate levels of sulphur especially when taking into consideration their solubility and susceptibility to leaching.

ELEMENTAL SULPHUR FERTILIZERS

Elemental sulphur based fertilizers with their high S analysis and minimal leaching properties should be considered as a cost effective alternative to sulphate-sulphur fertilizers. As these products are not water soluble, the sulphate is not immediately leachable but slowly releases sulphate to the growing crop, and as such can form part of the long term sulphur fertilizer management programme for soils low in available sulphur or for crops with high sulphur requirements. The elemental sulphur must first be converted into the sulphate form in the soil before it can be taken by the plant, and this conversion process is governed by several soil and environmental factors.

Particle size is important and the finer the particle size the faster the conversion process due the increased surface area available for microbial activity. The formation of fine sulphur particles is the modus operandi of sulphur-bentonite products such as Tiger 90CR. The addition of a swelling clay such as bentonite to a sulphur matrix, allows for the initial breakdown and subsequent dispersion of sulphur particles of varying sizes upon contact with soil moisture. The distribution in size of these sulphur particles is the key to controlling the rate of oxidation of elemental sulphur into the plant available sulphate form as shown in Figure 5 below.

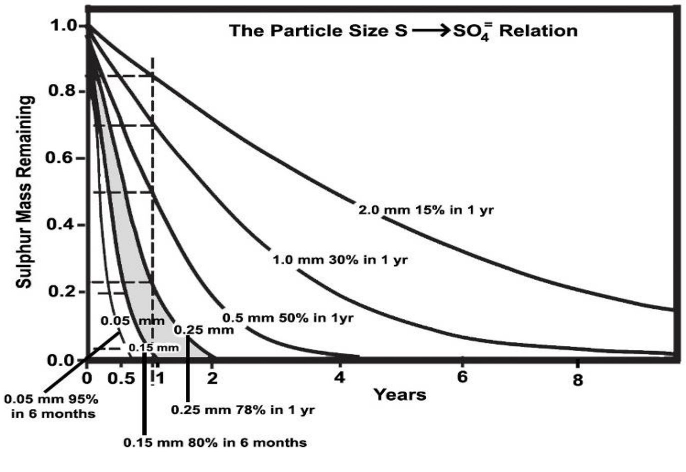

Figure 5. Effect of particle size on rate of oxidation of elemental sulphur

Oxidation of elemental sulphur is facilitated by soil borne organisms, including autotrophic bacteria such as *Thiobacillus*, heterotrophic bacteria, fungi and actinomycetes [43, 44]. The activity of these organisms is in turn determined by the oxygen and moisture content, temperature and pH of the soil. *Thiobacillus* occurs naturally in all soils and studies have shown that the addition of sulphur to the soil as a food source can have a dramatic effect on increasing the population and hence on the rate of oxidation [45]. Hence repeat applications of elemental sulphur products can have the desired effect of maintaining a long term balance of immediately available sulphate-sulphur and non-leachable elemental sulphur for later conversion to meet the crops’ requirement throughout the growing season.

Oxidation rates are also dependent upon environmental factors such as oxygen availability, soil temperature and moisture content. Simplistically considered, the same conditions which encourage crop growth also facilitate the oxidation of elemental sulphur. The advantage of this is that elemental sulphur based products can be applied early in the season, prior to planting, and also used to rebuild soil sulphur levels without the fear of loss to leaching.

Ideally elemental sulphur based products should be broadcast, especially in the first year of application as the oxidation process takes place quicker when mixed with soil compared to banded application.

Elemental sulphur fertilizers can be safely banded with seeds due to its low salt index and special grades of the product are available to be used as a seed extender for small seeds to improve seed distribution.

New formulations of elemental sulphur with micronutrients in the oxide form have also become available. These products work on the principle that the sulphurous acid created in the soil by the oxidation of sulphur reacts with the micronutrient oxide to form the corresponding sulphate. Once again, the advantage of this formulation is the season long availability of both the sulphur and micronutrient to the growing crop.

CONCLUSIONS

There can be no question that sulphur plays an important role in plant physiology and crop quality through the building of proteins. Sulphur availability and its impact on protein yield and quality in crops therefore has an important impact on human health.

Maximising crop yields, enhancing disease resistance and protein levels are very dependent upon following a balanced nutrition programme. Identifying the crops' needs and the soils' ability to deliver this nutrition along with quantifying the supplementation required through fertilizers is the cornerstone of improving the economics of farming.

Sulphur is taken up by the crop in the form of a sulphate and converted into the amino acids cysteine and methionine. These two amino acids are the building blocks of sulphur based proteins and downstream compounds which play key roles in multiple plant functions such as photosynthesis, disease resistance and plant growth.

The sulphur requirements of a growing crop can be met through a combination of atmospheric SOx deposition, soil organic carbon mineralization and applied fertilizers. This paper has attempted to quantify the typical amounts of sulphur delivered to crops through the deposition and mineralization processes and evaluated the various mineral fertilizer options used to supplement sulphur nutrition.

As sulphur is not mobile in the plant, the steady supply of sulphur throughout the growing season is a prerequisite in order to meet the requirements through to seed filling. Sulphate based fertilizers have the advantage of meeting the initial requirements of the crop but can be prone to excessive losses through leaching, whilst elemental sulphur based fertilizers must first be converted into plant available sulphate form - a process which requires a variety of soil and environmental conditions. The advantage however, is that these conditions are typically the same conditions required for optimum growth by the crop and hence elemental sulphur based fertilizers are viable alternatives to the traditional sulphate based fertilizers.

Each form of sulphur used for crop nutrition has its benefits and disadvantages. What remains clear however is that sulphur should form part of a balanced nutritional programme to meet the needs of the crop and the demands of the farmer for improved returns on investment.

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CROP NUTRIENT SULPHUR: SUPPLY AND DEMAND

FSSA Technical Symposium
22nd August 2012

by
Lawrence van Rensburg

fppt.com

SULPHUR BACKGROUND

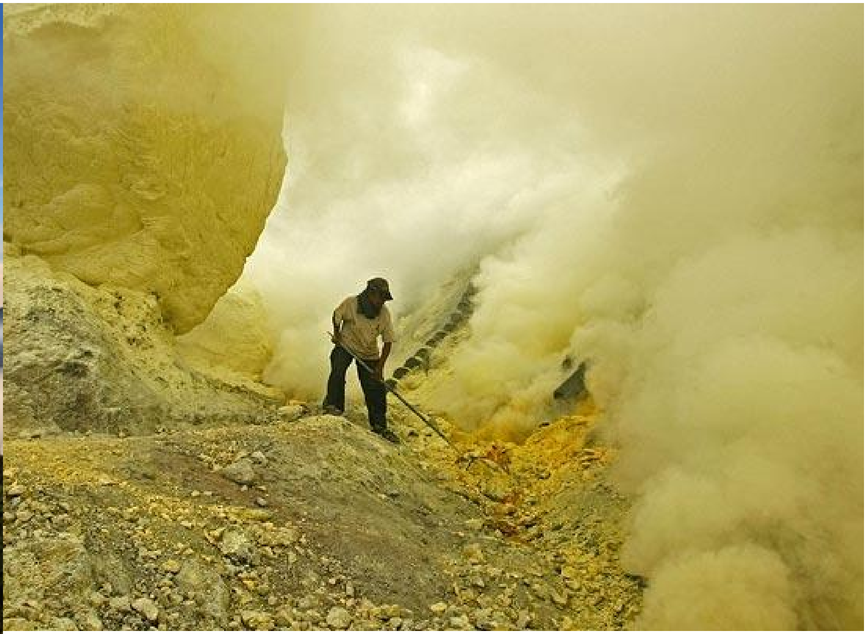
SULPHUR BACKGROUND

- Found in nature as the pure element S_8 or as sulphide and sulphates.

- 13th most abundant element in the earths' crust.

- History associated with "**fire and brimstone**".

SULPHUR BACKGROUND



SULPHUR BACKGROUND

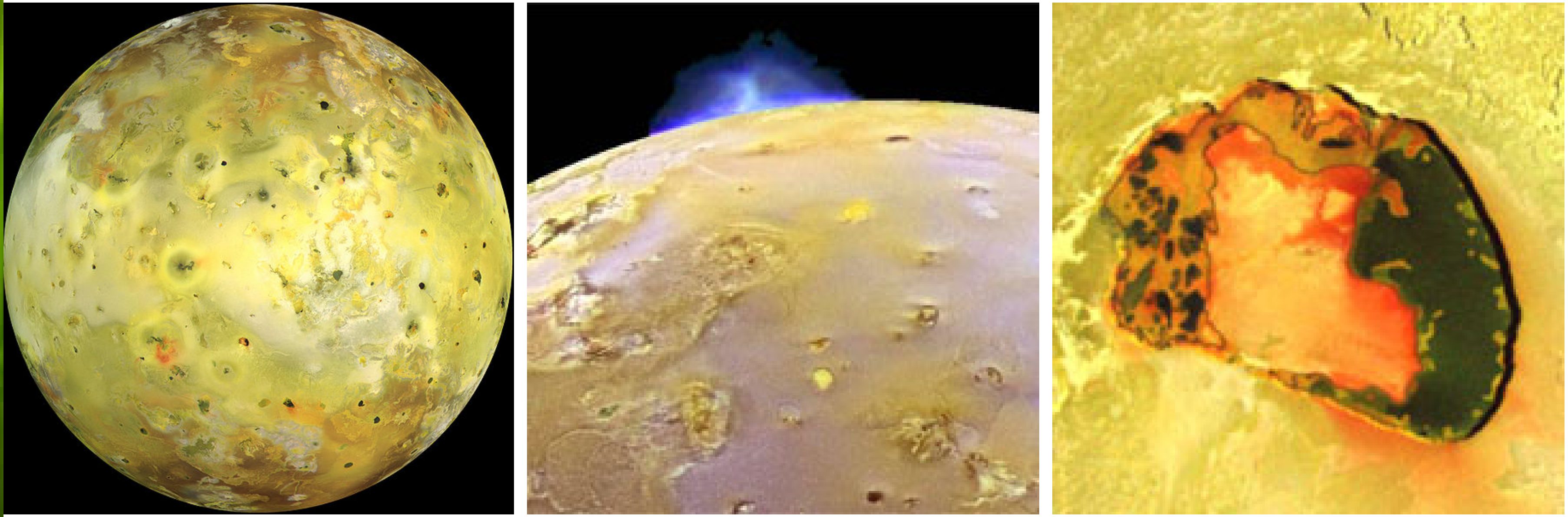
Things haven’t improved much

SULPHUR BACKGROUND

SULPHUR BACKGROUND

But there is a beauty and purpose to sulphur

SULPHUR BACKGROUND



NASA's Galileo spacecraft images of Jupiter's moon Io on 3 July 1999 during its closest pass

SULPHUR BACKGROUND

SULPHUR

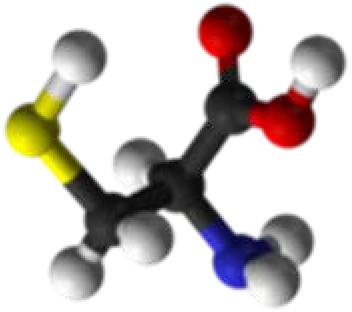
- Sulphur, like nitrogen is an essential element in the growth of all living things
  - The 7th most abundant element in the human body.
  - Found in proteins and organosulphur compounds - the majority of which are taken up through the food we eat or synthesised in-situ from building blocks supplied in our food.

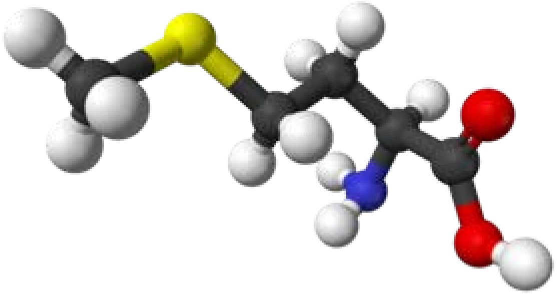
ROLE OF PROTEINS

- Proteins are important molecules in our cells – they are involved in virtually every cell function.
- Each has a specific function
  - **Enzymes** - carry out chemical reactions;
  - **Structural proteins** – provide support and strength;
  - **Storage protein** – store amino acids;
  - **Hormonal proteins** – messenger proteins which co-ordinate bodily activities;
  - **Transport proteins** – carrier proteins which move molecules through cell membranes;
  - **Antibodies** – special proteins for combating disease and attack.

SULPHUR BUILDING BLOCKS

- Sulphur is a building block in the amino acids, **cysteine** and **methionine** which are used for:
  - Protein formation;
  - Enzyme and vitamin production;
  - Facilitating photosynthesis;
  - Fixing nitrogen;
  - Growth hormones e.g. ethylene.



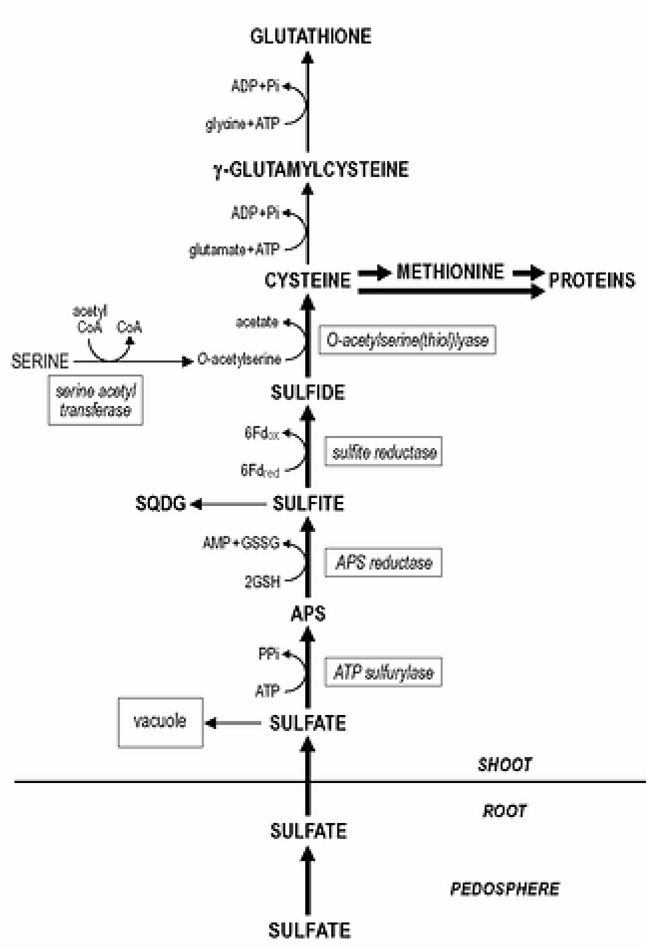


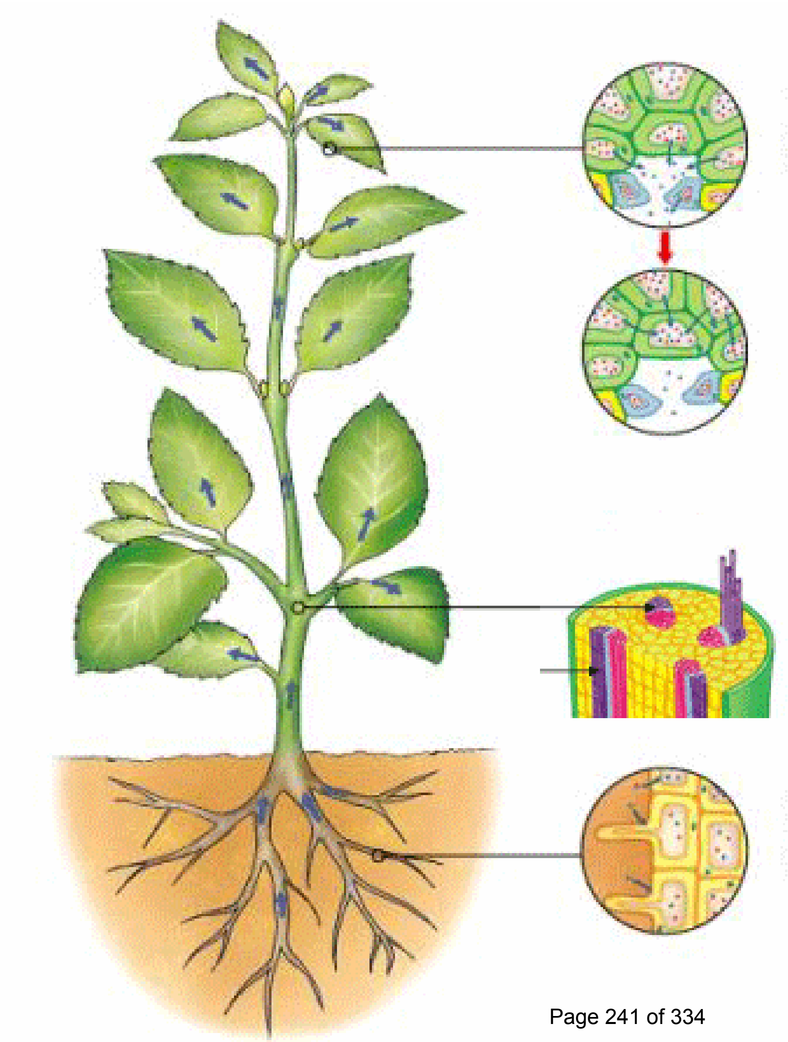
WHY ARE SULPHUR AMINO ACIDS IMPORTANT?

- Plants, bacteria and fungi can assimilate sulphur as the sulphate (+6) for reduction to sulphide (-2) leading to the synthesis of sulphur containing amino acids.

Humans and animals lack the capacity to reduce sulphate and hence rely on plants in their diet for the provision of these two essential amino acids.

SULPHUR UPTAKE





SULPHUR REQUIREMENTS

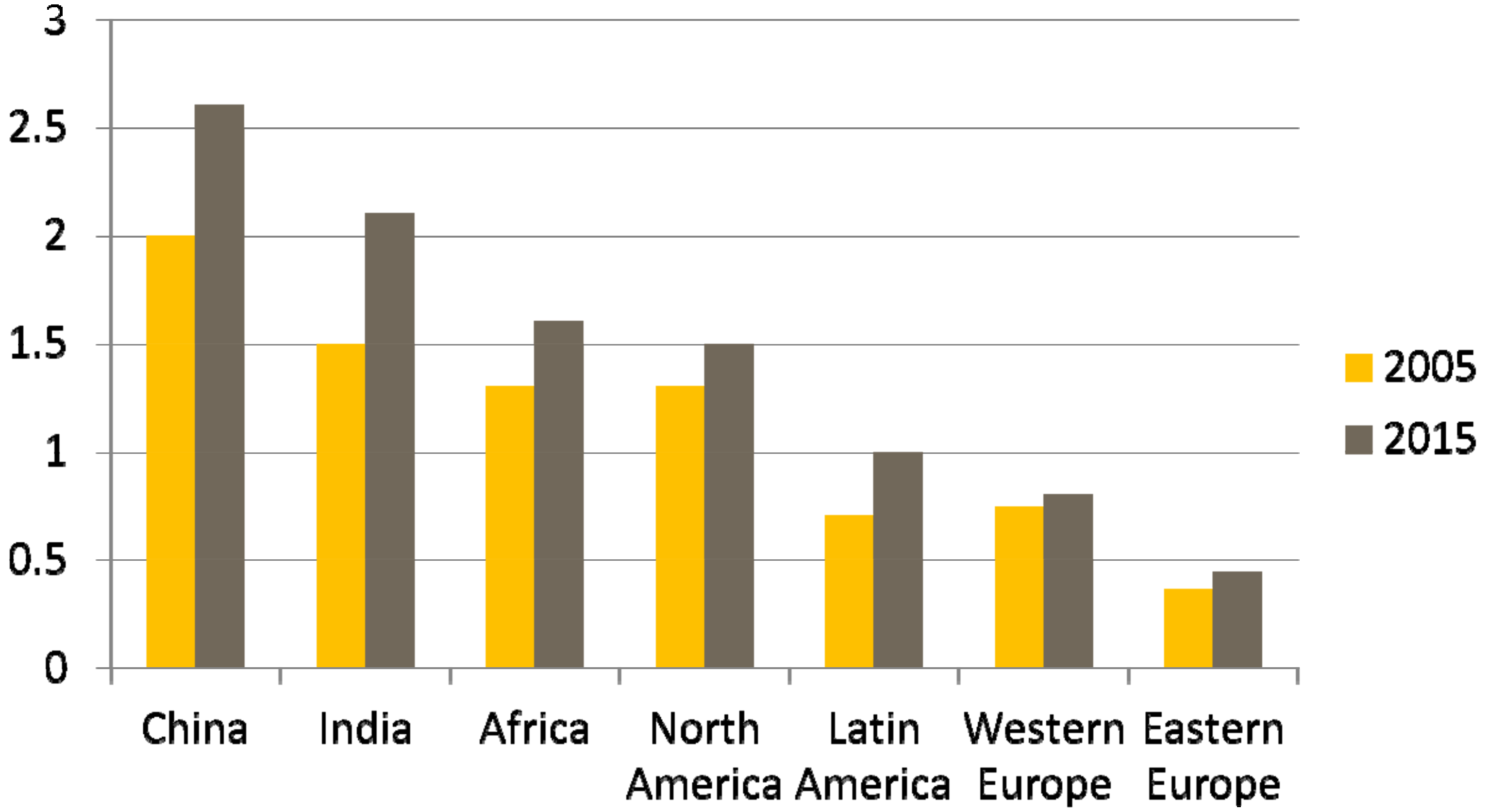
SULPHUR REQUIREMENTS

- Considered the fourth macronutrient after N, P and K
  - Required in similar quantities to P

	Sulphur requirement for crop growth (kg S/tonne grain produced)	Sulphur removal in grain (kg S/ tonne grain produced)
Cereals	5	2
Pulses	8	3
Canola	20	10

  - S concentrations in plants largely determined by the S content in the seed
- S is not mobile in the plant and so a continuous supply is required throughout the growing season.

