Introduction

Despite the daunting task of producing enough food for the expanding world population, historical trends indicate that agriculture is capable of doing this in an ecologically sustainable manner.

Based on a projection from 1995 data, the global annual demand of cereals will increase by about 40% or 700 million tons until 2020. About 80% of this additional food must come from already cultivated areas. Although mineral fertilizers and irrigation have, and continue to play a key role in world food production, threats are emerging. There are already serious constraints to agriculture from shortages of irrigation water both from over-utilization in agriculture and conflicts of interest between agricultural, industrial and urban use.

Abundant natural gas supplies assures plentiful feedstock for the production of nitrogenous fertilizers but increasing energy costs associated with the conversion of gas into ammonia are resulting in rapidly increasing costs of N. In many parts of the world N is applied inappropriately and/or in excess and this can result in leaching and surface runoff to water bodies and to denitrification.

Similarly, in parts of the world where fertilization has been practiced for a considerable period, or where high value crops are grown, excess phosphate applications can result in pollution of water bodies. By contrast, in large areas of the developing world, particularly Africa, P deficiency remains a major constraint to agricultural production. A significant constraint to world food production is emerging as high-grade phosphate reserves become scarce. This will likely result in a shift from di-ammonium phosphate (DAP) to mono-ammonium phosphate (MAP) because MAP can be made from rock with higher concentrations of impurities.

For many years, little attention was paid to sulphur as a plant nutrient mainly because it has been applied to soil in incidental inputs in rainfall and volcanic emissions, and as a component of nitrogenous, phosphatic and potassic fertilizers.

Intensification of cropping systems using high-yielding varieties has accelerated S removal from the soil, which is resulting in more soils becoming S-deficient. Increased use of high-analysis S-free fertilizers has aggravated the S deficiency problem in many cropping systems.

In many soils, particularly those with coarse texture and/or high pH, sulphate S is mobile and easily leached from the rooting zone as shown in Figure 1. By contrast, elemental S needs to be oxidized to sulphate by soil microorganisms, which are dependent on temperature and moisture for their activity, hence the supply of sulphate is in synchrony with plant demand and leaching losses can be less.Given the increasing demand for high analysis DAP and MAP fertilizers, which contain little or no S, a new group of Sulphur Enhanced Fertilizers (SEF), which contain elemental S has been developed by Shell.

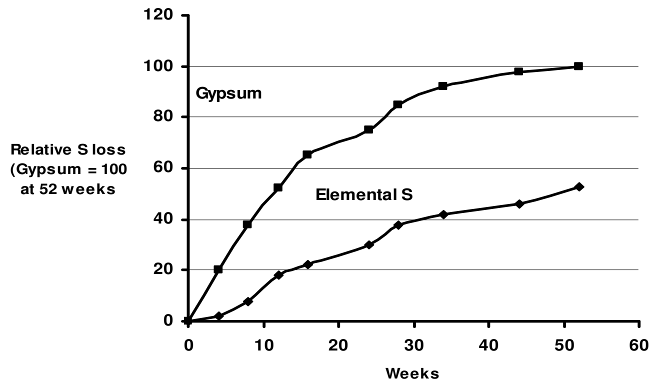

Figure 1. Relative loss of S from applications of gypsum and elemental S

Development of SEF fertilizers

Elemental S is an almost ideal fertilizer as it contains 100% nutrients. The elemental S must be oxidized to sulphate before it is available to plants and since microorganisms carry out this process it is moisture and temperature dependant, as is the crop demand for S. The rate of oxidation is also dependent on the particle size of S. This means that there is great scope to manage the release rate of sulphate to the plant to maximize plant uptake and minimize losses by surface runoff and leaching.

Research carried out by Blair et al (1979) has shown that plants require S and P early in growth and that oxidation rates are enhanced by intimate mixing of P and elemental S (Lefroy et al 1997), which makes S inclusion into P containing fertilizers an attractive proposition.

Shell Canada invented a process in 2001 to include microfine elemental S into DAP and MAP and a patent for this was filed in 2003 (International Publication Number WO 2004/043878 A1). Much of the developmental work on SEF was undertaken at IFDC where the process has been used with pre-neutralizers (PN) and pipe cross reactors (PCR) and combined PN/PCR units with S concentration ranging up to 20%. A significant feature of the process is that the elemental S is distributed throughout the fertilizer granule.