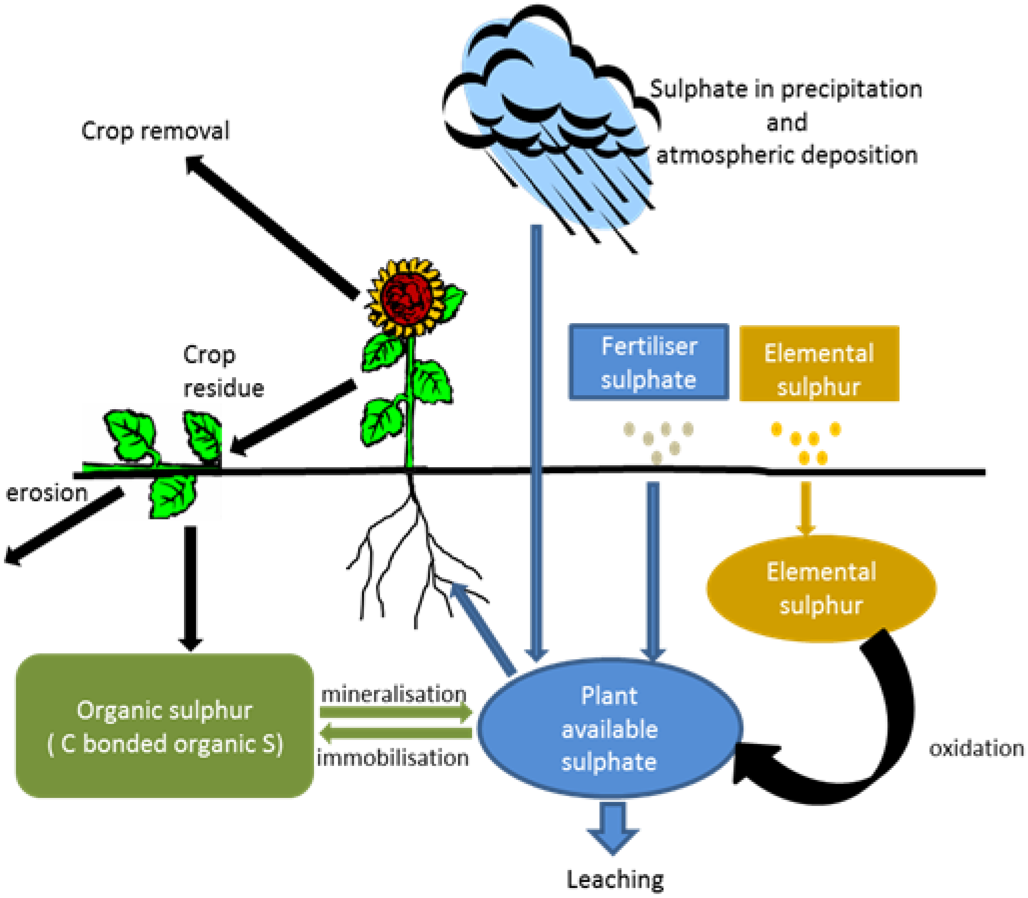
PROJECTIONS OF SULPHUR DEFICIT BY REGION



Source: TSI Report, April 2009.

SULPHUR CYCLE

THE SULPHUR CYCLE



SULPHUR SOURCES

- Atmospheric deposition
- Soil organics
- Fertilizers

ATMOSPHERIC DEPOSITION

- Every year approximately 2.1 million tons of SO_2 is emitted into the atmosphere in RSA – “free S”

Source: www.info.gov.za: State of the Air Report 2005 – Atmospheric emission sources.

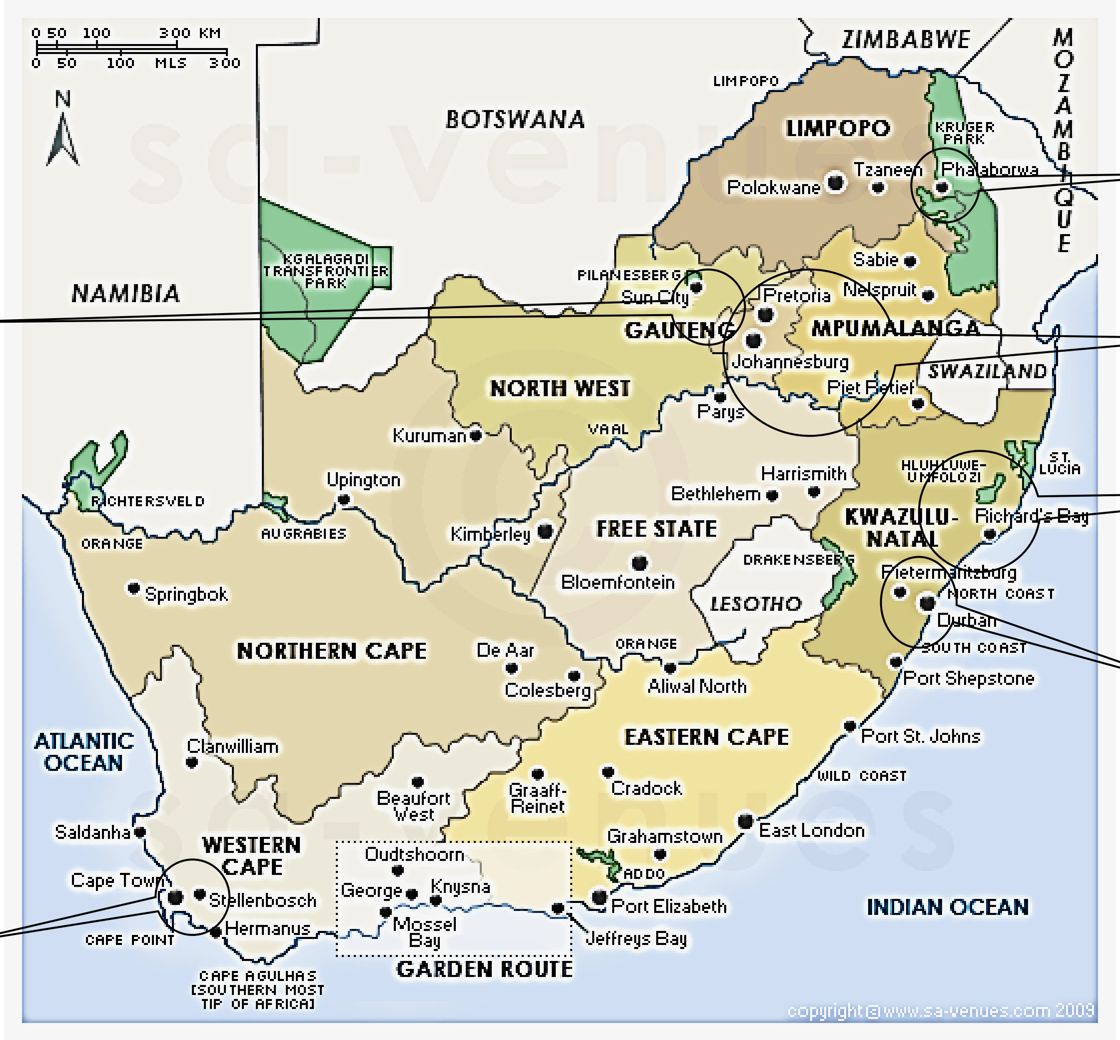
–SO_x species emitted from anthropogenic activities.

–Power stations, refineries, smelters and industrial sectors > 95% of the total.

–Distribution dependent upon:

  - Prevailing winds
  - Season and inversion layer
  - Rainfall
  - Emitting height

SO_2 EMISSIONS



40,000 t/annum

50,000 t/annum

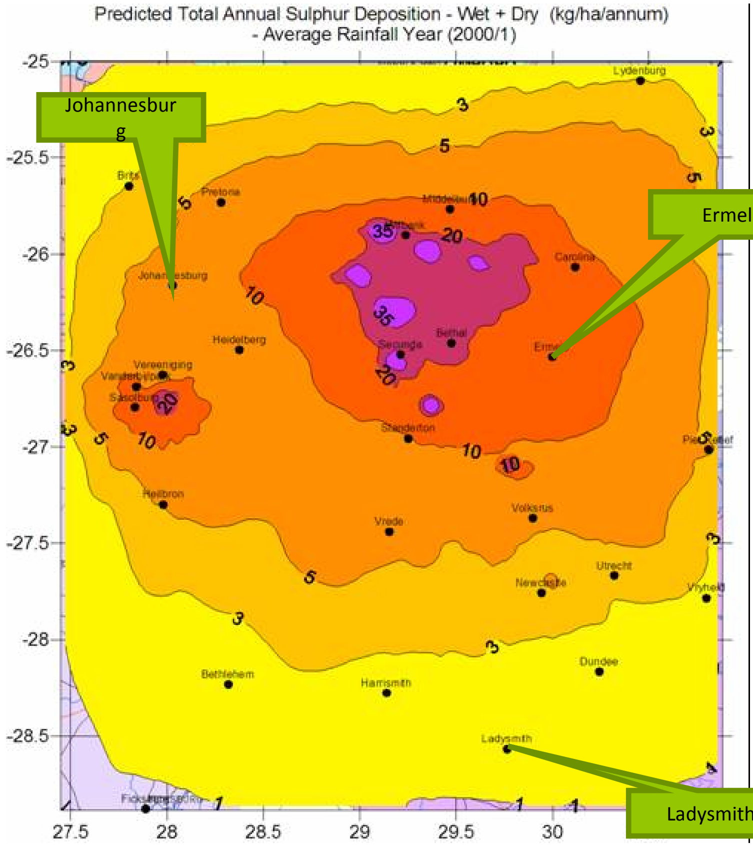
1,800,000 t/annum

27,000 t/annum

35,000 t/annum

? t/annum

PREDICTED TOTAL S DEPOSITON - HIGHVELD

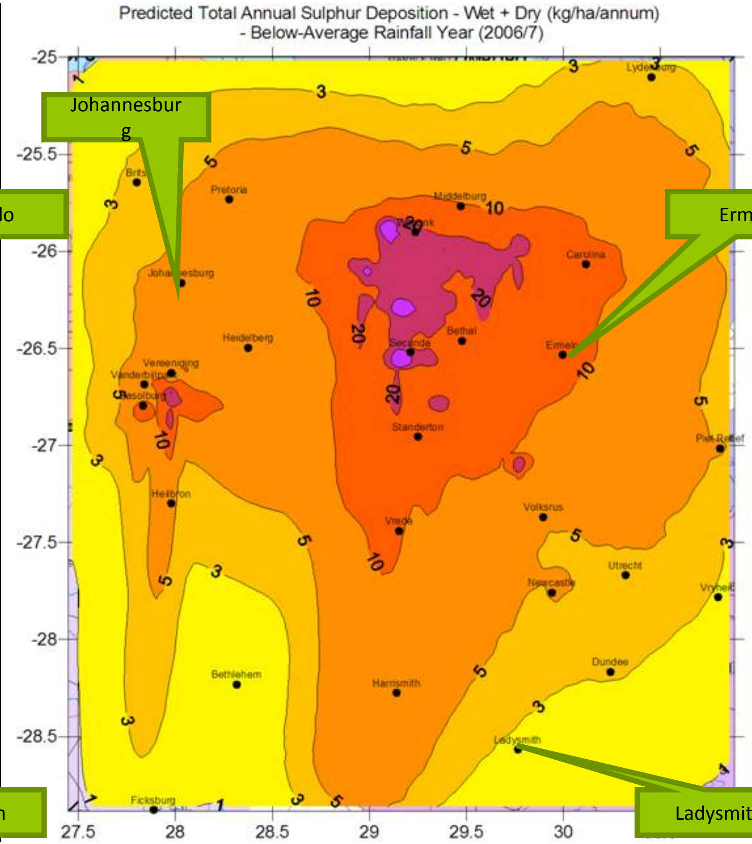


Predicted Total Annual Sulphur Deposition - Wet + Dry (kg/ha/annum) - Average Rainfall Year (2000/1)

Johannesburg

Ermelo

Ladysmith



Predicted Total Annual Sulphur Deposition - Wet + Dry (kg/ha/annum) - Below-Average Rainfall Year (2006/7)

Johannesburg

Ermelo

Ladysmith

Source: Airshed Planning (Pty) Ltd Modelling Results NACA Annual Conference ,15 Oct. 2009

ATMOSPHERIC DEPOSITION

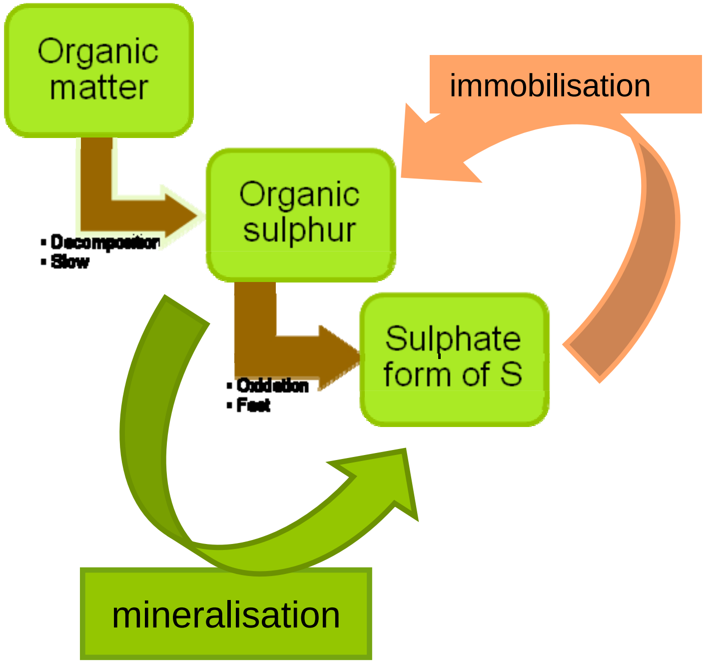
- Dry atmospheric SO_2 can enter a leaf stomata directly or be absorbed in moisture on the leaves – in both cases forming either SO_3 or SO_4
  - This SO_2 can partially offset some of the SO_4 typically absorbed through the roots;
  - SO_2 concentration (and duration) is important in determining whether atmospheric SO_2 is beneficial or injurious to the plant.

- Wet deposition of SO_2/SO_3 on the soil and subsequent uptake through the roots.

But, atmospheric deposition alone cannot meet the total S requirement of the growing crop.

ORGANIC CONTENT OF SOIL

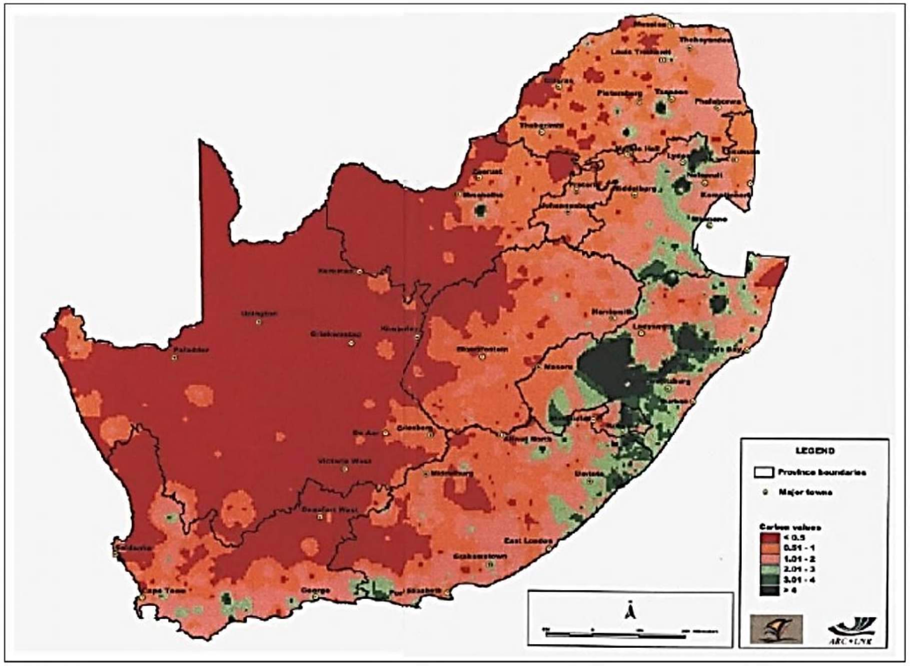
- Organic matter in the soil:
  - Physically – aggregation of colloids;
  - Chemically – improves CEC and nutrient supply;
  - Biologically – promotes microbial life and diversity.
- The organic component of soil can act as a source or sink for sulphur
  - The decomposition of low S organic matter can result in micro-organisms initially tying up S before finally being released in the sulphate form.



ORGANIC CONTENT OF SOUTH AFRICAN SOILS

- South African soils typically have very low organic matter levels(1)
  - 58% of the soil contains <0.5% organic C
  - 38% between 0.5 to 2% organic C

(1) Du Preez, C.C., Van Huyssteen, C.W. & Mnkeni P.S. Land use and soil organic matter in South Africa.



Source: Barnard[14]

FIGURE 1: Generalised organic carbon map for virgin topsoils in South Africa.

ORGANIC CONTENT OF SOUTH AFRICAN SOILS

- Total sulphur levels declined between 4% and 70% as a result of cultivation (3)
  - but inorganic S levels increased compared to uncultivated soils
  - hence decline in total S due to accelerated mineralisation of organic sulphur as a result of cultivation

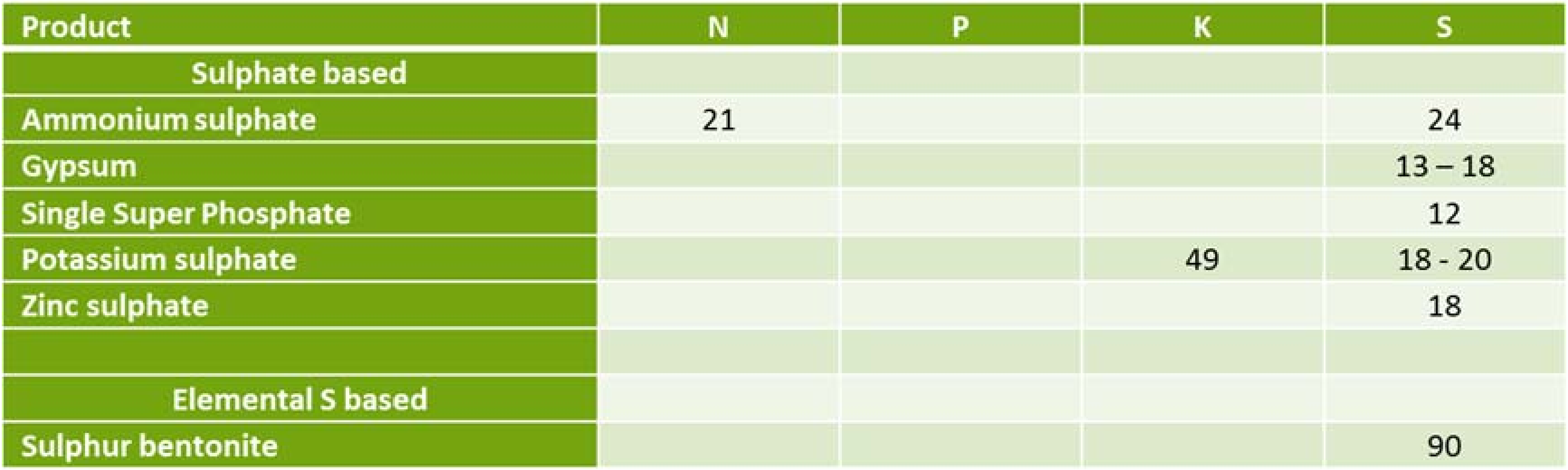
Du Toit, M.E. Effect of cultivation on the sulphur fractions in selected dryland soils. MSc Agric dissertation, Bloemfontein, University of the Free State, 1993.

- Typically, every 1% of organic matter in soil can release approximately 3.6 kg/ha/annum of S in the sulphate form

TSI Bulletin No. 23. Atmospheric Sulphur – The Agronomic Aspects.

SULPHUR FERTILIZERS

- The final balancing of the S demand must therefore come from the addition of S –based fertilizers



Product	N	P	K	S
Sulphate based				
Ammonium sulphate	21			24
Gypsum				13 – 18
Single Super Phosphate				12
Potassium sulphate			49	18 - 20
Zinc sulphate				18
Elemental S based				
Sulphur bentonite				90

ELEMENTAL SULPHUR

- Sulphur in the sulphate form is easily leached from soils - whereas elemental S is a slow release as the S is insoluble in water;
- Requires microbial activity to convert to SO_4^{2-}

- Product formulated with bentonite clay to overcome the reactivity issues of granular elemental S.

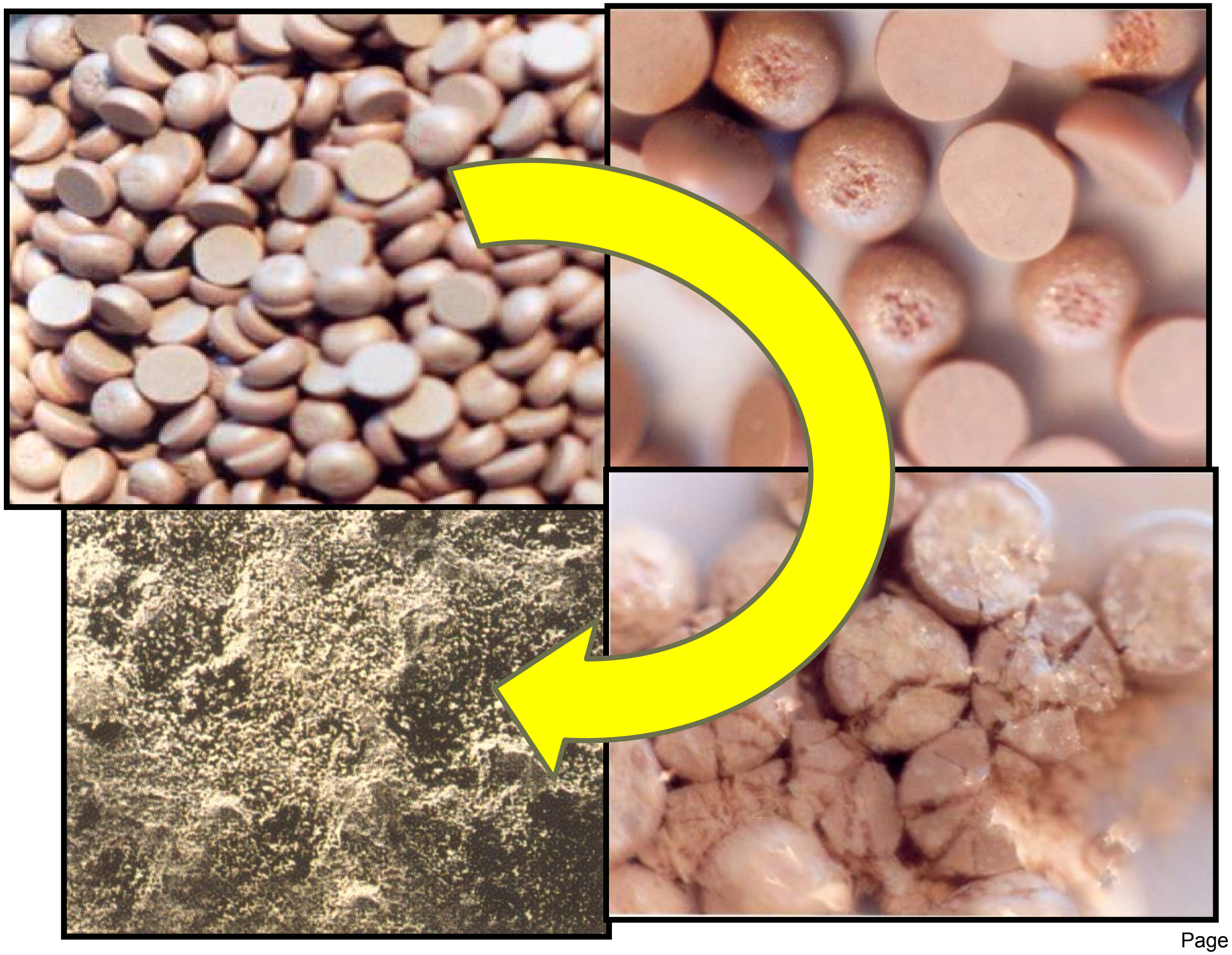
5 KEY FACTORS AFFECTING S OXIDATION

1. **Microbial activity –** *Thiobacillus* population. Repeat S applications have higher *Thiobacillus* populations.
2. **Particle Size –** Sulphur needs to be broken down into fine particles to increase surface area for *Thiobacilli.*
3. **Soil Temperature –** Oxidization occurs at > 5°C and peaks at around 35°C.
4. **Soil Moisture –** Moist soil promotes oxidization. Dry and flooded soils slow oxidization.
5. **Oxygen –** Needs to be present for conversion. Placing sulphur deep into soil slows SO_4^{2-} production.

SULPHUR BENTONITE

- Analysis: Typically (0-0-0-90);
- Homogeneous pastille of sulphur with a proprietary swelling clay to give S particle size distribution;
- Slow conversion to sulphate form dependent upon particle size;
- Low dusting and homogeneous sizing;
- Acid forming in the soil;
- Ease of blending;
- Incorporation of micronutrients possible.

PASTILLE BREAKDOWN

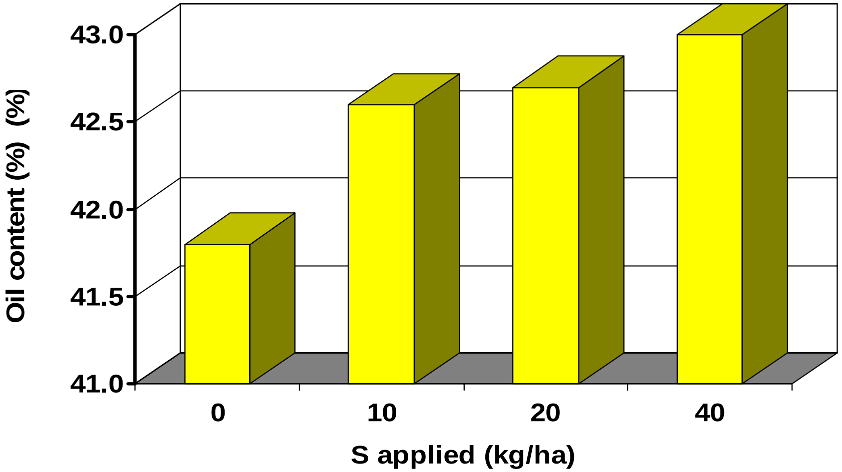


FIELD TRIAL RESULTS

EFFECTS OF S ON CANOLA OIL CONTENT

Sulphur Fertilizer Effect on Synthesis of Oil: IACR, Rothamsted Research Group, UK.

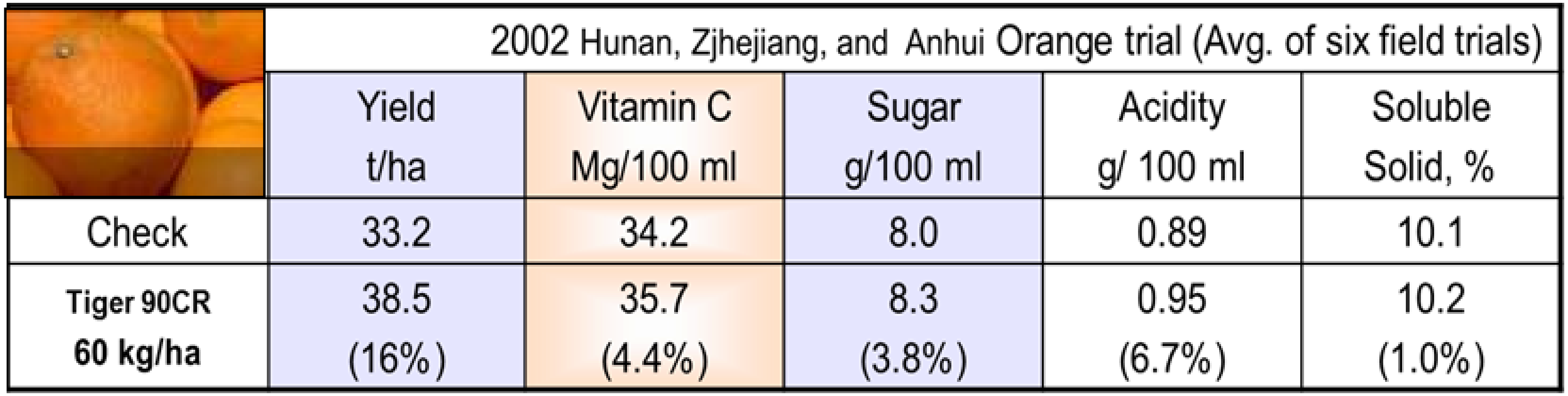
Sulphur fertilization **increased oil** content of canola seed **oil** content in the UK by **3.02%**



TSI RESEARCH

Sulphur Fertilizer Effect on Vitamin C & Sugar content:

<u>Increased Sugar content</u> *in* ***Sugarcane*** *and* ***Banana*** *by* ***10-23%*** *in Guangdong, Guangxi, and Jiangxi*



	2002 Hunan, Zjhejiang, and Anhui Orange trial (Avg. of six field trials)				
	Yield t/ha	Vitamin C Mg/100 ml	Sugar g/100 ml	Acidity g/ 100 ml	Soluble Solid, %
Check	33.2	34.2	8.0	0.89	10.1
Tiger 90CR 60 kg/ha	38.5 (16%)	35.7 (4.4%)	8.3 (3.8%)	0.95 (6.7%)	10.2 (1.0%)

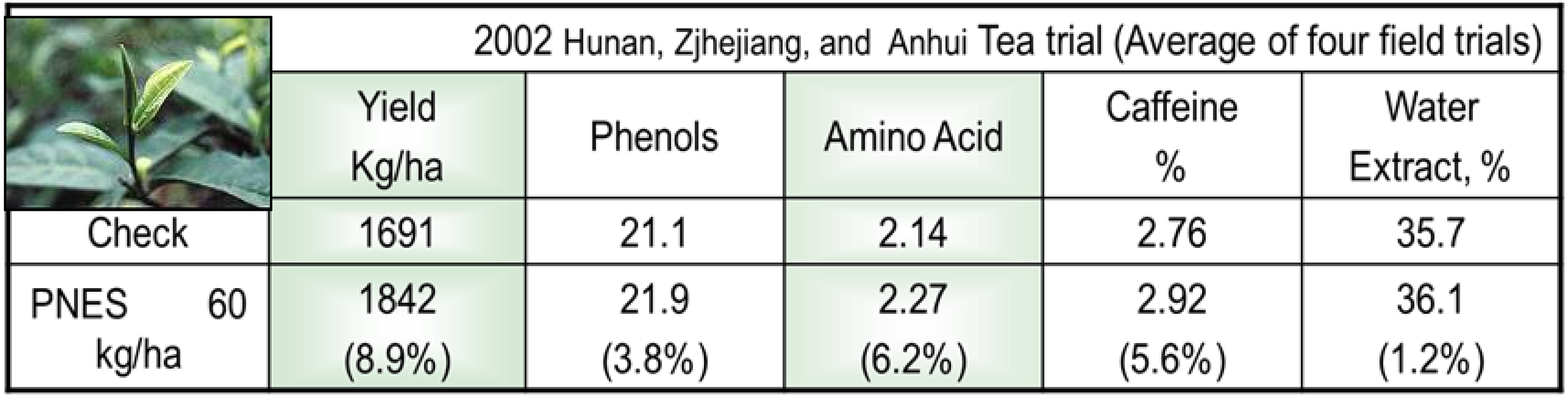
The Sulphur Institute 1997 - 2003 S trials

TSI RESEARCH

Sulphur Fertilizer Effect on Protein:

Increased **Crude Protein** content in **Rice and Wheat by 10-27%** in Anhui and Jiangsu;

Increased **Amino Acid (Methionine)** content in **Peanut by 40%** in Fujian and Jiangxi Provinces.



2002 Hunan, Zjhejiang, and Anhui Tea trial (Average of four field trials)

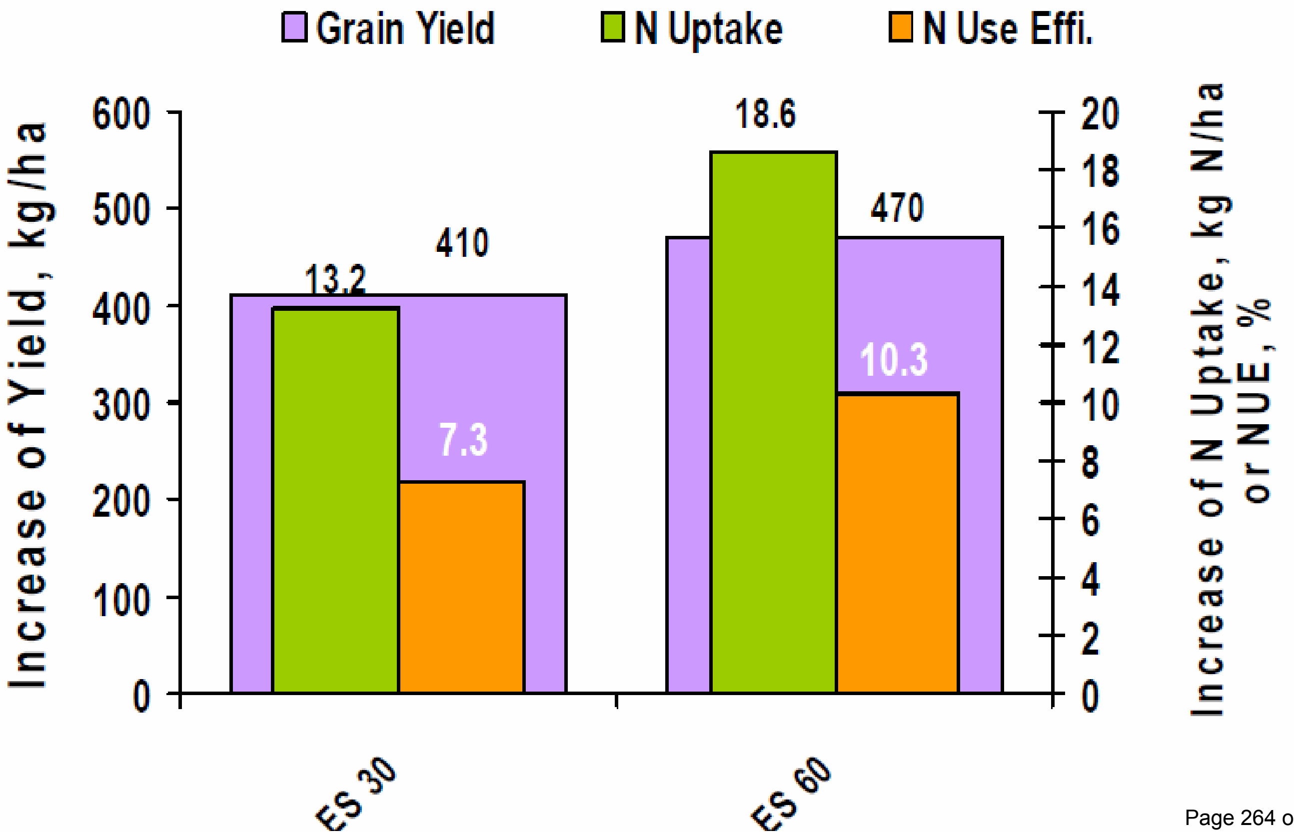
	Yield Kg/ha	Phenols	Amino Acid	Caffeine %	Water Extract, %
Check	1691	21.1	2.14	2.76	35.7
PNES 60 kg/ha	1842 (8.9%)	21.9 (3.8%)	2.27 (6.2%)	2.92 (5.6%)	36.1 (1.2%)

The Sulphur Institute 1997 - 2003 S trials

TSI RESEARCH

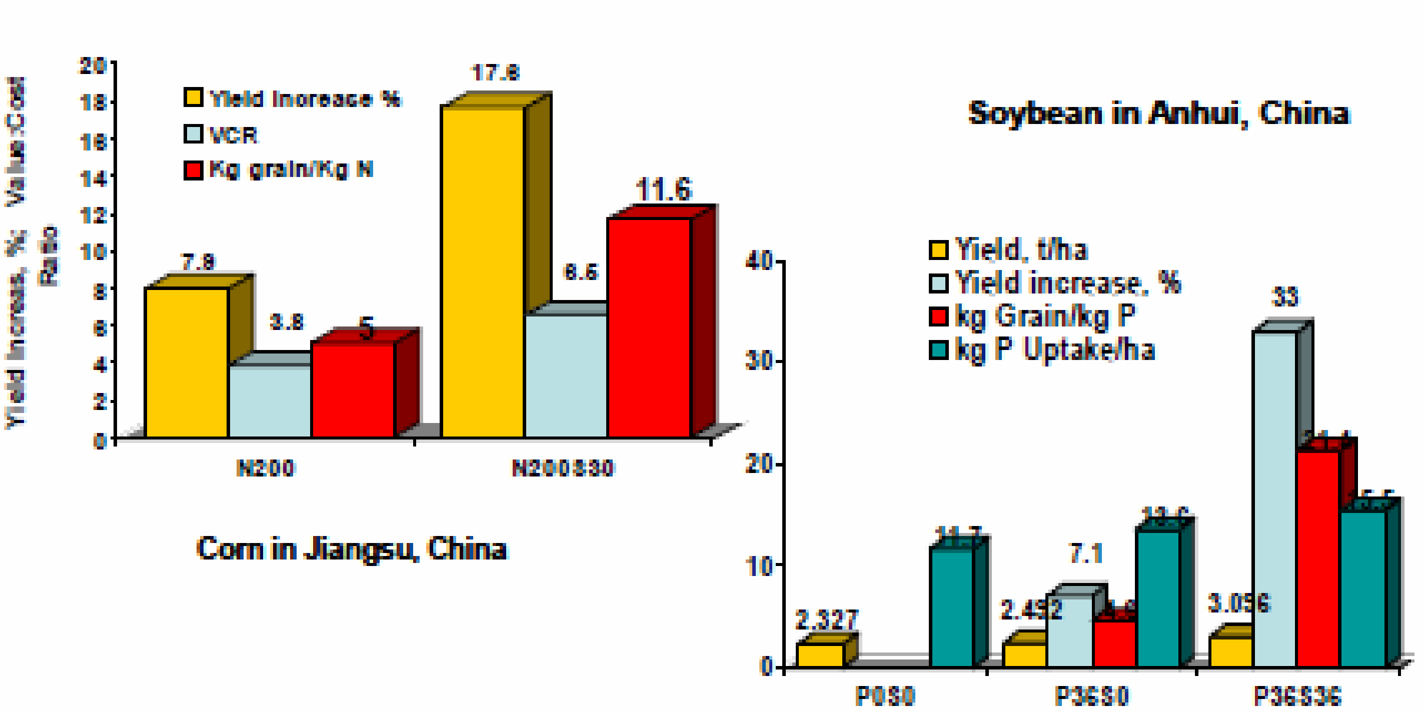
Sulphur Increased Rice Yield and N Uptake and Efficiency

Shangao, Jiangxi, 2000



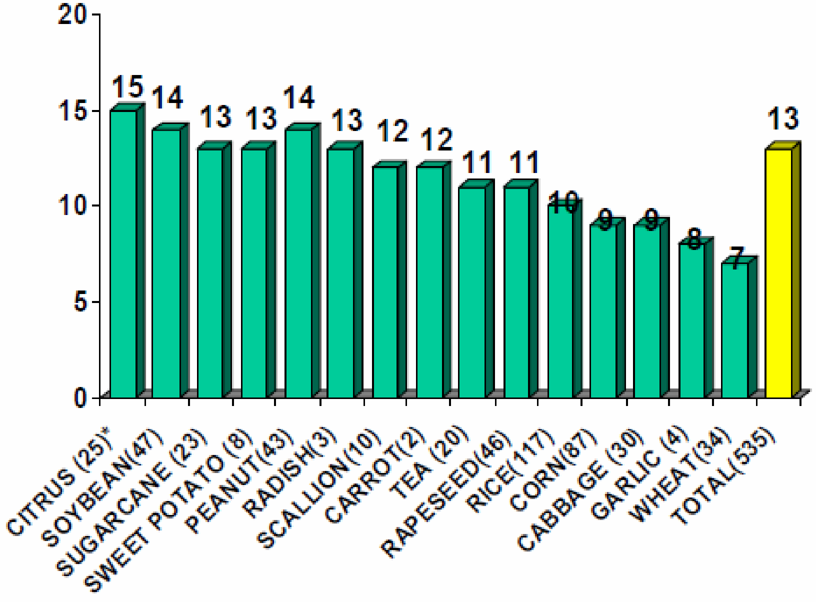
TSI RESEARCH

Sulphur Increased Crop Yield and Efficiency of N and P Fertilizers



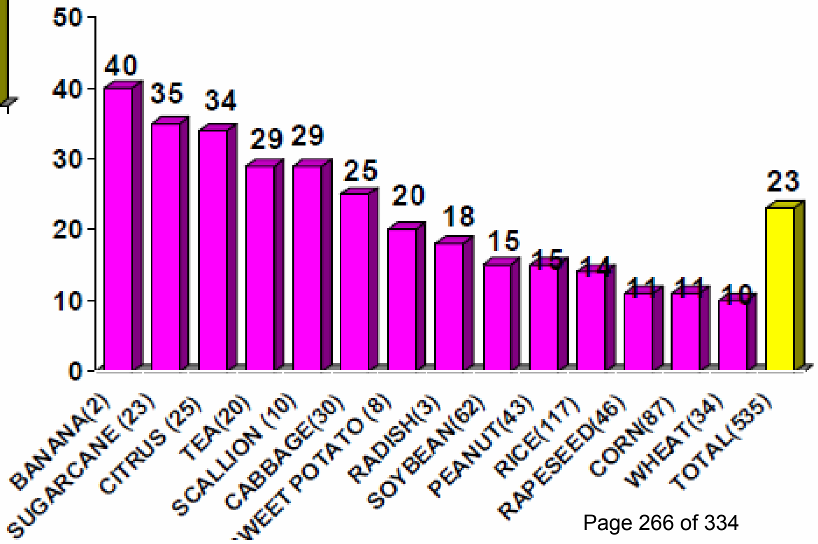
TSI RESEARCH

Sulphur Fertilizer Increases Crop Yield and Economic Returns: TSI Projects in China



Average Crop Yield Increase:13%

Average Economic Returns on Fertilizer Investment: 23 to 1
(Value : Cost Ratio)



SUMMARY

- Explored the role of S in plant physiology and building proteins;
- Quantified S requirements in crops;
- Evaluated the efficacy of S delivery via
  - Atmospheric deposition;
  - Mineralization;
  - Fertilizer application in sulphate and elemental form.
- Looked at international data on the effect of S in fertilization programmes.

CONCLUSIONS

- S should form part of a balanced fertilization programme in order to achieve higher productivity and fertilizer efficiency
  - Evaluate crop requirements and potential deficit
  - Check that sulphur is not the limiting nutrient
  - If in doubt – “trial it”
- Africa has yet to experience the “Green Revolution” and sub-Saharan Africa’s potential to improve yields and fertilizer efficacy must be explored.

THANK YOU

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unlocking nature's potential

LIMING AND THE RELEVANCE OF SOIL CALCIUM AND MAGNESIUM RATIOS

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INTRODUCTION

For more than a decade, the basic cation saturation (BCSR) concept, also referred to locally as the “Albrecht” system or formula, has been actively promoted in South Africa as a more “biologically friendly” and sustainable system for making lime and K fertilizer recommendations than the nutrient sufficiency level approach. Simplistically, the nutrient sufficiency level principle is derived from long-term, field-based calibration studies relating yield to soil test data, in order to identify soil test values above which yield increases in response to further increments of lime or a particular nutrient, are unlikely to occur (Olson *et al.*, 1982; Eckert, 1987).

The cation ratio concept, on the other hand, originated from greenhouse studies with lucerne on 20 of New Jersey’s most important agricultural soils over an 8-year study (Bear & Troth, 1948). This research led to the suggestion that for optimum nutrition of lucerne, 65% of the cation exchange capacity (CEC) should be saturated with Ca, 10% by Mg, 5% by K, and 20% by H – i.e. Ca+Mg should constitute 75% of the CEC and be present in an equivalent Ca to Mg ratio of 6.5. According to Liebhardt (1981), the findings reported for New Jersey soils were modified to suit soils from Missouri by Graham (1959) who recommended 75% saturation with Ca, 10% with Mg, 2.5 to 5% with K, and the remaining 10 to 12.5% with acidity – i.e. 85% Ca+Mg saturation, with an equivalent Ca to Mg ratio of 7.5. Graham (1959) suggested, however, that ranges from 65 to 85% saturation with Ca and 6 to 12% with Mg would have little impact on yield. In South Africa, proponents of the Albrecht system define minimum and maximum tolerance levels for exchangeable Ca and Mg saturation but, nevertheless, seemingly target a single ratio. The most widely promoted ratio is 68% Ca and 12% Mg – i.e. 80% Ca+Mg saturation with an equivalent Ca to Mg ratio of 5.7.

In so far as it pertains to soil acidity and liming, the BCSR / Albrecht approach hinges on two cardinal assumptions: (1) that yields are maximized when the exchangeable Ca+Mg saturation represents 71 to 97% of the CEC (extremes indicated by Graham, 1959), and (2) that, even if the first assumption is satisfied, additional calcitic lime and/or gypsum is required to adjust the exchangeable Ca to Mg ratio to achieve the “optimum” balance.

The purpose of this paper is to present an overview of the implication and relevance of these assumptions with regard to lime recommendations being advocated to South African farmers, by both foreign and local consultants who religiously endorse, and actively market the use of the “Albrecht” formula.

RELATIONSHIP BETWEEN pH AND CEC

As a first approximation, liming soils to achieve a Ca+Mg saturation of 80% (the locally targeted value) may not seem unreasonable. In this regard, however, it is doubtful that local farmers using the Albrecht approach, including the consultants who make lime recommendations on the basis of the system, fully appreciate the complexities of the soil chemistry surrounding CEC determination, or its implication with regard to soil acidity and the need for lime.

Owing to the presence of variable charge surfaces in soils such as organic matter, sesquioxides and clay mineral edges, which adsorb or desorb H^+ ions as pH is varied (Uehara & Gillman, 1981; Kamprath, 1984), the CEC of soils has been shown to vary with pH (Pratt, 1961; McLean *et al.*, 1965; Reeve & Sumner, 1971). Proton desorption (equivalent to OH^- sorption) is promoted by increasing pH, and results in an increase in CEC. In addition, neutralization of CEC blocking positively charged hydroxy-Al interlayers or surface coatings through pH elevation creates additional basic cation adsorption capacity (McLean *et al.*, 1965; Thomas & Hargrove, 1984).

Variation in the CEC of naturally acid soils with pH is illustrated by field-generated buffer curves relating effective CEC (∑ exchangeable Ca^{2+}, Mg^{2+}, K^{+}, and KCl-exchangeable acidity i.e. Al+H) to pH (Fig. 1).

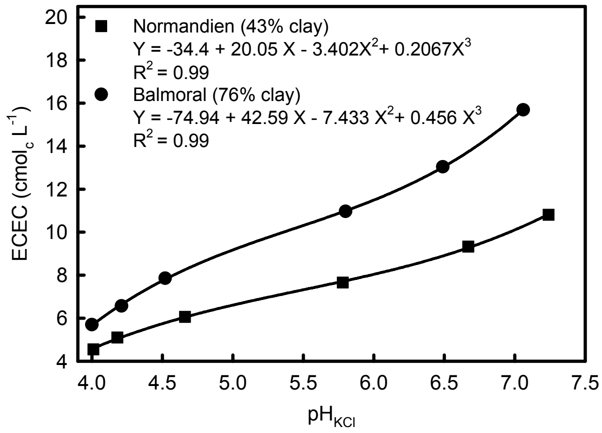

Figure 1. Relationship between soil pH and effective cation exchange capacity derived from field-based liming studies (M. Farina, unpublished data).