Recently the scope of the project has been expanded to include S enhanced triple superphosphate (TSPS) (0:45.8:0:9.2S) and a range of NPKS fertilizers namely: 15:15:15:15S, 15:15:15:5S, 12:24:12:12S, 12:24:12:5S.

S oxidation from SEF

S oxidation from SEF has been determined in plant growth chambers at the University of New England, Armidale using the carrier free $Ca^{35}SO_4$ reverse dilution technique. Ryegrass (*Lolium perenne*) and rhodes grass (*Chloris gayana*) were grown at temperatures of 22/14 °C and 34/26 °C (14 hour day/10 hour night), respectively, for 9 weeks. At the end of the 9 week growth period an average of 23.6% of fertilizer S was recovered in the plant tops from DAP and MAP based SEFs with no significant effect of temperature. This compares with 73.2% from gypsum in rhodes grass and 54.1% in ryegrass. This demonstrates the metered oxidation of the microfine elemental S at the start of growth, leaving more S for uptake at a later stage of development.

Agronomic evaluation of SEF fertilizers.

A total of 138 replicated (3 to 5 reps depending on crop) randomised block plot experiments have been conducted to evaluate SEF (

Table 1). Experiments have been conducted in China (101 experiments), Brazil (22 experiments), Argentina (10 experiments) and Australia (7 experiments). Two experiments in Australia did not produce results due to drought or hail damage meaning that results are available from 136 experiments.

Of the 136 experiments 84 were responsive to S (difference between minus S control and SEF treatment significant at p=0.05 according to Duncan's Multiple Range Test) with a weighted mean yield increase to SEF of 14%, compared to the zero S control (

Table 1). The comparison treatment consisted of a mixture of MAP and gypsum used to simulate an addition of single superphosphate (SSP) and comparisons shown below are with this treatment. Nitrogen and all other nutrients were balanced between treatments so that S was the only variable. SEF produced yield responses equal to SSP at 50 sites, responses exceeding SSP at 28 sites and responses inferior to SSP at 6 sites (

Table 1).

Table 1. Summary of crop responses to SEF**.**

Country	**S responsive site**		**% response to SEF**	**SEF v SSP**		
	Yes	**No**		**Equal**	**Superior**	**Inferior**
China	72	29	13	45	24	3
Brazil	8	14	17	5		3
Argentina	3	7	34		3	
Australia	1	4	9		1	
TOTAL OR AVERAGE	**84**	**54**	**14 (weighted mean)**	**50**	**28**	**6**

Agronomic evaluations in China

Seventy two percent of the trials in China responded to S with the highest response recorded in soybeans (Figure 2) because they are generally grown on lighter textured soils which are more prone to leaching of S. A snapshot of the trial results from China is presented in Figure 3. A trial conducted with four successive crops in Jiangsu Province showed a superior yield from SEF over SSP in 3 of the 4 crops (Figure 3). The rice was grown in flooded soils and this crop was followed by soybeans planted in the same plots in unflooded soil.

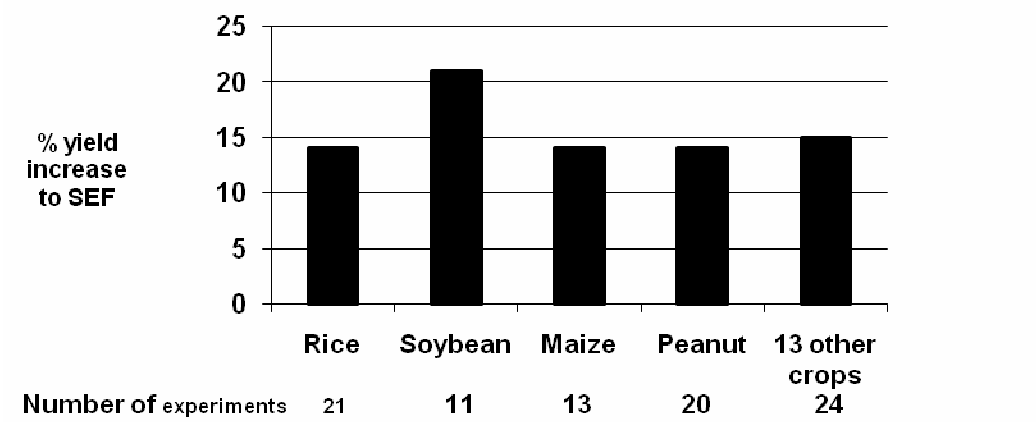

Figure 2. Average yield responses to Sulphur Enhanced Fertilizer (SEF) in a range of crops in China.