An increase in pH_{KCl} from 4 to 7, through liming, resulted in a 2.2 and 2.7-fold increase in the effective CEC (ECEC) for the Normandien and Balmoral soils, respectively, with inflection points (maximum buffering) occurring at pH 5.4 to 5.5.

Thus, for acid soils with appreciable pH-dependent charge, traditional procedures which measure CEC at pH 7.0 or 8.2 often result in highly inflated values of the soil's actual capacity to retain cations at the prevailing soil or "field" pH – i.e. ECEC (Thomas & Hargrove, 1984; Sumner & Miller, 1996). This is illustrated by the topsoil data for eight Natal Oxisols (Table 1) used in the study by Reeve & Sumner (1970b). For these soils, which had $CaCl_2$ pH values ranging from 4.4 to 5.0, ECEC varied from 14 to 34% of the CEC at pH 7, with an average of 24%.

Table 1. The organic carbon, pH, effective CEC, and CEC at pH 7.0 for eight surface Natal Oxisols (after Reeve & Sumner, 1970b).

Soil Type	**Organic carbon**	**pH 0.002 M $CaCl_2$**	**Cation exchange capacity**	
			"Field" pH	**pH 7.0**
	---- g kg^{-1}----		**--------------- $cmol_c\ kg^{-1}$ --------------**	
Griffin	68	4.4	5.5	39.6
Clovelly	33	4.4	6.4	18.8
Lidgetton	44	4.5	7.3	31.7
Farmhill	42	4.6	5.6	22.0
Hutton	41	4.7	6.0	21.2
Farningham A	37	4.6	4.5	23.0
Farningham B	45	5.0	6.7	30.0
Balmoral	19	4.7	3.7	14.3

Data from an investigation into the charge characteristics of 17 acid topsoils (Grove *et al.*, 1982) showed that "field" CEC averaged 32% of CEC (pH 7) for soil types dominated by kaolinite and chloritized vermiculite (pH_{KCl} 3.7 - 5.2). For four montmorillonitic soils (pH_{KCl} 3.4 - 4.7), the average was 68%. Similarly large differences between CEC determined using neutral unbuffered salts, or calculated as the sum of exchangeable cations extracted by such solutions, and CEC measured at pH 7 or 8.2, have been reported in a number of other studies (Coleman *et al.*, 1959; Pratt & Bair, 1962; McLean *et al.*, 1965). The extent to which CEC is inflated when determined at pH 7 or pH 8.2 depends on the difference in pH between the soil and the pH at which CEC is determined, as well as on the amount of pH-dependent charge, which is a function of the quantity and type of clay minerals present and the organic matter content.

A direct consequence of defining CEC using solutions buffered at pH 7 or 8.2 is that it results in unrealistically low values for Ca+Mg saturation, relative to those found when using ECEC (Coleman *et al.*, 1959; Grove *et al.*, 1982). This is especially true for acid soils with a high proportion of variable charge components, relative to permanent charge minerals. The relationship between Ca+Mg saturation based on ECEC versus CEC (pH 7) for 13 acid soils dominated by either kaolinite or chloritized vermiculite, drawn from data published by Grove *et al.* (1982), is shown in Figure 2. On average, Ca+Mg saturation expressed as a percentage of CEC (pH 7) was 2.5-fold lower than that obtained using ECEC. For four montmorillonitic soils (data excluded from Fig. 2), the average Ca+Mg saturation of CEC (pH 7) was 1.4-fold lower than that obtained using ECEC.

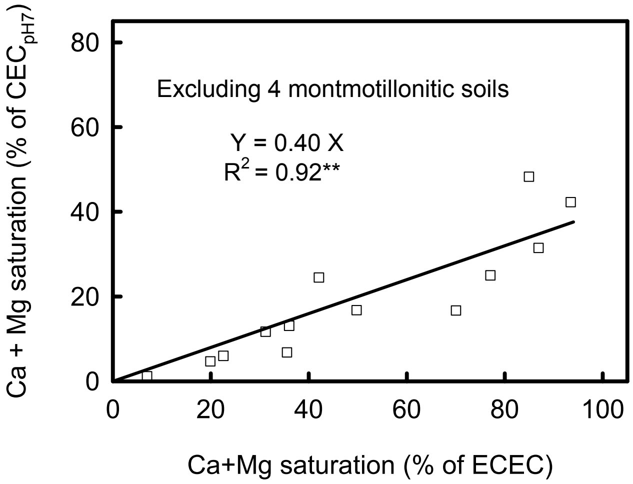

Figure 2. Relationship between Ca+Mg saturation calculated using either ECEC or CEC (pH 7). Drawn from data published by Grove et al. (1982).

Since the BCSR / Albrecht formula utilizes CEC (pH 7) as its basis, and requires a Ca+Mg saturation of 80% according to local consultants, it is perhaps not surprising that large and questionable amounts of lime are recommended to farmers in order to increase the Ca+Mg saturation to this targeted value, particularly on soils with appreciable pH-dependent charge. The relevance of this is considered in more detail in the following section.

RELATIONSHIP BETWEEN pH AND PERCENTAGE CA+MG SATURATION

Liebhardt (1981) developed an equation relating Ca+Mg saturation to pH_w for sandy Coastal Plain soils in Delaware ($Y = 20.1X – 45.8$, $R^2 = 0.74$). This equation was used by Liebhardt (1981) to identify soil pH values required to achieve the various degrees of Ca+Mg saturation proposed by different philosophies (Fig. 3).

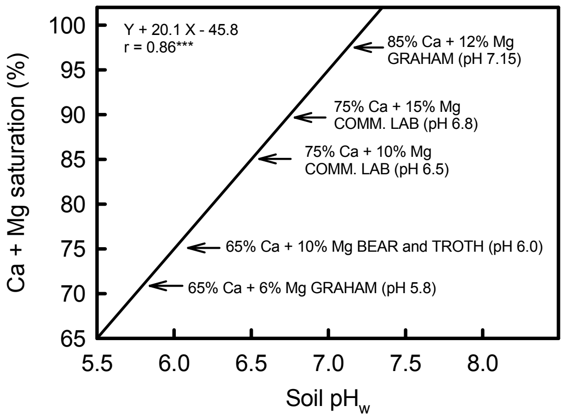

Figure 3. Calcium + Magnesium saturation as affected by pH (redrawn from Liebhardt, 1981).

On the basis of the relationship shown in Figure 3, to achieve a Ca+Mg saturation of 80%, as recommended by local proponents of the Albrecht system, it would require liming soils to a pH_w of 6.3. Owing to manganese deficiency when soils were limed to pH >6.0, Liebhardt (1981) recommended that Ca+Mg saturation of 65 to 75% (pH 5.5 to 6.0) were adequate for Delaware's Coastal Plain soils. Liming to achieve Ca+Mg saturation ratios suggested by some commercial laboratories in Delaware – i.e. 85 to 90% (Fig. 3) result in soil pH values of 6.5 to 6.8 for the sandy Delaware soils, and lead to yield reductions through lime-induced Mn deficiency (Liebhardt, 1979, 1981).

For soils of widely differing mineralogy, and clay and organic matter content, the relationship between pH and Ca+Mg saturation is, understandably, less well defined than that reported by Liebhardt (1981) for Delaware's Coastal Plain soils (Fig. 4).

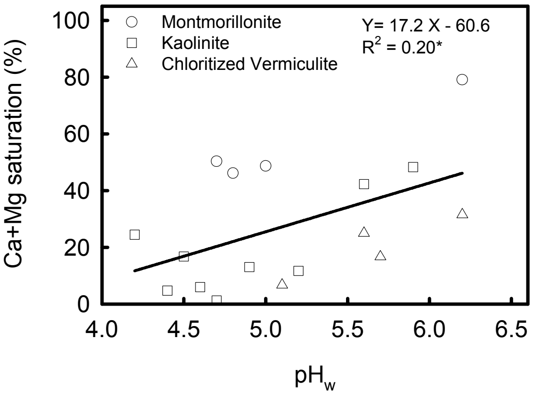

Figure 4. Relationship between pH_W and Ca + Mg saturation (% of CEC_{pH7}). Drawn from data published by Grove et al. (1982).

The importance of clay mineralogy is reflected by the fact that, for a given pH_w, soils with a dominance of montmorillonite (permanent charge) have an appreciably higher degree of Ca+Mg saturation than soils dominated by kaolinite or chloritized vermiculite (variable charge). It is also apparent from Figure 4 that, at pH_w values of 5.5 to 6.0, which were sufficient to achieve Ca+Mg saturations of 65 to 75% for the sandy soils studied by Liebhardt (1981), only resulted in Ca+Mg saturation levels of 20 to 50% for the acid soils containing kaolinite and hydroxy - Al interlayered minerals, used in the study by Grove *et al.* (1982). The data suggests that, to achieve a Ca+Mg saturation of 80% on these soils, they would need to be limed to pH_w values above 7.0. Similarly, from the relationship between pH_{KCl} and Ca+Mg saturation expressed as a percentage of field CEC at pH 7.0 (derived from Fig. 1), it is apparent that, to achieve a Ca+Mg saturation of 80%, the soils would need to be limed to a pH_{KCl} of 6.4 (Fig. 5). The quantity of lime (CCE = 80%) required to elevate these acid soils to pH_{KCl} 6.4 amounts to nearly 15 and 20 Mg ha^{-1} for the Normandien and Balmoral soils, respectively (Fig. 6).

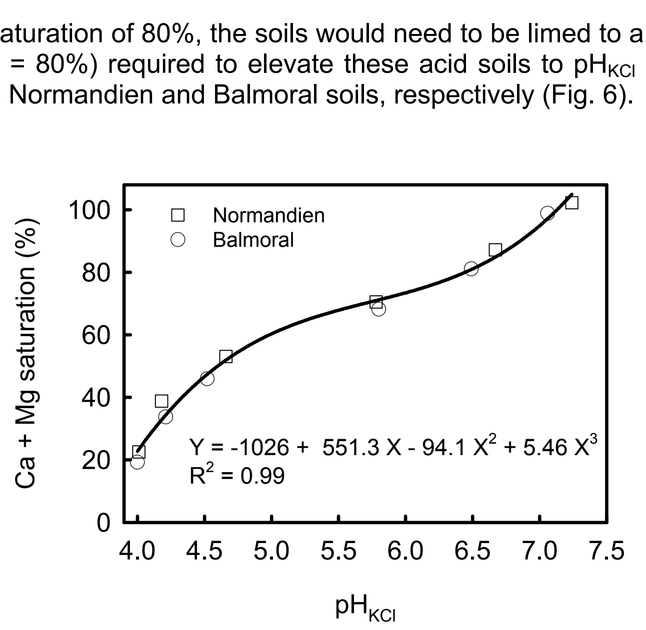

Figure 5. Relationship between pH_{KCl} and the degree of Ca+Mg saturation at a field pH of 7.0 (M. Farina, unpublished data).

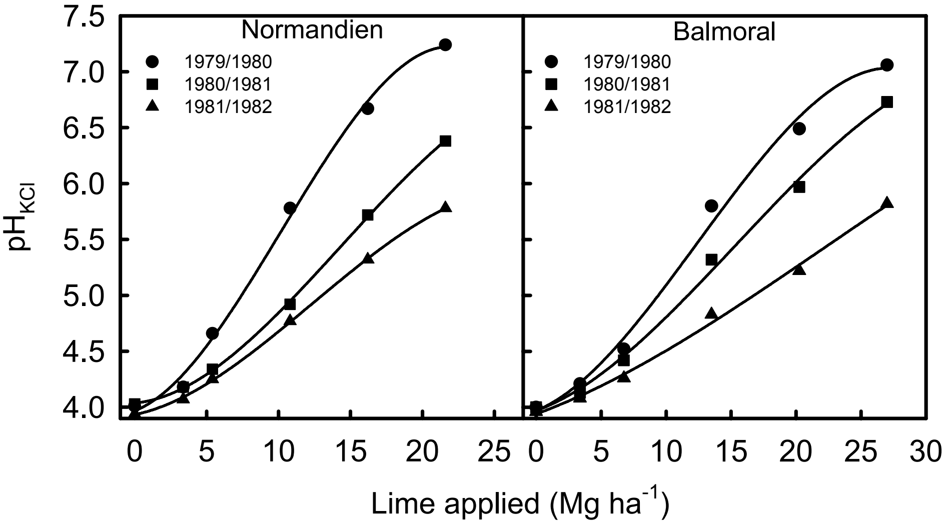

Figure 6. Relationship between lime applied and soil pH_{KCl} (M. Farina, unpublished data).

With continued mixing of the initially limed soil through annual ploughing and disking operations and high N use, zones of higher alkalinity presumably contact areas of more acid soil resulting in continued reaction/consumption of alkalinity, causing a decrease in pH (Fig. 6). As a consequence, further lime would need to be applied to restore the soils back to pH_{KCl} 6.4 (i.e. Ca+Mg saturation = 80%). For both soils, the amount of extra limed required one season after its initial application equates to 4 Mg ha^{-1}, giving a total potential lime application of 19 and 24 Mg ha^{-1}, in two seasons, for the Normandien and Balmoral soils, respectively.

The sustainability and justification of using such large amounts of lime to maintain Ca+Mg saturation at 80% of CEC (pH 7) for crops like maize, soybean and wheat must be challenged, especially since both soils are more than 95% base (Ca+Mg+K) saturated at a pH_{KCl} of 4.5, if ECEC rather than CEC (pH 7) is used. Magdoff and Bartlett (1985) similarly questioned the theoretical relevance of pH vs % base saturation for predicting lime requirement, since all 51 Vermont soils studied by them were 100

+% base saturated at pH_s >4.9, if neutral salt rather than CEC at pH 7.0 or 8.2 was used. In this regard, the issue of liming soils to near neutral pH, necessitated by targeting 80% Ca+Mg saturation of CEC (pH 7), as opposed to liming soils to alleviate Al, and possibly Mn toxicity, will be considered in the next section.

LIME REQUIREMENT TARGET: NEUTRAL pH, "SAFE" pH OR Al SATURATION

The beneficial effect on crop growth resulting from lime application to low pH soils is widely documented in the literature. However, liming strategies based on soil pH and, especially those which target pH_w values of 6.5 to 7.0, as opposed to liming to reduce exchangeable Al to sufficiently low levels, have been a controversial topic for several decades (Kamprath, 1970a,b; McLean, 1970; Reeve & Sumner, 1970a,b; Kamprath, 1971; McLean, 1971; Pearson, 1975; Farina & Sumner, 1979; Fox, 1979; Farina *et al.*, 1980; Farina *et al.*, 1981; Farina *et al.*, 1982; Farina & Channon, 1991; Sumner & Yamada, 2002).

The poor growth of most crops in low pH soils results primarily from the phytotoxic nature of high concentrations of soluble Al (Foy, 1984). Since Al solubility decreases exponentially with an increase in pH, its concentration at pH_w 5.5 and above is reduced to sufficiently low levels to have minimal detrimental impact on the growth of all but perhaps the most Al-sensitive or high Ca-requiring crops. Manganese toxicity has also been implicated as a cause of poor growth on some acid soils (Foy, 1984), but its occurrence and severity as a yield-limiting factor is much less widespread and problematic than Al toxicity. In KwaZulu-Natal, for example, isolated cases of Mn toxicity have been observed with crops such as lettuce and cabbage on anthropogenically acidified soils, but not on naturally occurring acid soils.

McLean (1970, 1971) strongly promoted liming soils to near neutral pH on the grounds that nutrient availability was optimized at these pH values and that biological activity is enhanced, resulting in more rapid turn over of organic matter, with a release of essential plant nutrients including N, P and S. McLean, (1971) conceded, however, that on well fertilized soils, liming to eliminate toxicities of Al and Mn was likely to be sufficient to achieve maximum yields with most crops. For acid-sensitive, high Ca-requiring crops such as lucerne, liming topsoils to pH 7.0 where subsoils are strongly acid, was not considered unreasonable by McLean (1971). Likewise, Brown and Stecker (2003) endorsed the merits of liming Missouri topsoils to higher pH values than ordinarily required for legume production if subsoils were highly acid, on the premise that this would neutralize some of the subsoil acidity. By comparison, lime rates of up to 20 Mg ha^{-1} were found to have a minimal ameliorative effect on subsoil acidity four years after application, on a kaolinitic clay soil containing an appreciable quantity of an hydroxy Al-interlayered mineral (Farina, 1997). In this regard, Farina *et al.* (2001a, b) showed that the use of gypsum was a highly effective and economical strategy for ameliorating subsoil acidity, relative to conventional topsoil incorporation of lime alone.

In order to resolve some of the discrepancy between lime requirements, as opposed to frequently recommended lime rates, Sumner and Yamada (2002) delineated soils on the basis of their pH. For soils with pH_w values < 5.2 to 5.4, positive effects of lime application were considered to be primarily due to alleviation of Al and Mn toxicity. For soils with pH_w >5.5, on the other hand, positive responses to lime were considered to be a more likely consequence associated with the alleviation of potential nutrient deficiencies, including N, P, S, Ca, Mg and Mo. An abundance of examples for many crops, including lucerne, were presented by Sumner and Yomada (2002), showing that economic responses to lime were unlikely to occur above a pH_w of 5.5, the pH at which exchangeable Al is effectively neutralized.

As far as nutrient deficiencies are concerned, Mikkelsen (1963), demonstrated that liming increased organic matter mineralization, and alleviated N and S deficiencies in three Cerrado soils in Brazil. Since organic matter is also an important storehouse for P, increased rates of organic matter mineralization may similarly be expected to contribute to plant available P. Notwithstanding this, the rapid rise in the concentration of phytotoxic Al as pH_w falls below 5.5 for many soils, results in increasingly depressed root growth and proliferation, which reduces P uptake, creating the impression that P solubility is enhanced by pH elevation (Sumner & Yamada, 2002). Studies cited by Sumner and Yamada (2002) show that P solubility is, in fact, reduced through pH elevation, and that P uptake may accordingly be diminished by liming to pH >5.0.

High concentrations of soluble Al in soils depress the uptake of Ca and Mg. However, absolute deficiencies of Ca in acid South Africa soils have not, unambiguously, been shown to be a major cause of depressed yields at low pH for field grown crops such as maize and soybean (M. Farina, personal communication). In any event, the use of dolomitic lime to neutralize all exchangeable Al present would be sufficient, in most cases, to provide adequate amounts of Ca and Mg to satisfy crop requirement (Sumner & Yamada, 2002).

Molybdenum solubility and its availability to plants increase as pH is elevated through liming (Sumner & Yamada, 2002). The interactive effects between lime and Mo are illustrated in Figure 7. For one of the seasons represented in Figure 7, the combination of lime and Mo significantly decreased soybean yield. Notwithstanding this, to eliminate Mo deficiency through liming, it was necessary to elevate soil pH to 4.7. The cumulative amount of lime applied to raise and maintain the soil at this pH equates to 20 Mg ha^{-1}. Conversely, lime had no significant benefit on yield when Mo treated seed (equivalent to 70g sodium molybdate per hectare) was used. Thus, small and relatively inexpensive amounts of Mo can substitute for large and costly inputs of lime, if the main reason for poor growth on acid soils is Mo deficiency rather than Al toxicity.

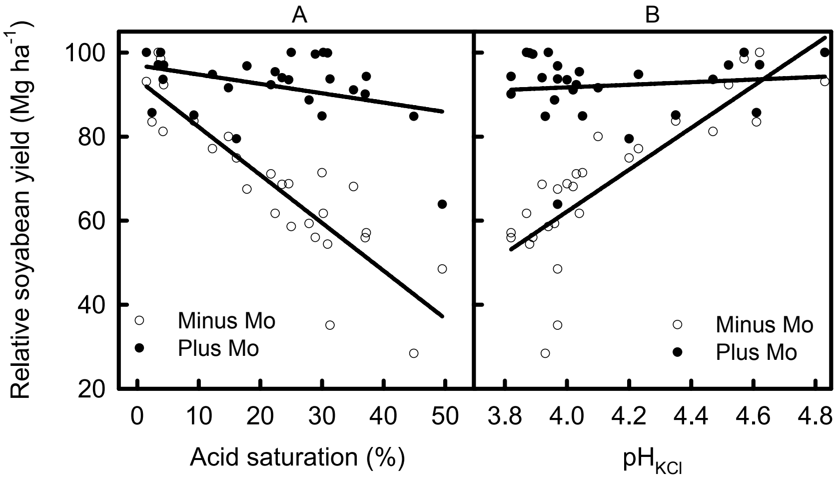

Figure 7. Relationship between (A) acid saturation and (B) pH, and the relative yield of soybean as influenced by Mo seed treatment on a Balmoral clay soil at Greytown (Thibaud & Farina, 2001).

Apart from the obvious economic advantage of liming soils to pH values no higher than the point at which exchangeable Al is effectively neutralized (pH_w 5.5), as opposed to targeting pH_w values of 6.5 to 7.0, Sumner and Yamada (2002) discussed numerous other benefits that accrue, including reduced nitrification, reduced incidence of diseases and pests, reduced clay dispersion and soil crusting, and improved water infiltration. Other advantages not discussed by Sumner and Yamada (2002) include reduced leaching losses of S (Korentajer *et al.*, 1983) and reduced potential for N loss from soil through ammonia volatilization, especially if urea is used (Adams & Martin, 1984). Kamprath (1971) similarly discussed a number of detrimental and yield-limiting effects by liming highly weathered soils to pH 7.0, such as induced deficiencies of P, B, Zn and Mn, and the formation of smaller aggregates which reduce the rate of water infiltration.

The long-held view, that nutrient availability is maximized at soil pH values near 6.0, was challenged by Farina *et al.* (1981), who noted significant decreases in the uptake of P, Zn, Mn and B by maize with liming. In this same study, liming soils to pH_{KCl} values > 5.0 did not significantly improve maize yields while, for some of the soils, near maximum yields occurred at appreciably lower pH values than in others. For six of the nine soils used, liming beyond the pH at which maximum yields occurred significantly decreased yield. These findings concur with those reported in a later study (Farina *et al.*, 1982).

Similarly, Reeve and Sumner (1970b) showed that the yield of trudan increased with liming up to the point at which exchangeable Al was eliminated, after which a significant reduction in yield occurred. In addition, the amount of lime required for maximum growth of trudan was, on average, only 17% of that required to achieve a SMP buffer pH of 6.5. While liming soils to a pH_w of 5.5 eliminates possible Al toxicity, many soils with pH_w values lower than this do not contain toxic amounts of Al, resulting in unnecessary liming. Thus, pH *per se* is a poor indicator of the need for lime across a wide range of soils (Farina *et al.*, 1980). In this study, correlation of the relative yield of maize with pH_s, pH_w, % Al saturation and percentage Al+H saturation resulted in R^2 values of 0.22, 0.18, 0.81 and 0.81, respectively. In a field study involving 22 site-years with maize (Farina & Channon, 1991), neither pH_{KCl} (Fig. 8) nor exchangeable acidity (Fig. 9) were found to be reliable indicators of lime response on soils varying from 10 to 70% and 0.4 to 4.3% with respect to clay and organic carbon content.

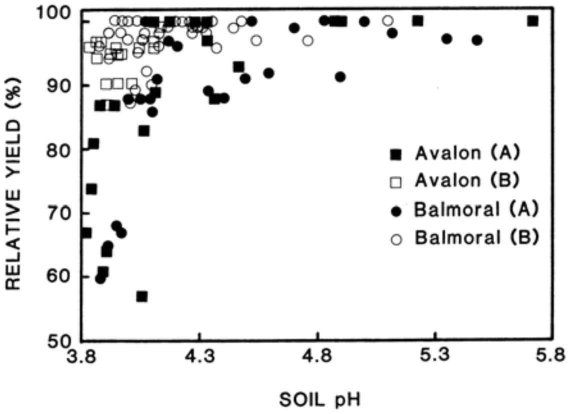

Figure 8. Relationship between pH and relative yield of maize on sandy and clay soils in KwaZulu-Natal. Reproduced with permission from M.P.W. Farina and P. Channon, "A field comparison of lime requirement indices for maize". In: Plant & Soil 134: 127-135, copyright Kluwer Academic Publishers, 1991.

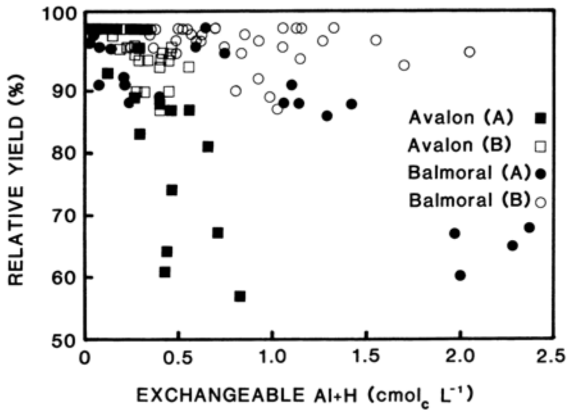

Figure 9. Relationship between exchangeable acidity and relative yield of maize on sandy and clay soils in KwaZulu-Natal (Reproduced with permission from M.P.W. Farina and P. Channon, "A field comparison of lime requirement indices for maize". In: Plant & Soil 134: 127-135, copyright Kluwer Academic Publishers, 1991).

By comparison, the use of Al or acid saturation – i.e. exchangeable Al or Al+H expressed as percentage of the ECEC, resulted in an appreciable improvement in the relationship between soil test and relative yield (Fig. 10). A remarkably similar relationship between Al saturation and the relative yield of maize (Fig. 11) was reported by Fox (1979).

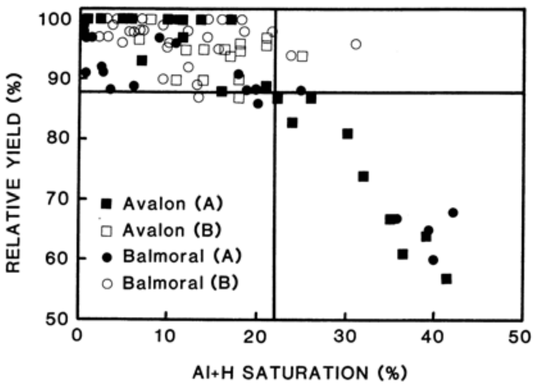

Figure 10. Relationship between acid (Al+H) saturation and relative yield of maize on sandy and clay soils in KwaZulu-Natal. (Reproduced with permission from M.P.W. Farina and P. Channon, "A field comparison of lime requirement indices for maize". In: Plant & Soil 134: 127-135, copyright Kluwer Academic Publishers, 1991.

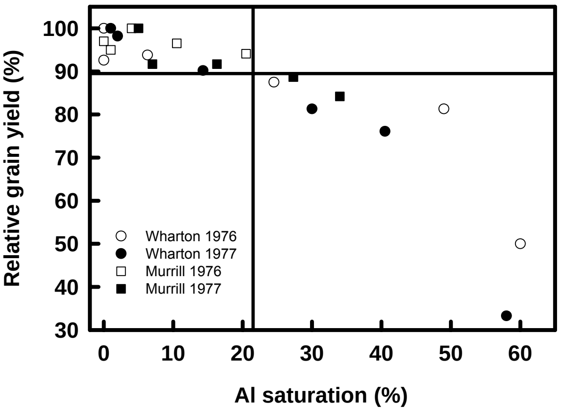

Figure 11. Relationship between Al saturation and relative maize grain yield (redrawn from Fox, 1979).

The amount of Al in the soil solution has been shown to be related to aluminium saturation for mineral soils (Evans & Kamprath, 1970), while Farina and Channon (1991) indicated that exchangeable acidity (Al+H) or Al saturation provide an empirical index of soil solution Al activity. It is perhaps not surprising, therefore, that use of either Al or exchangeable acidity, expressed as a percentage of the ECEC, should relate so well to yield.

The use of acid saturation as a basis for making lime recommendations has been used by the Cedara Fertilizer Advisory Service in KwaZulu-Natal for more than three decades (M. Farina, personal communication), and takes into account the fact that crops vary in their tolerance to Al, by targeting different values for the permissible acid saturation (PAS), depending on the crop to be grown. PAS values for a number of crops are illustrated in Table 2. For the establishment of highly acid-sensitive legumes such as lucerne and clovers, a pH_{KCl} of at least 5.0 is considered necessary to ensure adequate persistence of the legume.

Table 2. Permissible acid saturation levels used by Cedara for a number of pastures and crops

Crop	PAS (%)
Eragrostis curvula	50
Kikuyu	40
Fescue	40
Cynodon	40
Potato	30
Maize	20
Soyabean	20
Wheat	10
Most vegetables	1 - 5
Perennial ryegrass	1

Finally, the main advantage of using acid saturation as an index of lime requirement, rather than use of a “safe” pH, is that it precludes the unnecessary liming of soils – i.e. soils where an increase in yield through liming would not be expected. Since lime recommendations based on acid saturation are more conservative than those based on pH, similar yield benefits can be achieved more economically, an important consideration in cases where lime is either in short supply or very costly. Liming on the basis of PAS may, however, require more frequent lime applications, especially on sandy soils, which tend to reacidify more rapidly because of their low buffer capacity.

The second assumption relating to this review, namely that an ideal exchangeable soil Ca to Mg ratio exists will now be briefly addressed in the following section.

SOIL Ca TO Mg (Ca/Mg) RATIOS: HOW CRITICAL ARE THEY?

The relevance of exchangeable soil Ca/Mg ratios as a basis for making lime and fertilizer recommendations is an issue that has been raised many times over the past 100 years (Kelling *et al.*, 1996; Kopittke & Menzies, 2007). From these two reviews, it is apparent that there is a total dearth of published scientific studies to show that the Ca/Mg ratios encountered in most soils are as critical as sales people promoting the Albrecht system in South Africa would like to believe. In addition, flawed experimental design and misinterpretation of data in some of the studies conducted by Albrecht were pointed out by Kopittke and Menzies (2007).

The irrelevance of Ca/Mg ratios, but the importance of liming acid soils is shown in Table 3, using data published by Moser (1930).

Table 3. Initial and final pH and exchangeable Ca to Mg ratio, and the percentage yield response to calcitic lime (adapted from Moser, 1933).

Soil	pH_w[a]	Exch. Ca/Mg[a]	pH_w[b]	Exch. Ca/Mg[b]	% increase in yield due to lime
1	5.25	2.63	7.30	4.90	52
2	4.65	1.02	7.00	3.40	194
3	6.27	1.08	7.00	1.51	6
4	5.72	1.28	6.70	2.65	6
5	5.15	3.11	6.75	7.00	62
6	5.00	2.10	6.80	5.00	21
7	5.44	4.59	7.15	4.13	49
8	4.96	1.67	6.80	4.26	186

[a] Initial values, [b] after liming and cropping with barley, red clover, fodder corn and timothy.

Soils 3 and 4 had similarly low initial Ca/Mg ratios as soils 2 and 8 but, because the former two soils were less acid (pH 6.27 and 5.72) compared to the latter two (pH 4.65 and 4.96), they showed a small yield response to the application of calcitic lime (6% versus 186 to 194% for soils 2 and 8). Research conducted in the eastern USA (Hunter, 1949) showed that varying the exchangeable Ca/Mg ratio from 0.25 to 32 had no significant effect on the yield of lucerne, weight of roots or lignin content. The range of Ca/Mg ratios used in this study was considered extreme, compared to those normally found in soils. The results of a study by Key *et al.* (1962) in Illinois showed that, provided Ca and Mg were present in adequate amounts to satisfy plant growth, maize and soybean yields were not significantly affected by the ratio, provided that it was not less than 1.

Data from Martin and Page (1969) relating exchangeable soil Ca/Mg ratio and the yield of citrus plants is shown in Figure 12. Depending on soil type, yields were maximized at equivalent exchangeable Ca/Mg ratios of 0.9 to 2.4, values appreciably below the ratio of 5.7 targeted by local proponents of the Albrecht system. Below a Ca/Mg ratio of 0.5, yields dropped sharply while, for the Merriam soil, a significant reduction in yield occurred at a ratio of 16.3. Similarly, in a study with onions (van Lierop, 1979) yields decreased rapidly as the Ca/Mg ratios decreased below 0.5. However, such low ratios are not typical of most soils. While serpentine-derived soils often have very low Ca/Mg ratios, these soils are rare and not widespread in South Africa, at least not from an agronomic point of view (J. Hughes, personal communication).

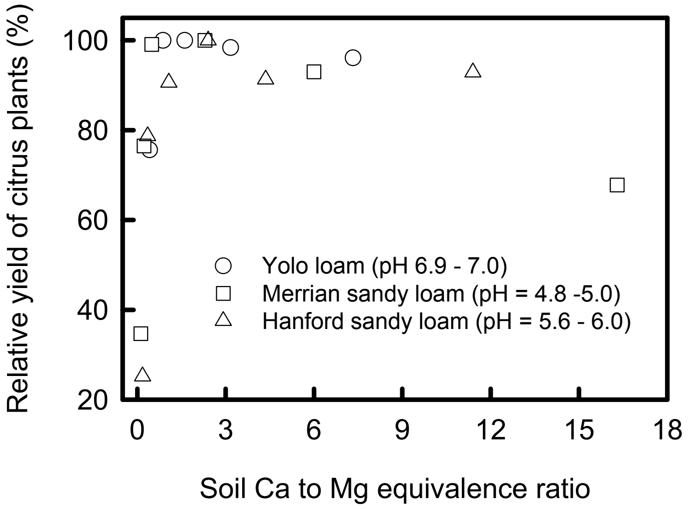

Figure 12. Relationship between exchangeable Ca/Mg ratio and the relative yield of citrus plants (drawn from data published by Martin and Page (1969).

On both soil types used in the study by McClean and Carbonell (1972), the yield of German millet and lucerne was unaffected by soil treatments in the range of Ca 75% - Mg 5% to Ca 55% - Mg 25% – i.e. Ca/Mg ratios varying from 2.2 to 15. In later work (Eckert & McLean, 1981), it was concluded that “there is no *ideal* basic cation saturation ratio or range for crops on the whole. Instead, the individual nutrient cations should be supplied in adequate but not excessive amounts, depending on the response of the crop in question”. McLean *et al.* (1983) stated that “in fertilizer and lime practice, emphasis should be placed on providing sufficient but non-excessive levels of each basic cation rather than attempting to adjust to a favourable basic cation saturation ratio which evidently does not exist”.

Likewise, researchers in Nebraska (Olson *et al.*, 1982) concluded that “the nutrient sufficiency approach to soil testing, when adequately calibrated, promises the surest method of achieving most economic yields while conserving non-renewable resources and preserving environmental integrity”. The nutrient sufficiency approach seeks to supply adequate amounts of individual nutrients, without making adjustments for nutrient ratios. It is pertinent to mention that the lime and fertilizer recommendations given by the Soil Fertility Laboratory at Cedara are based on yield response curves generated from data obtained through extensive field experimentation and soil testing, and concur with the nutrient sufficiency level principle.

In support of the experimental findings mentioned above, Simson *et al.* (1979), working in Wisconsin, found that variation in the exchangeable Ca/Mg ratio between 0.8 and 5.0 had no effect on maize and lucerne yields when adequate amounts of Ca and Mg were present in the soil. They suggested that even wider ratios than those used in their study were unlikely to affect yields. The results for lucerne are shown in Figure 13. Studies with ryegrass and Kikuyu in KwaZulu-Natal (N. Miles, personal communication) likewise showed that yields were not significantly influenced by widely varying exchangeable soil Ca/Mg ratios (Fig. 14). In a two year study with maize near Winterton, adjustment of Ca/Mg ratios to 2.7 to 4.5 using calcitic lime, MgO and $MgSO_4$, on a Hutton soil with a pH_{KCl} of 5.94, had no significant effect on grain yield (G. Thibaud, unpublished data).

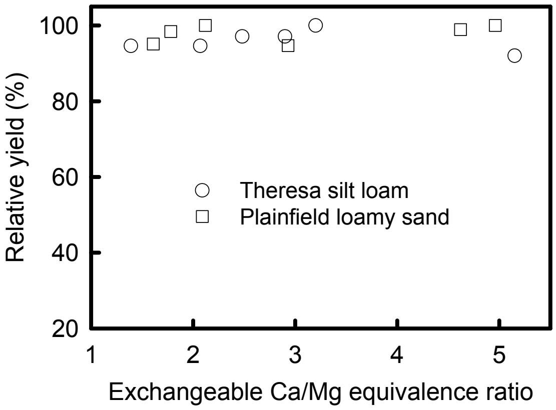

Figure 13. Relationship between exchangeable Ca/Mg ratio and relative yield of lucerne (drawn using data from Simson et al., 1979 and Schulte & Kelling, 1985).

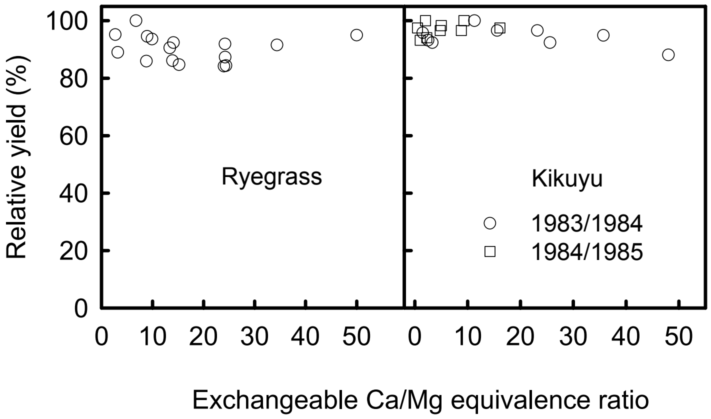

Figure 14. Relationship between soil Ca/Mg ratio and the relative yield of ryegrass and kikuyu (N. Miles, personal communication).

Similarly, Liebhardt (1981), in studies conducted in Delaware, showed that maize yields were unaffected by varying the Ca/Mg ratio between 2.5 and 4.5, while Fox and Piekielek (1984), in Pennsylvania, found no evidence that Ca/Mg ratios as low as 1.8 or as high as 36.9 had any negative or positive impact on maize yields (Fig.15). Studies conducted in New York (Reid, 1996) showed that the yields of both lucerne and birdsfoot trefoil were not influenced by varying the Ca/Mg ratio from 1 to 267, provided that soil pH was not excessively low, and the soil contained sufficient Mg. In a recent study with cotton (Stevens *et al.*, 2005), in which the soil Ca/Mg ratios were adjusted to cover the range of 2.5 to 7.6 through application of $CaSO_4$ or $MgSO_4$, it was found that neither cotton fibre properties nor lint yield were significantly influenced by the Ca/Mg ratio.

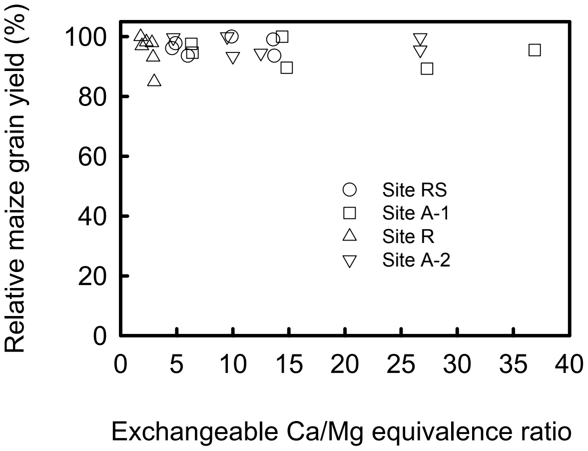

Figure 15. Relationship between exchangeable Ca/Mg ratio and the relative yield of maize grain at four sites (drawn from data published by Fox & Piekielek, 1984).

According to Kinsey (2001), maize yields are reduced by 0.63 Mg ha^{-1} if the exchangeable Mg saturation on medium to heavy textured soils is 15%, and are reduced by a further 0.32 Mg ha^{-1} if Mg saturation exceeds 20%. In the case of soybean, yields are reduced by 0.67 Mg ha^{-1} at 13 to 14% Mg saturation. There is no published scientific evidence to support this claim. The relationship between Mg saturation and the relative yield of maize grain is shown in Figure 16.

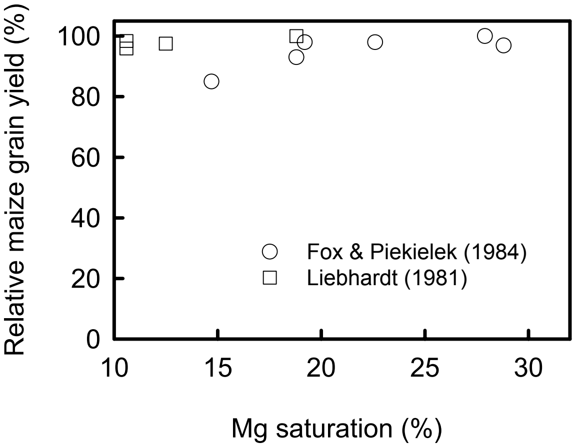

Figure 16. Relationship between Mg saturation and relative yield of maize (drawn from data published by Liebhardt (1981) and Fox & Piekielek (1984)). Data where yields were depressed by over liming in the study by Liebhardt (1981) are excluded.

While in both studies, Mg saturation did not significantly influence yield, it is interesting to note that a relative yield of 100% occurred at 18.8 and 27.9% Mg saturation in the study by Liebhardt (1981) and Fox and Piekielek (1984), respectively.

To lend further support to the fact that farmers should not be concerned about their soil Ca/Mg ratios or the Mg saturation, yield data from the Ten Ton Maize Club and Super Soya Competition in KwaZulu-Natal are shown in Figures 17 and 18, respectively.

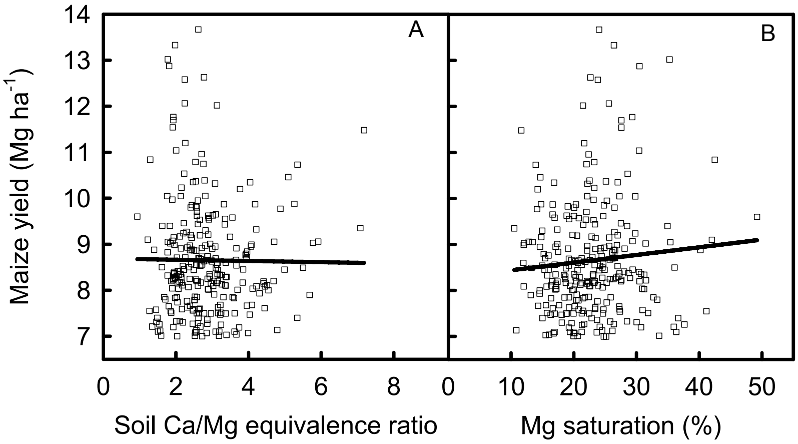

Figure 17. Relationship between between (A) Ca/Mg ratio and (B) Mg saturation and maize yield.

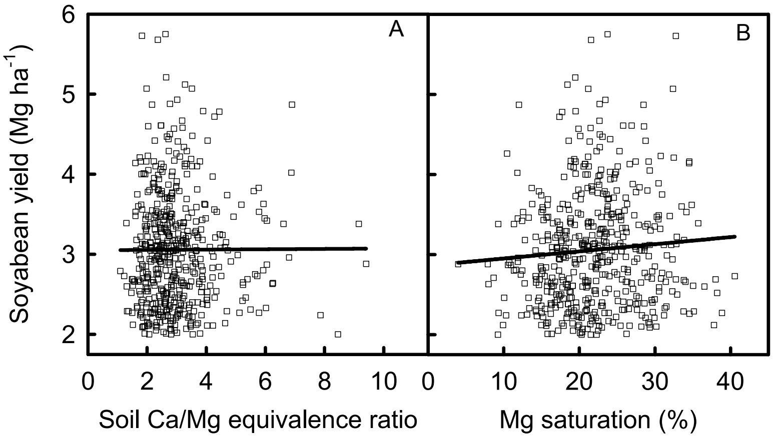

Figure 18. Relationship between (A) Ca/Mg ratio and (B) Mg saturation and soybean yield.

In order to reduce yield variability associated with factors such as poor control of weeds, pests and diseases, late plantings, and drought or hail, or otherwise generally poor management on the part of participating farmers, only data points corresponding to maize and soybean yields greater than 7 and 2 Mg ha^{-1} are shown. In all, there were 269 data points for maize and 501 data points for soybean. While it is accepted that yield is a function of many and often interacting factors, it is not unreasonable to assume that, if Ca/Mg ratios and Mg saturation are as critical as proponents of the Albrecht approach make them out to be, some trend would at least be evident in Figures 17 and 18. Clearly this is not the case, and it supports the study by Liebhardt (1981). Brown and Stecker (2003) stated that "The Ca/Mg ratio idea has hung on far too long, as numerous studies have shown that the Ca/Mg ratio in soils can vary widely without detrimental effects upon crop performance" and "Toxicities of magnesium have not been documented in field studies, but allusions to poisonous levels of magnesium in soil still persist".

The effect on vegetable production and soil properties, through increasing the average soil Ca/Mg ratio from 2.6 to nearly 4, by applying calcitic lime and gypsum to soils with pH values ranging from 6.0 to 6.9 and clay contents varying from 18 to 42%, was investigated by Schonbeck (2000). The results did not support a number of the claims made by proponents of the Albrecht system, namely: increased availability and crop uptake of N, P or micronutrients; increased crop resistance to pests, diseases and environmental stresses; fewer weeds; higher soluble solids (Brix); and longer shelf life. Neither did increasing Ca/Mg ratio, on average, have any detectable effect on soil organic matter content, biological activity in the soil, soil bulk density, soil moisture content, water infiltration and soil strength. Similarly Kelling *et al.* (1996) reported that neither lucerne yield, incidence of weeds (grass or broadleaf), earthworm populations or lucerne quality (crude protein, ADF, NDF) were significantly correlated with exchangeable Ca/Mg ratios. On the basis of their study, they stated that "there is no justification for recommending calcitic lime over dolomitic lime or adding Ca or Mg to soils already containing adequate amounts of these elements". An even more pessimistic viewpoint relating to the use of Ca/Mg ratios was expressed by Rehm (2003) who stated that: "It's an outdated, antique concept that has no value in high yield, modern agriculture".

CONCLUSIONS

Elevating the Ca+Mg saturation to 80% of CEC (pH 7) as required by the BCSR / Albrecht approach, implies liming soils to questionably high pH values. On acid soils, with appreciable pH-dependent charge, unrealistically large rates of lime are required, and it is concluded that this not agronomically desirable or economically sustainable. Liming to reduce acid or Al saturation to levels which are not harmful to crops, on the other hand, is considered to be sufficient to maximize yields and offer appreciable economic advantage. Widely varying exchangeable soil Ca to Mg ratios are tolerated by crops with no detrimental effect, and applying calcitic lime and/or gypsum to manipulate the ratio to achieve what proponents of the Albrecht system regard as "balanced" is not justified.