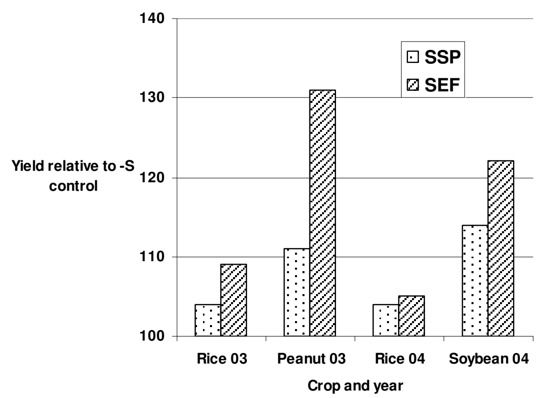

Figure 3. Yield response to S applied in SEF or SSP when all other nutrients are non-limiting.

Agronomic evaluations in Brazil

SEF evaluation trials have been conducted in the major cropping areas of Brazil and an example of the response obtained is presented in Table 2. There was a large response in soybeans to S and MAP-SEF produced a similar response to S supplied as gypsum (Table 2). When an oats crop was grown on residual S a large response to both MAP-SEF and gypsum was recorded.

Table 2. Initial and residual effect of fertilizers on soybean and oats yield at Marakau, Matto Grosso State, Brazil.

Fertilizer applied to crop 1	Relative yield of crop	Fertilizer applied to crop 2	Relative yield of crop 2
MAP	100a [1]	N only	100a
MAP-SEF	147b	N only	283b
MAP + Gypsum	177b	N only	309b

[1] Numbers followed by the same letter are not statistically different according to DMRT.

Agronomic evaluations in Argentina

There is a long history of S research in Argentina and responses have been recorded in most significant cropping areas. A total of 10 SEF trials have been completed in Argentina with a response to S recorded at 3 sites (

Table 1). SEF proved to be superior to gypsum and ammonium sulphate at the Oliveros 1 site and all three sources equal at the Oliveros 2 site (

Table 3). Heavy rain was recorded early in the season at Oliveros 1 and sulphate was most probably leached from the rooting zone. This did not occur at Oliveros 2.

Table 3. Response of corn to DAP-SEF containing elemental S and sulphate and gypsum and ammonium sulphate (AS) containing sulphate only, at two sites in Santa Fe Province, Argentina.

Fertilizer	Oliveros 1	Oliveros 2
	% response above DAP	
DAP-SEF	34	11
DAP + GYPSUM	12	6
DAP + Ammonium sulphate	12	11

Agronomic evaluations in Australia

Field evaluations of SEF have been completed at 5 sites and some 16 sites are currently under investigation. One evaluation of SEF fertilizer (MAP12) was undertaken on a native pasture oversown with clover near Armidale, NSW from August 2007 to November 2008. Fertilizers were topdressed onto the sward and four harvests taken over the period.

There was a significant effect of treatment on total grass+clover dry matter production ($p>0.05$) and most of this difference was from the clover contribution, particularly in the later harvests (

Figure 4)

Addition of S fertilizers increased the uptake of S in all treatments, except DAP pastille (Table 4). Highest uptake was with MAP12. Calculation of apparent fertilizer recovery (S uptake in S treatment - S uptake in MAP treatment)/ S applied) shows a recovery of 16% from SSP, 32% from MAP12 and no recovery from DAP pastille (Table 4). The increased yield resulting from S application resulted in an increase in the apparent recovery of fertilizer P (Table 4).