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Liming and the relevance of soil calcium and magnesium ratios

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PROVINCE OF KWAZULU-NATAL

In this presentation:

- Introduction.
- Relationship between pH and CEC.
- Relationship between pH and Ca+Mg saturation.
- Lime requirement target: neutral pH, “safe” pH or Al saturation.
- Soil Ca/Mg ratios: how critical are they?
- Conclusions.

Introduction

- Basic cation saturation ratio (BCSR) or Albrecht approach widely marketed in SA.
- BCSR developed from greenhouse studies with lucerne in New Jersey during the 1940s (F.E. Bear & coworkers).

- Published the following tentative statement (1945):

“For the ideal soil, it is suggested that 65% of the exchange complex should be occupied by Ca, 10% by Mg, 5% by K, and 20% by H”

i.e.

Ca+Mg should constitute 75% of CEC and be present in an equivalent Ca to Mg ratio of 6.5

- E.R. Graham (1959) - Univ. of Missouri suggested:

75 % Ca

10 % Mg

Ca+Mg = 85% & Ca/Mg ratio = 7.5

- Soil productivity not seriously affected if:

65 - 85 % Ca and 6 - 12 % Mg

i.e

Ca+Mg = 71 to 97 % & Ca/Mg ratio = 5.4 - 14.2

- **BCSR theory brought into the forefront by W. Albrecht (Univ. of Missouri, Brookside Laboratory).**

- **Albrecht endorsed the concept, developed some laboratory methods & the procedure became known as the <u>Albrecht system / formula</u>.**

W.r.t soil acidity and liming, BCSR / Albrecht approach hinges on two cardinal assumptions:

(1) That liming to saturate CEC with 80% Ca+Mg is necessary.

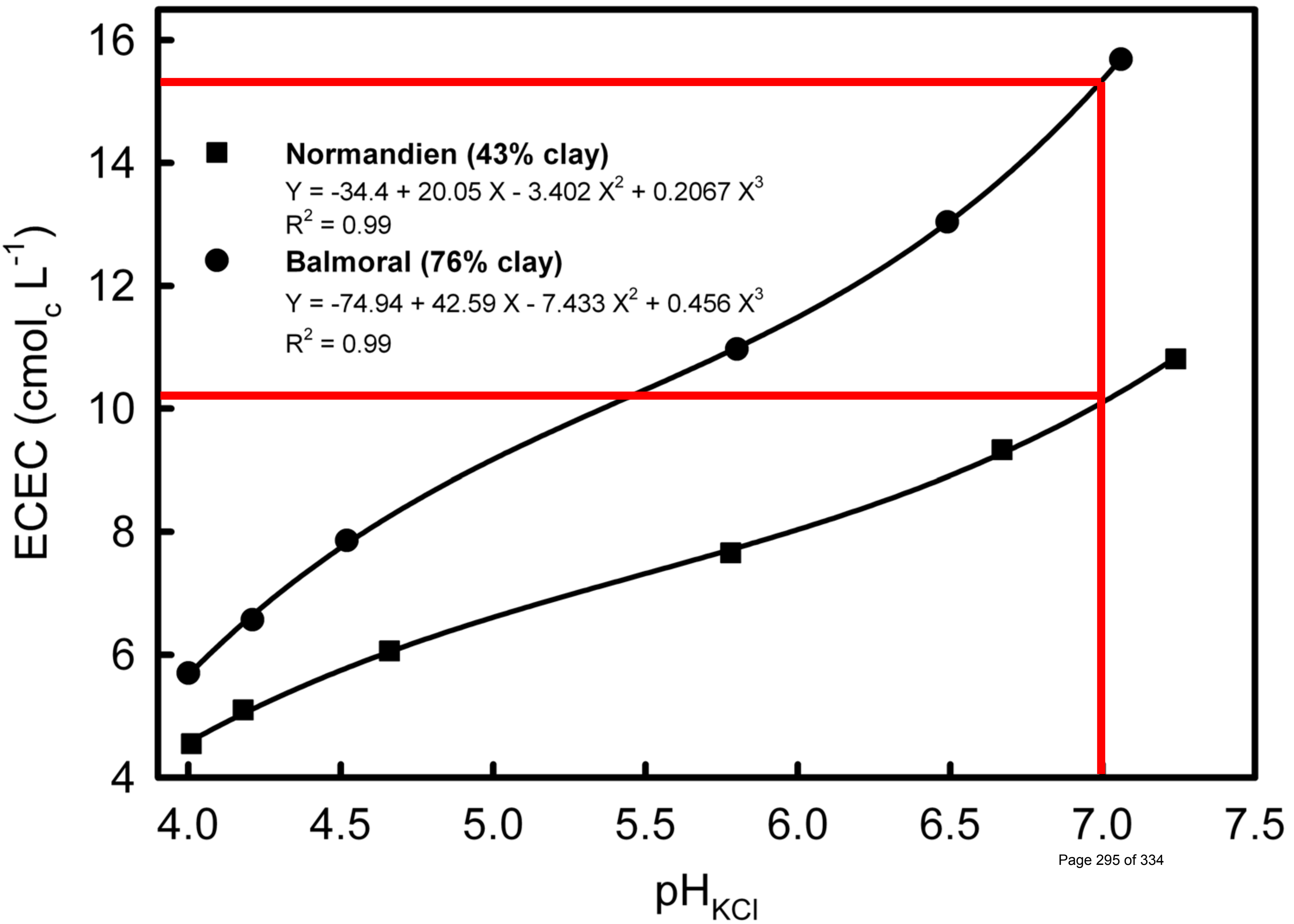
(2) That even if the first assumption is satisfied, calcitic lime and/or gypsum is required to "balance" Ca & Mg.

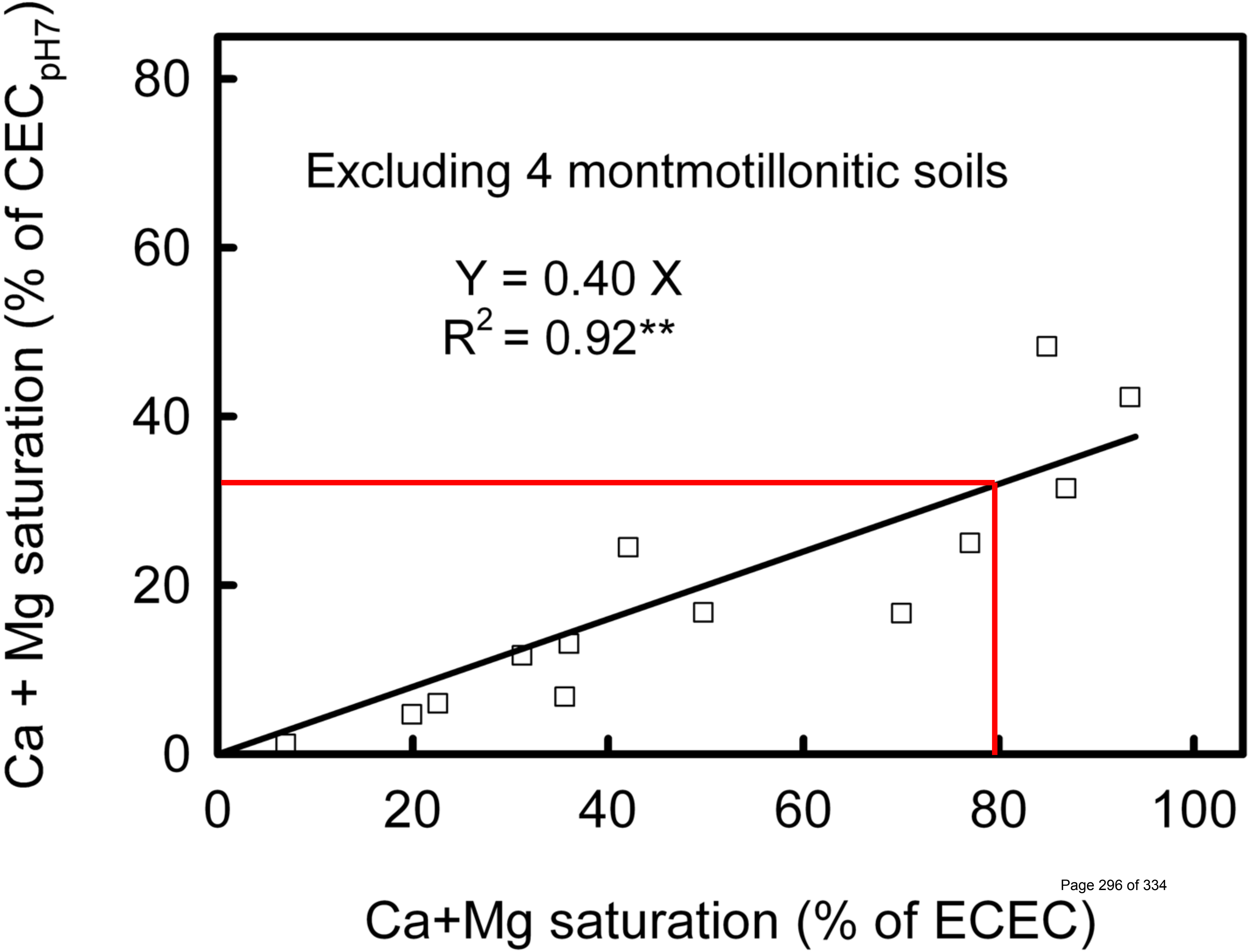
Relationship between pH and CEC

- At first sight, liming to a Ca+Mg saturation of 80% of the CEC may not seem unreasonable.

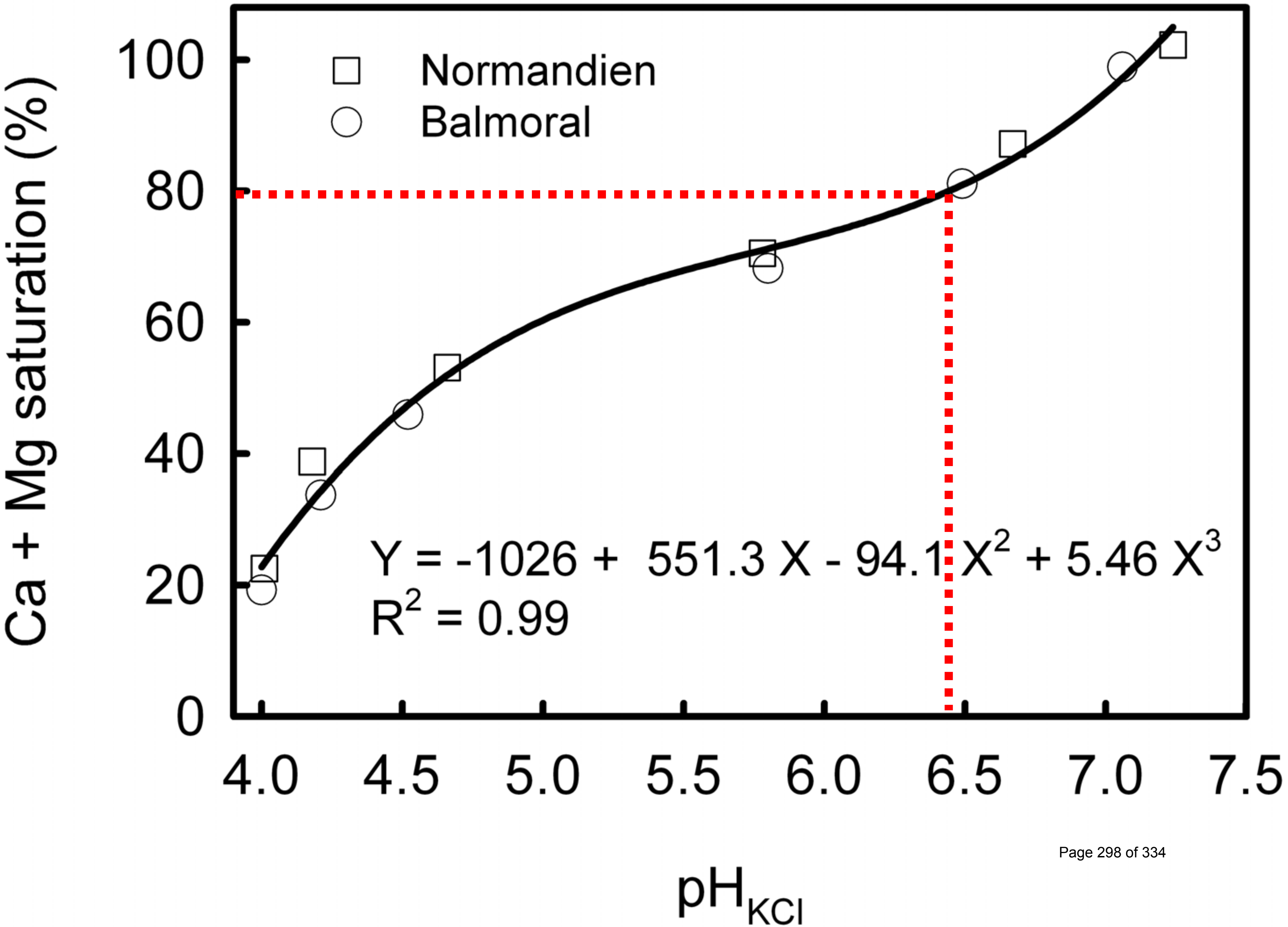
- **BUT** the **CEC** referred to is that at **pH 7.0 !!**

- Variable charge surfaces (OM, sesquioxides, clay mineral edges) adsorb or desorb H^+ - i.e. CEC is pH-dependent.


16
14
12
10
8
6
4
ECEC (cmol$_c$ L^{-1})
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
pH$_{KCl}$
■ Normandien (43% clay)
$Y = -34.4 + 20.05 X - 3.402 X^2 + 0.2067 X^3$
$R^2 = 0.99$
● Balmoral (76% clay)
$Y = -74.94 + 42.59 X - 7.433 X^2 + 0.456 X^3$
$R^2 = 0.99$

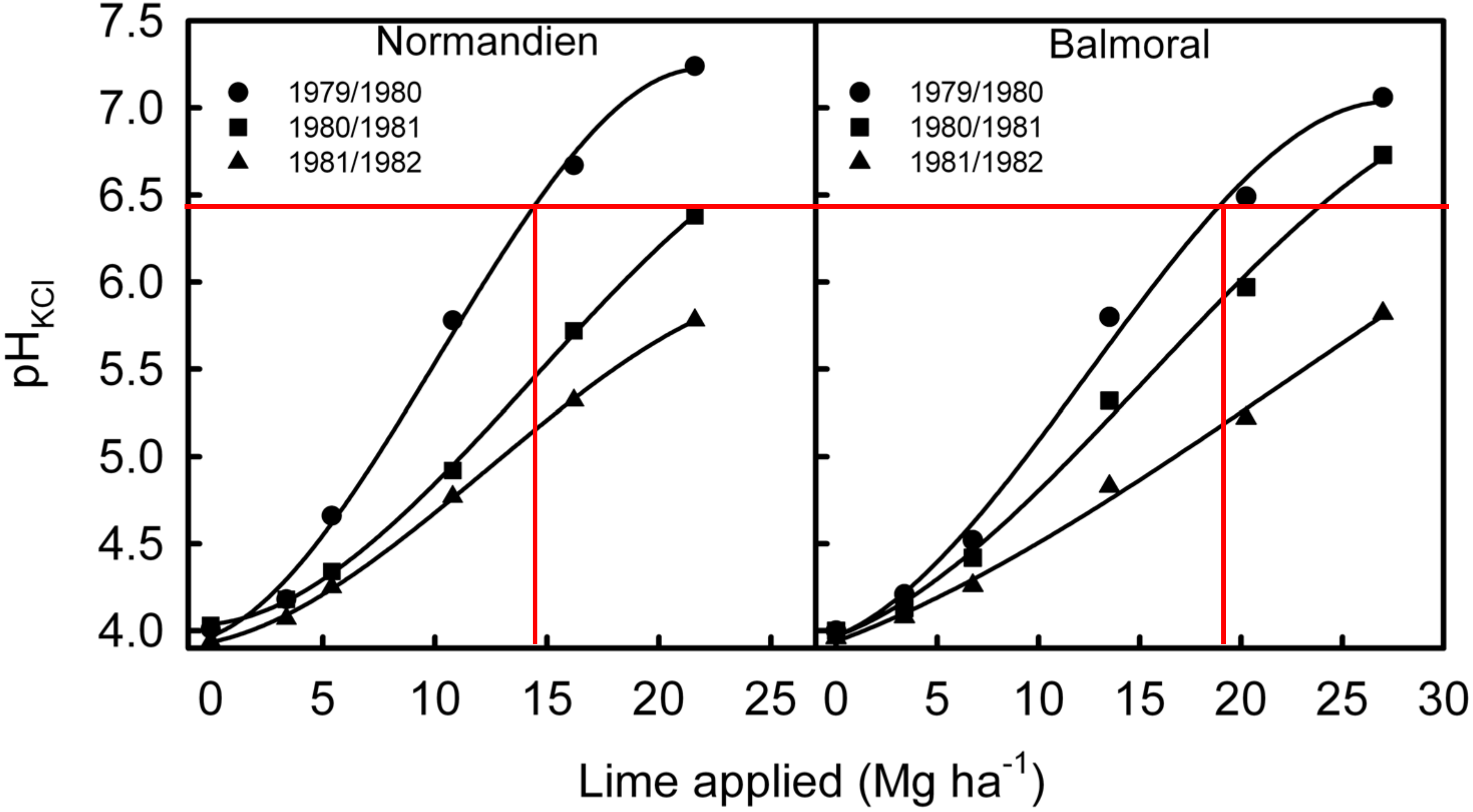

Excluding 4 montmotillonitic soils
Y = 0.40 X
R^2 = 0.92**
Ca + Mg saturation (% of CEC_{pH7})
0
20
40
60
80
0
20
40
60
80
100
Ca+Mg saturation (% of ECEC)

Relationship between pH and Ca+ Mg saturation



Ca + Mg saturation (%)
100
80
60
40
20
0
□ Normandien
○ Balmoral
$Y = -1026 + 551.3X - 94.1X^2 + 5.46X^3$
$R^2 = 0.99$
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
pH_{KCl}

Economic implications



Lime requirement target: neutral pH, “safe” pH or Al saturation ?

- Beneficial effect of liming acid soils well documented. However, lime requirement vs lime recommendations - a controversial topic.

- Poor growth of most crops at low pH primarily due to high concentrations of soluble Al^{3+}.

- Liming soils to near neutral pH strongly promoted by E.O. McLean on the grounds:
    - ► nutrient availability is optimized.
    - ► biological activity is enhanced – rapid decomposition of org. matter = release of N, P and S.

- Conceded that on well fertilized soils, liming to eliminate toxicities of Al^{3+} and Mn probably sufficient for maximum yield of most crops.

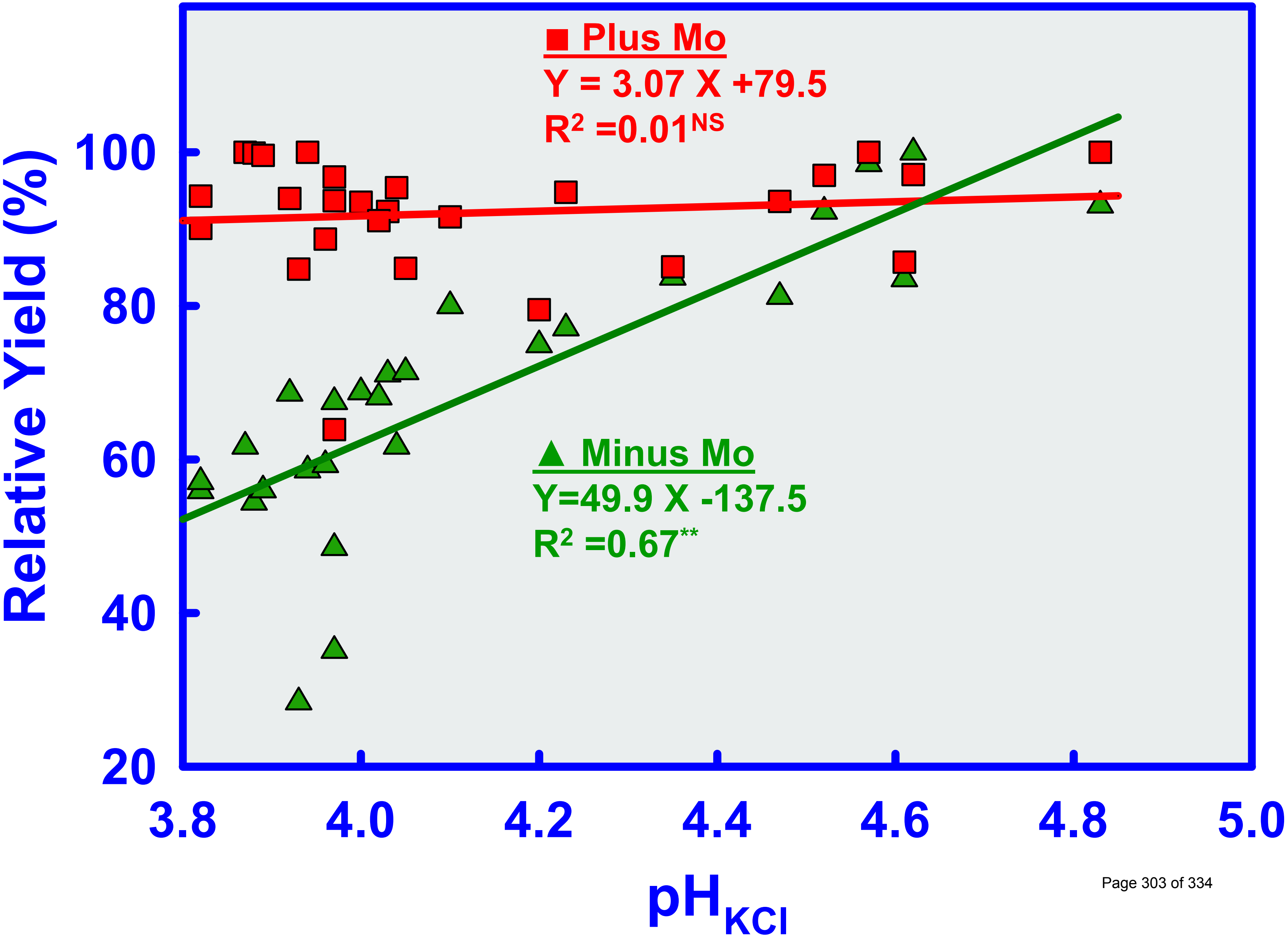
Sumner & Yamada (2002)

- Soil $pH_w < 5.5$ – positive lime response primarily due alleviation of Al & Mn toxicity.

- Soil $pH_w > 5.5$ – positive lime response more likely due to alleviation of deficiencies (N, P, S, Mg, Mo).