Among the S fertilizers evaluated MAP12 was the best, and it was superior to SSP in clover growth (

Figure 4). This is an important result as clover growth is essential in the pasture both to contribute fixed N and for animal protein. Total S uptake was also higher from MAP12 than SSP most likely due to leaching of sulphate from the SSP treatment two weeks after application.

Table 4. S uptake (kg/ha) and apparent fertilizer recovery (S or P uptake in S treatment – S or P uptake in MAP treatment)/ S or P applied) from the S fertilizers applied.

Treatment	S uptake (kg/ha)	Apparent % fertilizer S recovery	Apparent % fertilizer P recovery
DAP past	3.44 a[1]	0 a	34.7 a
MAP	3.65 a	0 a	35.7 a
SSP	5.05 b	16 b	40.4 b
MAP12	6.38 c	32 c	50.8 c

[1] Numbers followed by the same letter are not significantly different according to DMRT.

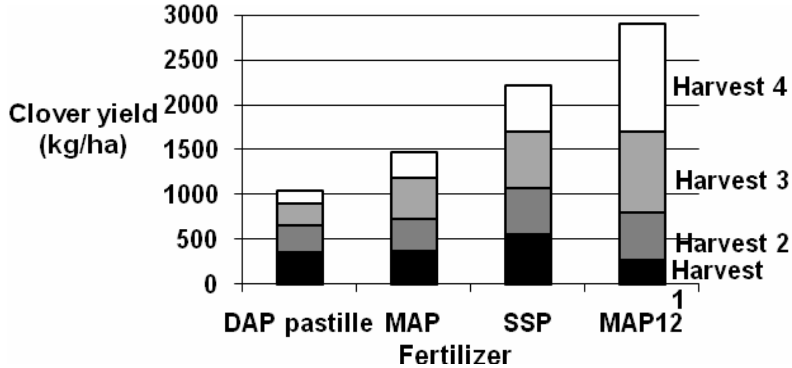

Figure 4. Effect of fertilizer on clover yield at each harvest. Treatments are di-ammonium phosphate with S° pastilles (DAP pastille) mono-ammonium phosphate (MAP), single superphosphate (SSP), and mono-ammonium phosphate with S in granule (MAP12).

S soil testing

Relationships between mono-calcium phosphate MCP) extractable soil S and S response were calculated for the data from the China field trials and no relationship was found. Similar lack of correlation between both MCP and $CaCl_2$ extractable soil S and plant response has been found in other trial data from China, Argentina and India.

Conclusions

As the world moves from sulphur containing fertilizers such as single superphosphate and ammonium sulphate to high analysis fertilizers, atmospheric inputs of S in rainfall and dry deposition decrease, and crop offtakes of S increase, the incidence of S deficiency is increasing. Much of the world's fertilizer production capacity is committed to the production of ammonium phosphate fertilizers and the opportunity to incorporate elemental S into these fertilizers was recognized by Shell Canada in 2001. Engineering and agronomic expertise were brought together to design and produce a range of sulphur enhanced N and P fertilizers and these have been evaluated in a wide range of climatic/soil/crop situations. Of the 136 experiments conducted to date, where nitrogen and all other nutrients were balanced between treatments so that S was the only variable, 84 were responsive to S with a weighted mean yield increase to SEF of 14%, compared to the zero S control. SEF produced yield responses less than SSP at 6 sites, equal to SSP at 50 sites and responses exceeding SSP at 28 sites.

The application of S to overcome soil sulphur deficiency improved the efficiency of utilization of applied fertilizer P.

This innovative Sulphur Enhanced Fertilizer Technologies program, undertaken by Shell, has produced a new generation of N, P, S fertilizers with the potential to contribute significantly to increased world food production, improve fertilizer use efficiency and reduce impacts of fertilizer management on greenhouse gas emissions.

References

Blair, G.J., Momuat, E.O., and Mamaril, C.P.(1979). Sulfur nutrition of Rice. II. Effect of source and rate of S on growth and yield under flooded conditions. Agronomy Journal, 71: 477-480.

Lefroy, R. D. B, Sholeh and Blair, G. (1997).Influence of sulfur and phosphorus placement, and sulfur particle size, on elemental sulfur oxidation and the growth response of maize (Zea mays). *Australian Journal of Agricultural Research*, 48, 485-495