- Abundance of examples presented showing that economic response to lime did not occur above pH_w of approximately 5.5

Lime x Mo interactive effects with soyabean at Greytown



Other benefits of liming to pH_w 5.5 – i.e. a “safe” pH rather than pH_w 6.5-7.0

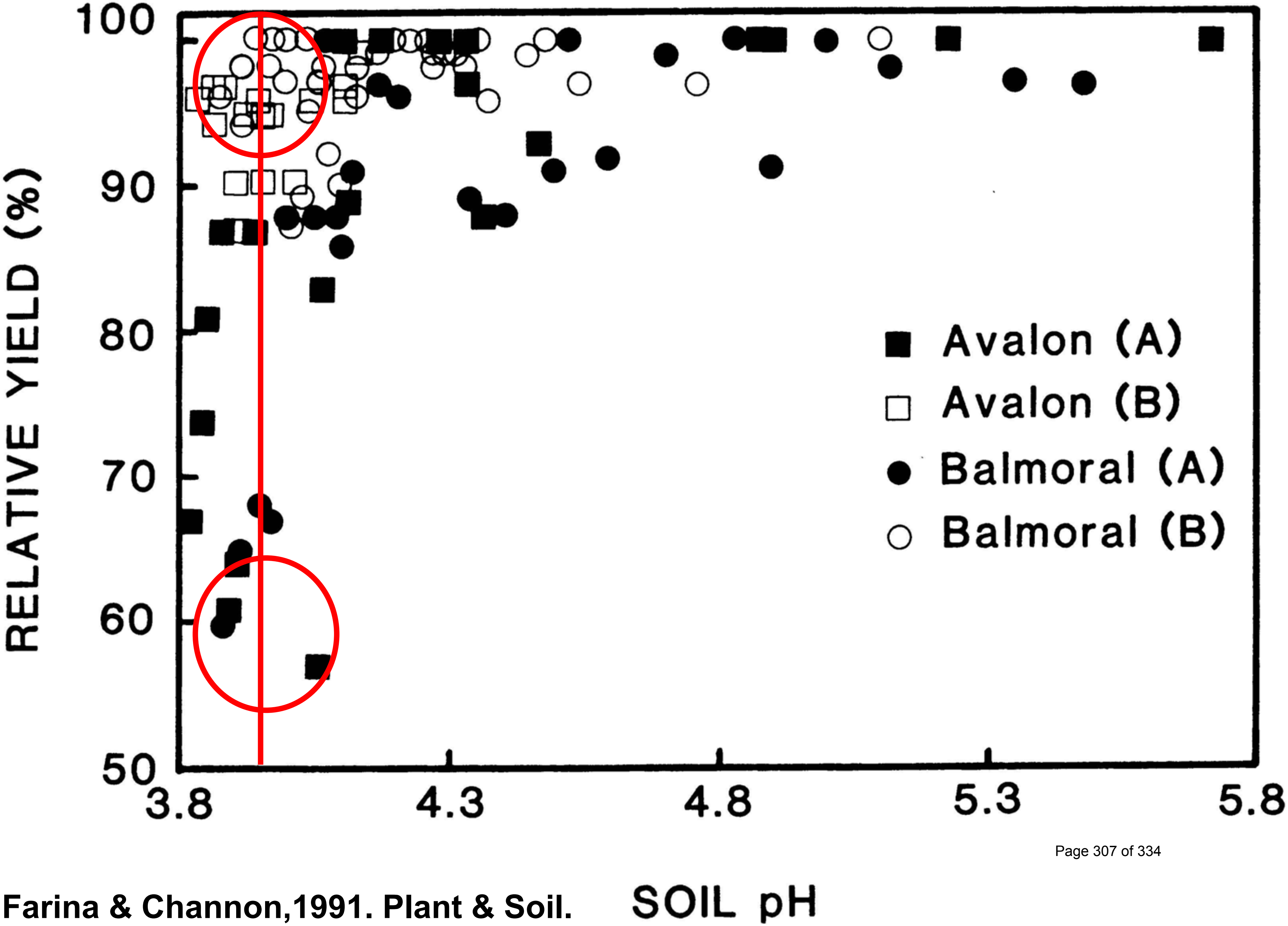
- Reduced rate of nitrification.
- Reduced incidence of diseases & pests.
- Reduced clay dispersion & crusting.
- Improved water infiltration.
- Reduced leaching losses of S.
- Reduced potential for NH_3 volatilization.
- Elimination of yield depressions due to induced deficiencies of P, B, Zn & Mn.

Lime-induced Mn deficiency in soyabean at Greytown

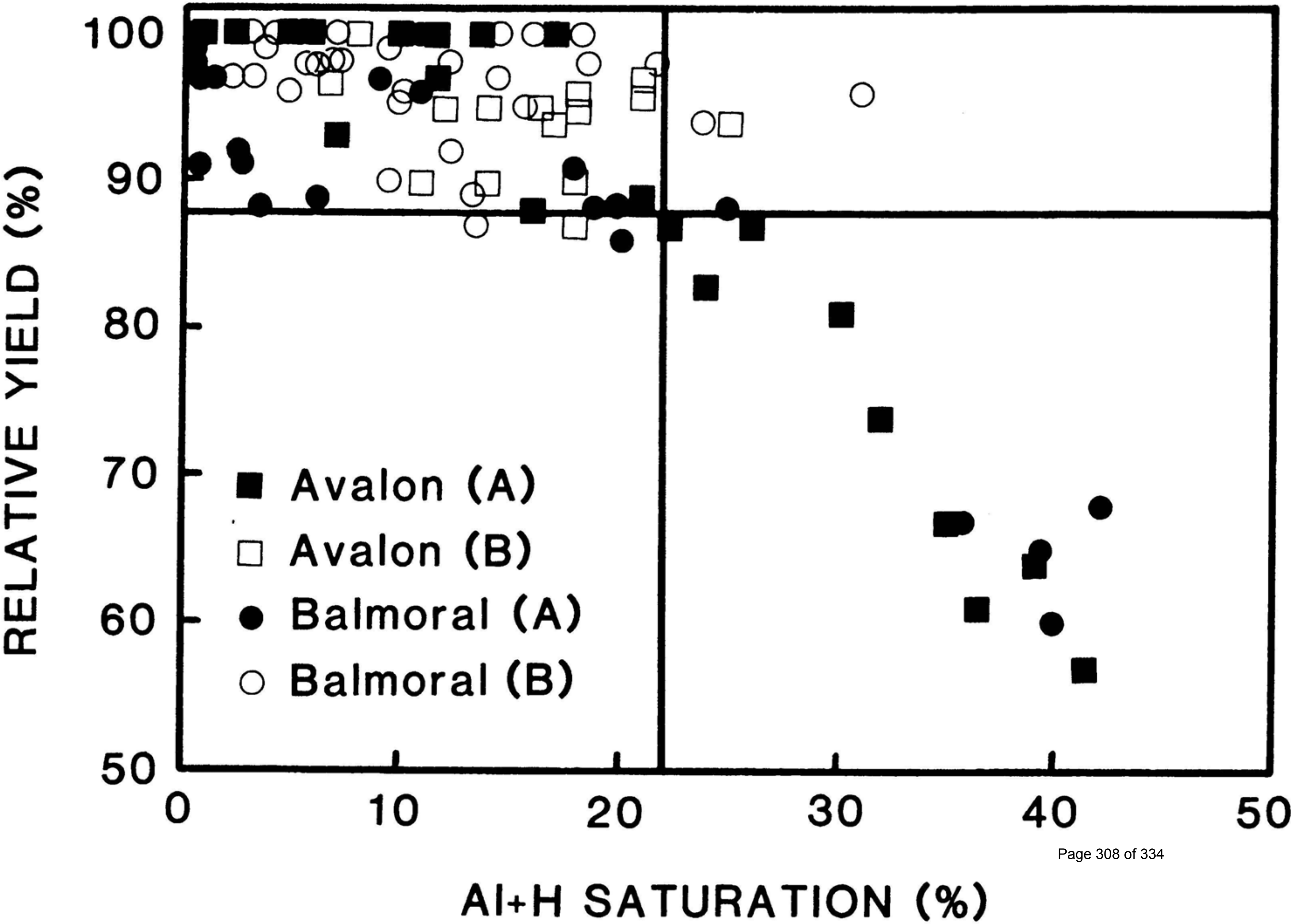
- Liming soils to pH_w 5.5 eliminates possible Al^{3+} toxicity – i.e liming to a “safe” pH.

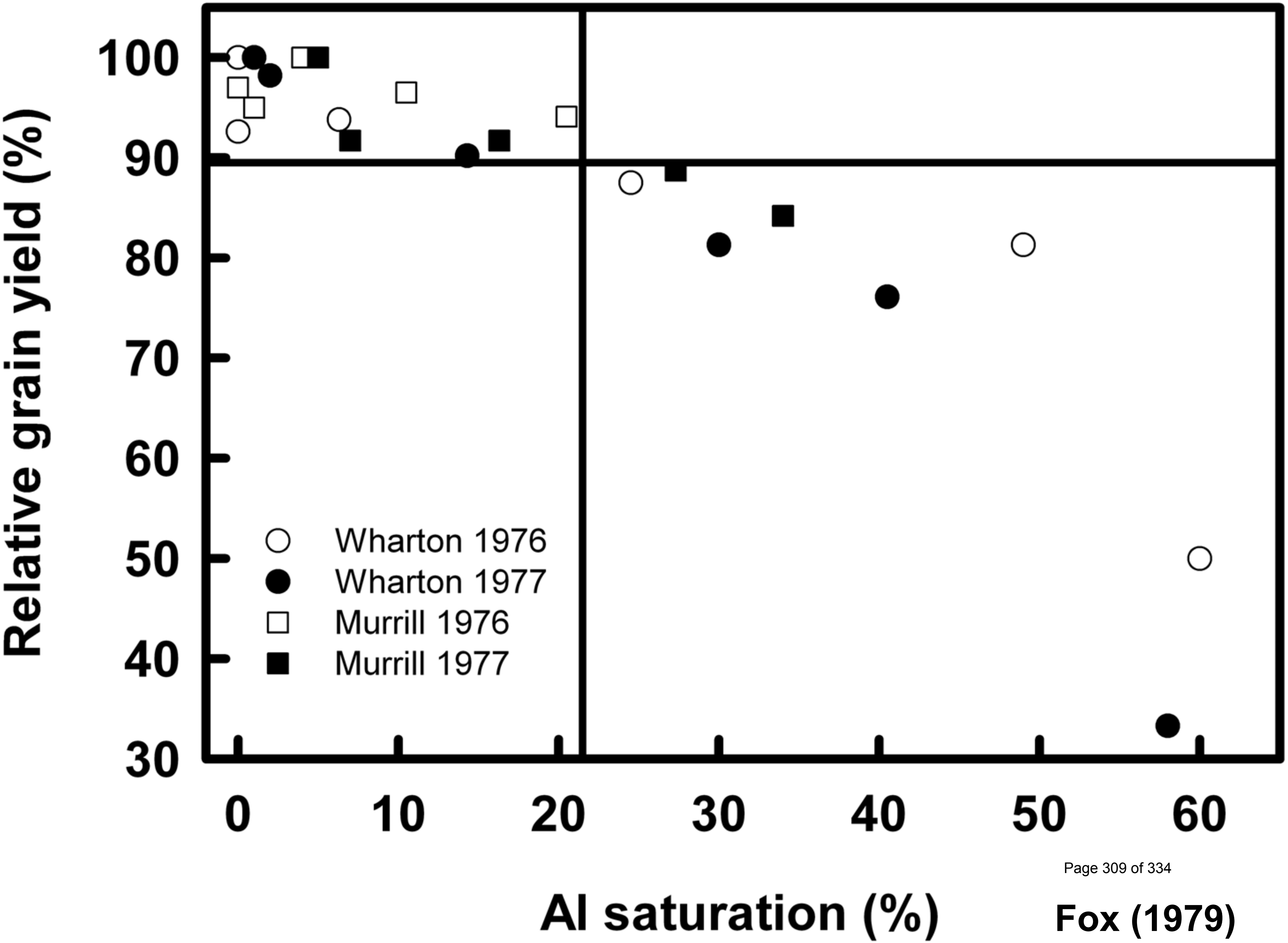
- Many soils with pH values < 5.5 don’t contain toxic amounts of Al^{3+}.

- Hence, pH *per se* is a poor indicator of the need for lime across a wide range of soils.



Farina & Channon,1991. Plant & Soil.


RELATIVE YIELD (%)
100
90
80
70
60
50
0
10
20
30
40
50
Al+H SATURATION (%)
■ Avalon (A)
□ Avalon (B)
● Balmoral (A)
○ Balmoral (B)


Relative grain yield (%)
100
90
80
70
60
50
40
30
0
10
20
30
40
50
60
Al saturation (%)
○ Wharton 1976
● Wharton 1977
□ Murrill 1976
■ Murrill 1977

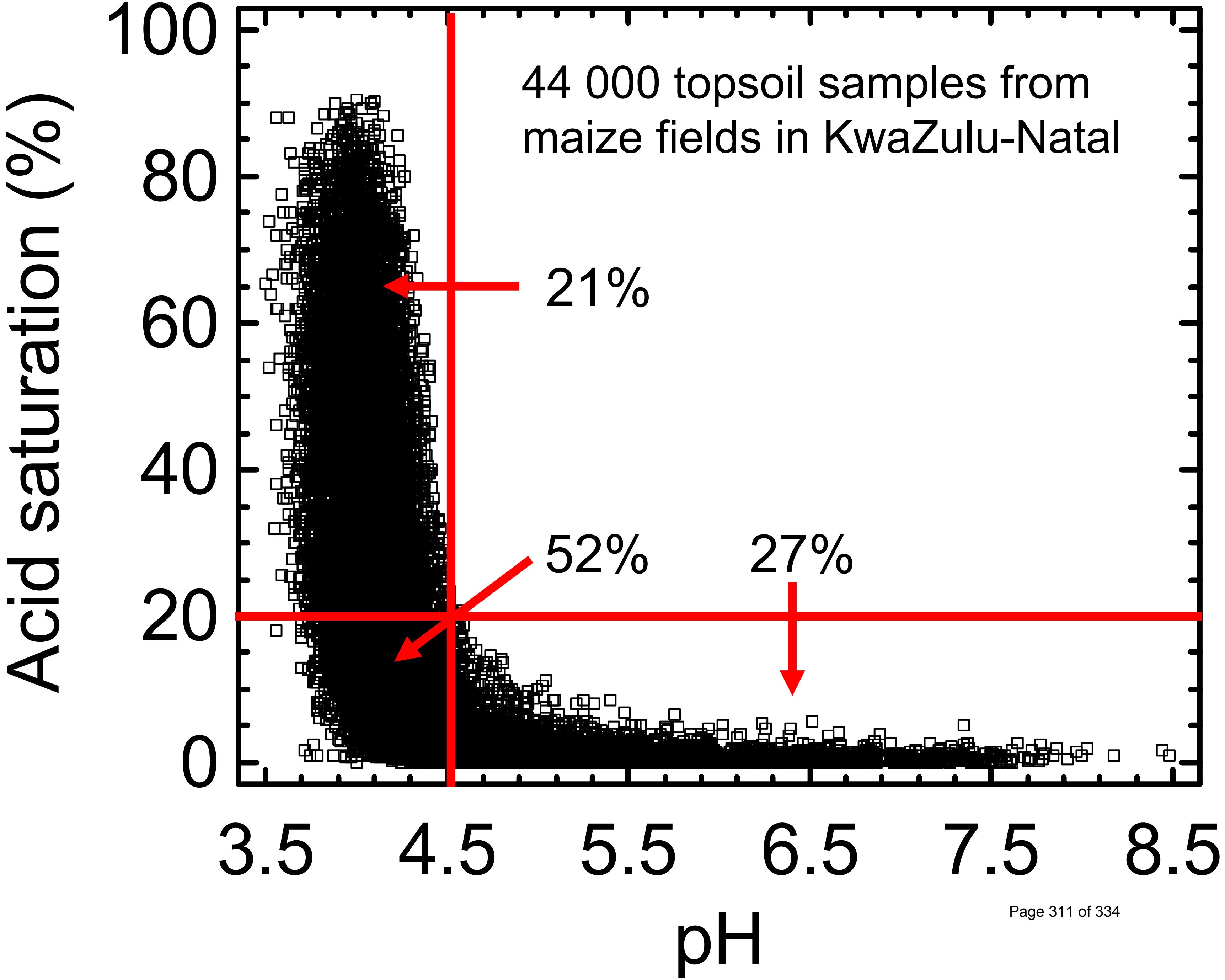
Fox (1979)

Acid Saturation (%)

$$\frac{\text{Exch. (Al + H)}}{\text{Exch. (Ca +Mg + K + Al + H)}} \times 100$$

Acid saturation used for making lime recommendations at Cedara, for more than 30 years.

In contrast to using a “safe” pH, use of acid saturation precludes unnecessary liming of soils.


44 000 topsoil samples from
maize fields in KwaZulu-Natal
21%
52%
27%
Acid saturation (%)
100
80
60
40
20
0
3.5
4.5
5.5
6.5
7.5
8.5
pH

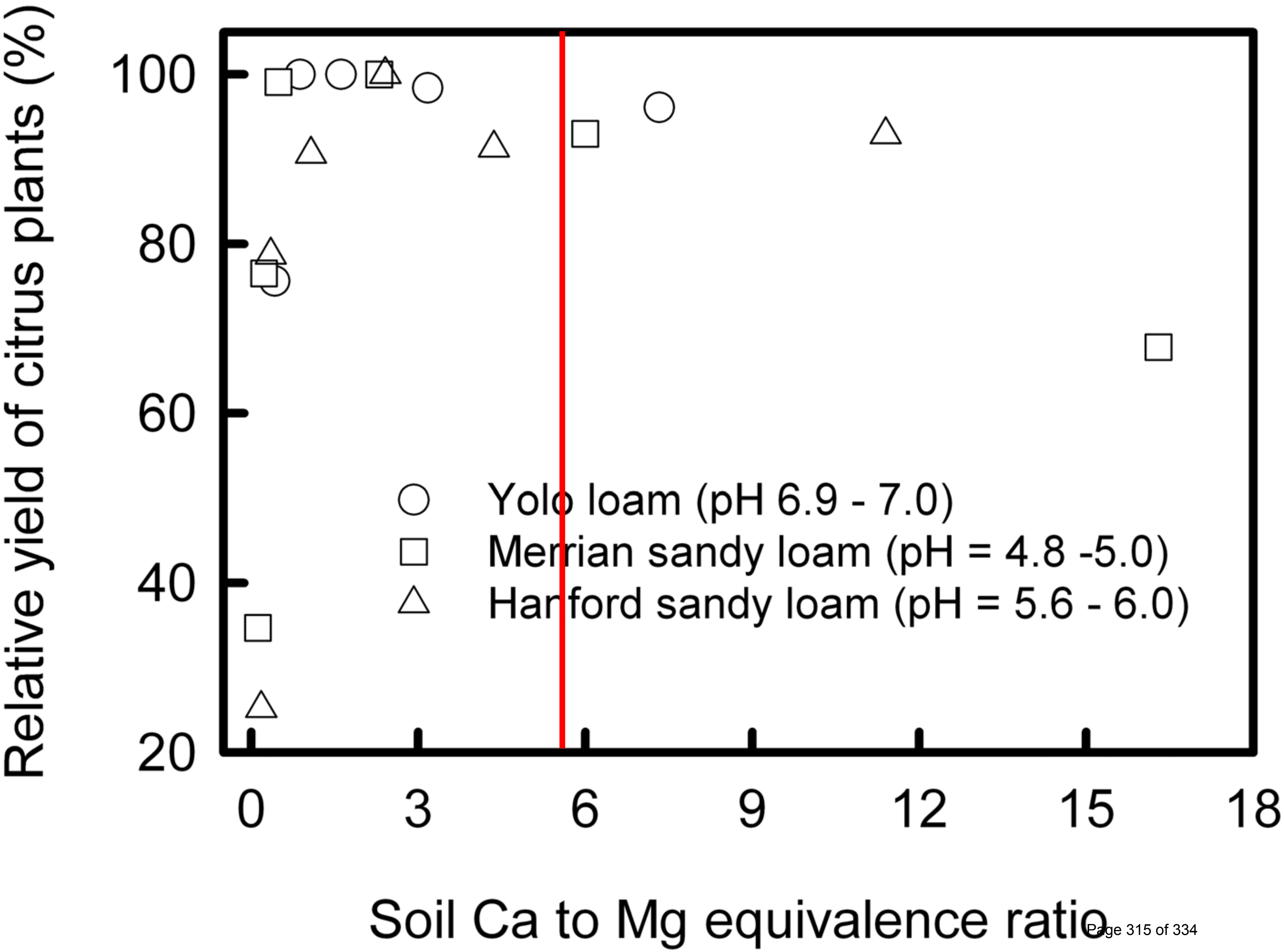
Crops vary in their tolerance to soil acidity

Permissible acid saturation levels used by Cedara

Crop	PAS (%)
Eragrostis curvula	50
Kikuyu	40
Fescue	40
Cynodon	40
Potato	30
Maize	**20**
Soyabean	20
Wheat	10
Most vegetables	<5
Perennial ryegrass	1

Soil Ca to Mg ratios: How critical are they?

- Supporters of the Albrecht formula in SA regard Ca & Mg to be in “balance” when Ca : Mg is 68% : 12% (Ca/Mg = 5.7)
- No published scientific evidence to show that Ca/Mg ratios are as critical as sales people promoting the Albrecht system in SA would like to believe.



Martin & Page (1969)

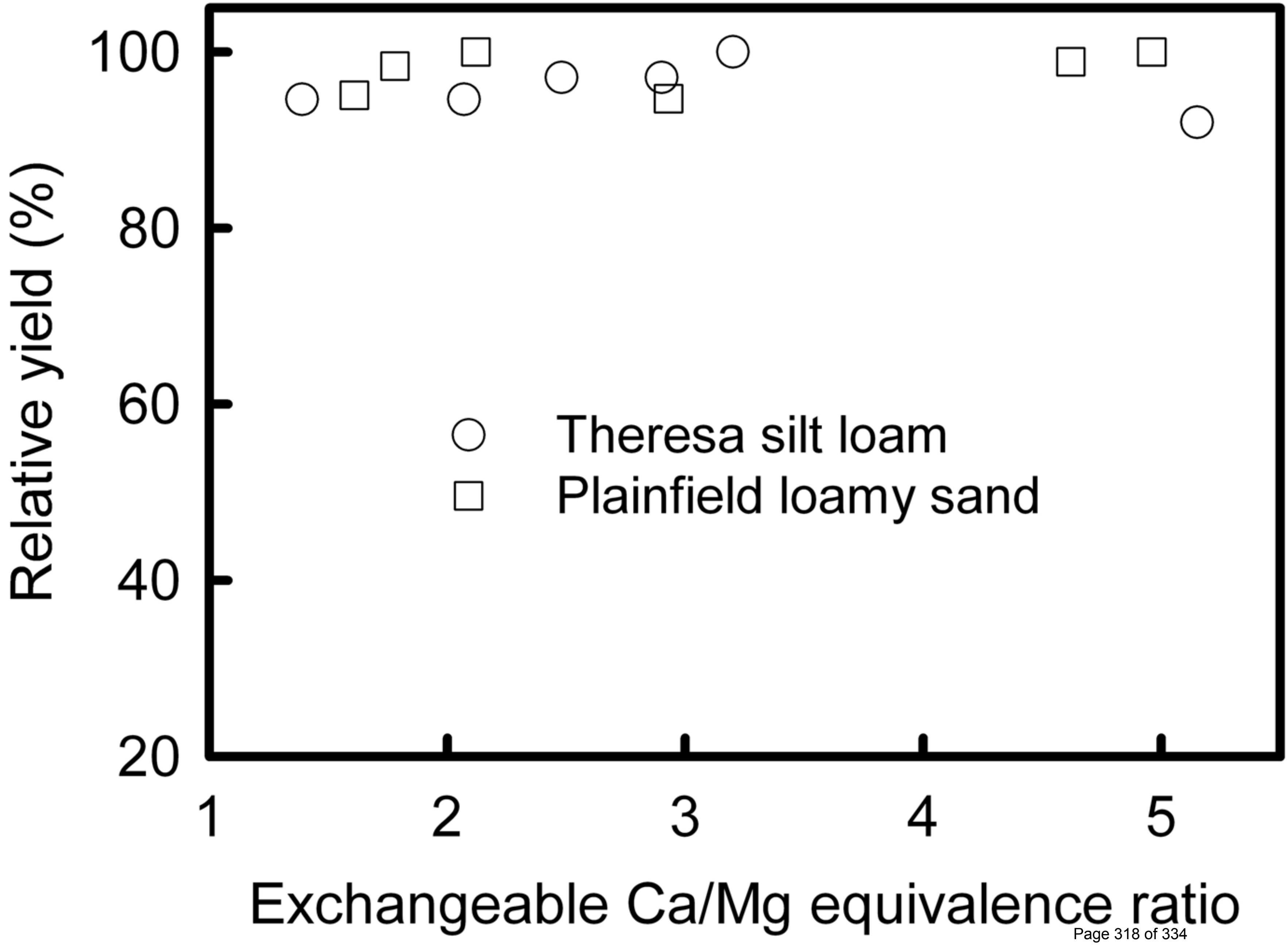
Eckert & McLean (1981)

“**There is no *ideal* basic cation saturation ratio** or range for crops on the whole. Instead, the individual nutrient cations should be supplied in adequate but not excessive amounts, depending on the response of the crop in question”.

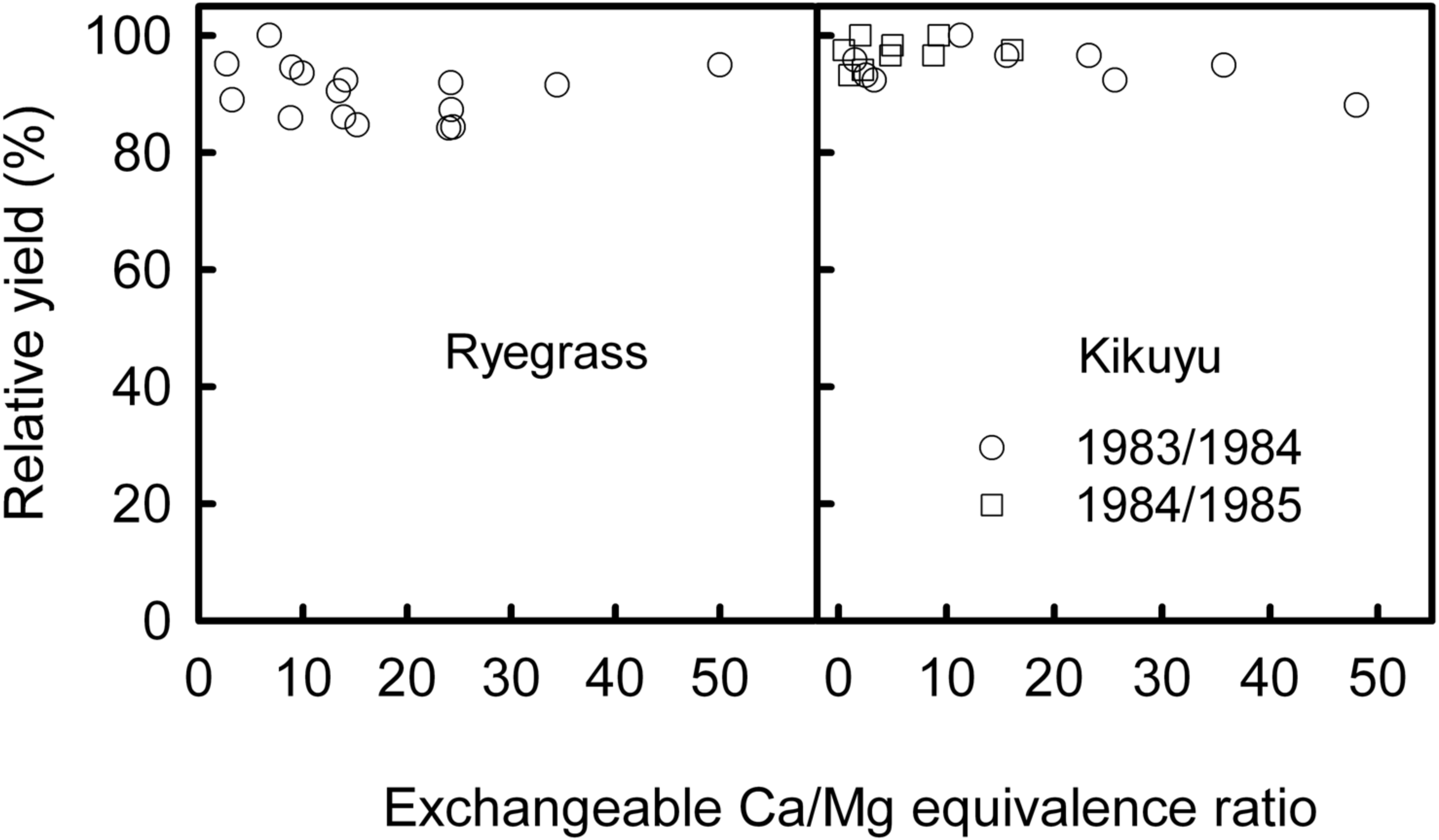
Further,

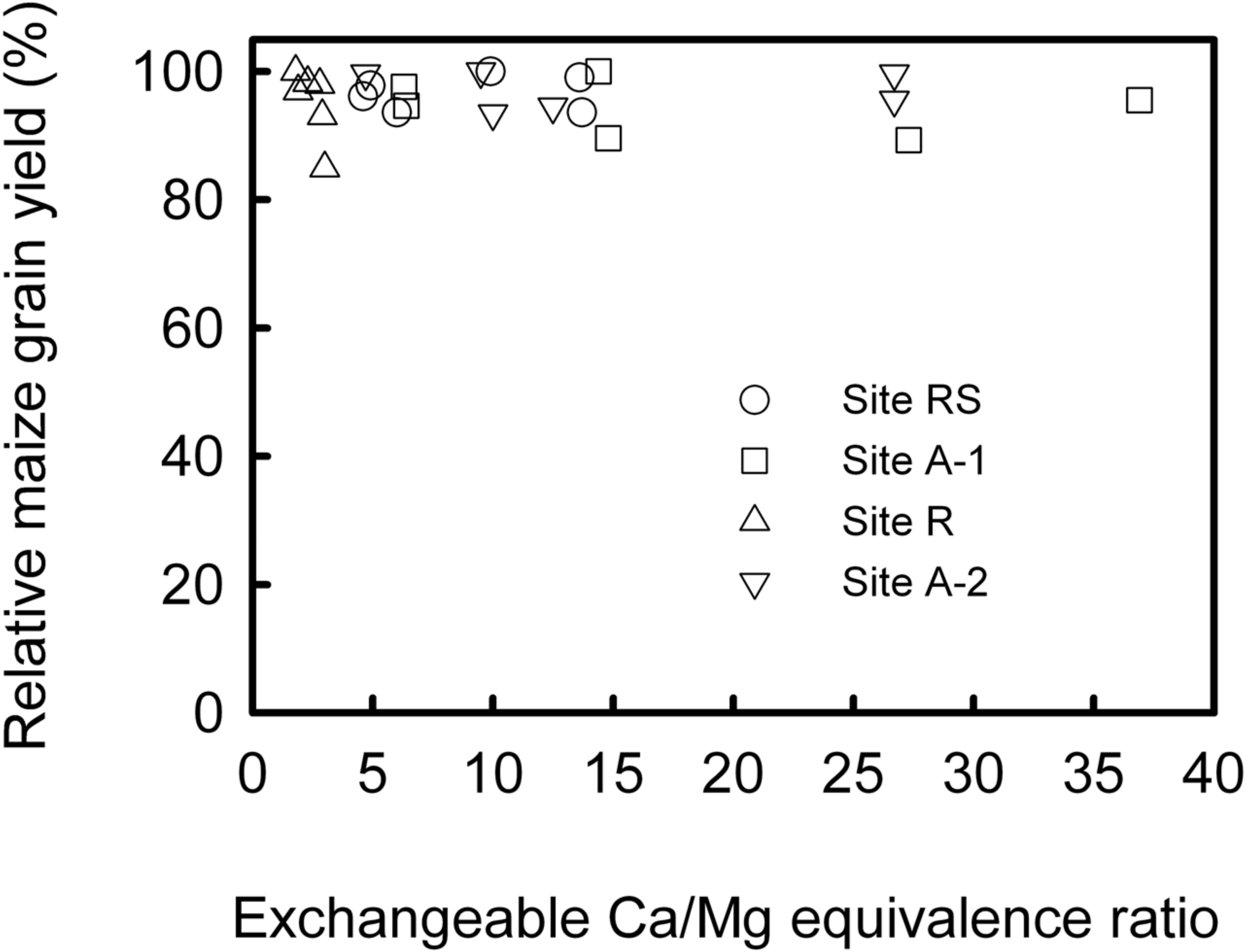
McLean *et al* (1983)

"In fertilizer and lime practice, emphasis should be placed on providing sufficient but non excessive levels of each basic cation rather than attempting to adjust to a **favorable basic cation saturation ratio** which evidently **does not exist**".



Simson *et al* (1979)


Relative yield (%)
100
80
60
40
20
0
0
10
20
30
40
50
Ryegrass
0
10
20
30
40
50
Kikuyu
○ 1983/1984
□ 1984/1985
Exchangeable Ca/Mg equivalence ratio



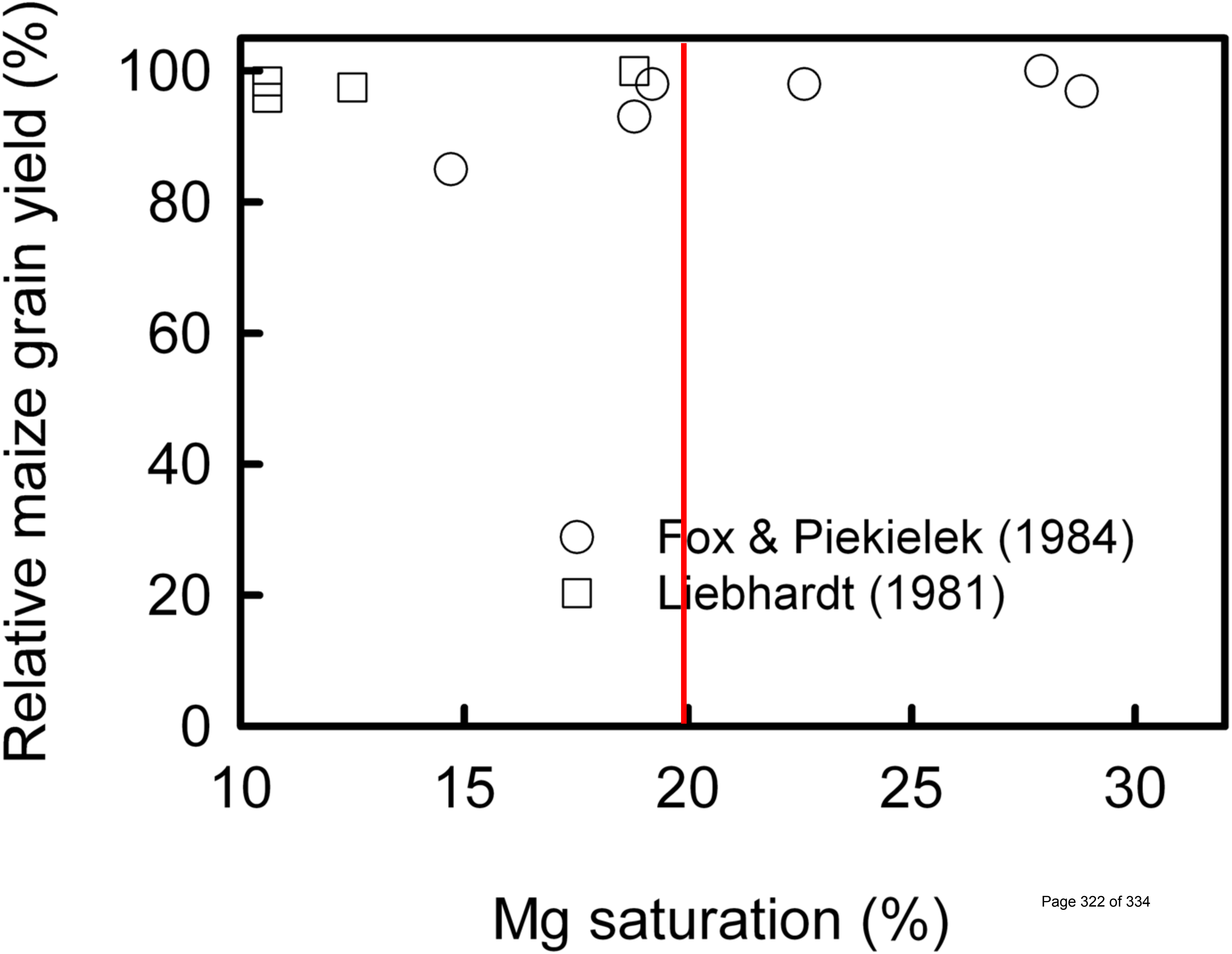
Fox & Piekielek (1984)

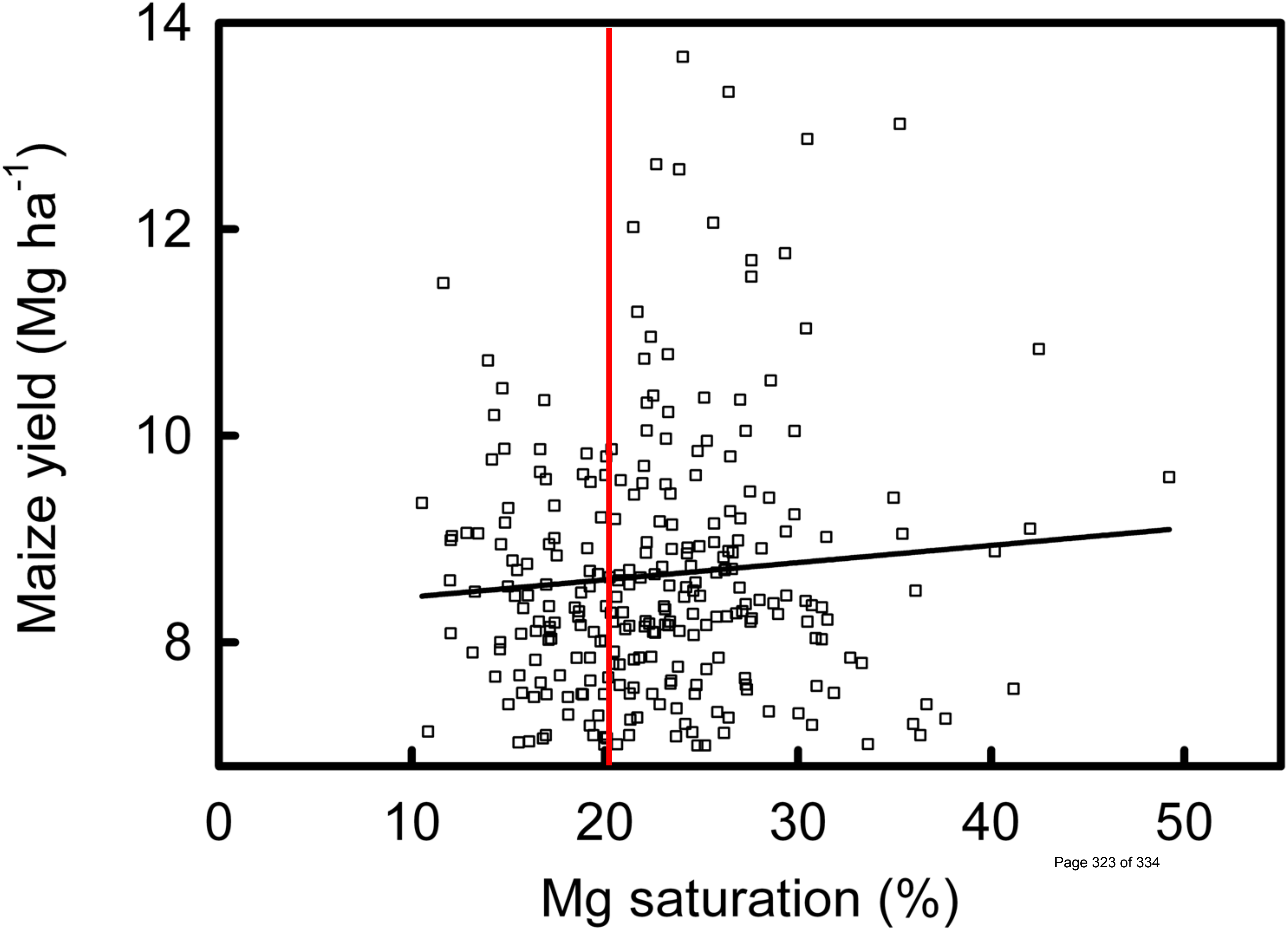
“Excess magnesium costs money”

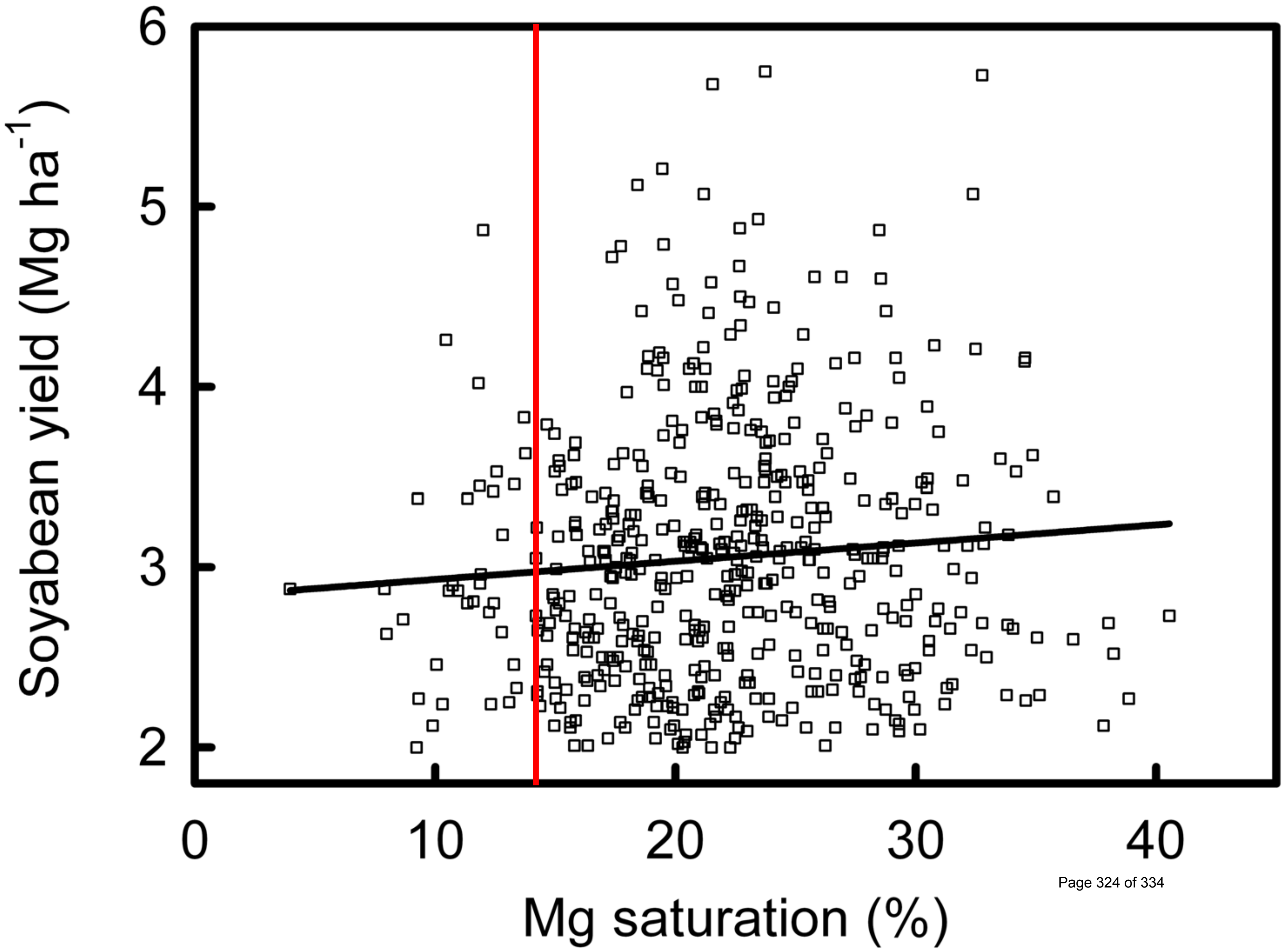
Kinsey (2001)

- Maize yields reduced by 0.63 Mg ha^{-1} if Mg saturation on medium to heavy textured soils is 15%, reduced by a further 0.32 Mg ha^{-1} if Mg saturation > 20%

- Soyabean yields reduced by 0.67 Mg ha^{-1} at 13 to 14 % Mg saturation.


Relative maize grain yield (%)
100
80
60
40
20
0
10
15
20
25
30
Mg saturation (%)
○ Fox & Piekielek (1984)
□ Liebhardt (1981)


14
12
10
8
Maize yield (Mg ha^{-1})
0
10
20
30
40
50
Mg saturation (%)


Soyabean yield (Mg ha^{-1})
6
5
4
3
2
0
10
20
30
40
Mg saturation (%)

Brown & Stecker (2003)

- “The Ca/Mg ratio idea has hung on far to long”

- “Toxicities of Mg have not been documented in field studies, but allusions to poisonous levels of Mg in soil still persist”

Mark Schonbeck (2000): VABF

Soil nutrient balancing in sustainable vegetable production

- Adjusted soil Ca/Mg ratios from 2.6 to 4, by applying calcitic lime & gypsum to soils with pH values of 6.0 to 6.9 & clay contents varying from 18 - 42%

Schonbeck (2000)

- Results **did not support** various claims made by Albrecht proponents, namely:

  1. Increased availability / crop uptake of N, P or micronutrients.
  2. Increased crop resistance to pests, diseases, environmental stresses.
  3. Fewer weeds.
  4. Higher soluble solids (Brix).
  5. Longer shelf-life.

Schonbeck (2000) study also showed that:

Increasing Ca/Mg ratio, on average, **had no effect on:**

Soil organic matter content

Biological activity

Soil bulk density

Soil moisture content

Water infiltration rate

Soil strength

Kelling *et al* (1996):

None of the following were significantly correlated with soil Ca/Mg ratio:

Lucerne yield

Incidence of weeds (grass or broadleaf)

Earthworm populations

Lucerne quality (crude protein, ADF, NDF)

Kelling et al (1996) concluded that:

“there is no justification for recommending calcitic lime over dolomitic lime, or adding Ca or Mg to soils already containing adequate amounts of these elements”

On the relevance of soil Ca to Mg ratios:

Rehm (2003)

“It’s an outdated, antique concept that has no value in high yield, modern agriculture”

Conclusions

- Elevating Ca+Mg saturation to 80% of CEC (pH 7) is not agronomically desirable & is economically unsustainable.

- No published evidence to support the use of critical BCSR / Albrecht formula .

- Sales literature ‘supporting’ liming programs to bring soils into better Ca-Mg ‘balance’ based on unverified farmer testimonials and anecdotal evidence.

Thank you

FSSA-MVSA

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Email: general@fssa.org.za
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