



Australian Society of Agronomy Inc. C.M. Donald Medal



awarded to an eminent Australian agriculturalist for a long and distinguished career. The award recognises contributions in all areas of agronomy including scientific and field research, development and extension.

The 2015 CM Donald Medal
was awarded to

Dr Graeme Blair - Plant nutritionist, international teacher and mentor



Citation for the 2015 Australian Agronomy Society, Donald Medal

Graeme John Blair is a most worthy candidate for the Donald medal due to his lifelong commitment to plant-soil research, research leadership and undergraduate and postgraduate teaching at the highest national and international level. Following in the great tradition of Colin Donald, Graeme has developed a truly international reputation, particularly in the area of mineral nutrition of pastures and crops, by using innovative experimental techniques combined with a great capacity to develop creative insights through both empirical and modelling approaches. He has been an inspiring teacher with an outstanding ability to explain complex interactions with clarity. He has conducted quality research and teaching on both national and international stages. One of Graeme's great strengths has been his ability to assemble and lead productive research teams which has magnified the impact of their collective research.

Throughout his career, Graeme has aimed to obtain a deeper understanding of soil fertility, plant nutrition and the relationships between them. To this end, he has made imaginative use of radioisotopes, particularly in studies of phosphorus and sulfur. In the 1990s he and his research team developed techniques which significantly enhanced our knowledge of the dynamics of soil organic matter and its role in plant nutrient supply. In 2000, the International Fertiliser Association (IFA) recognised his work on sulfur with the prestigious International Crop Nutrition Award.

Graeme's career began at the University of Sydney where he majored in agronomy; even as an undergraduate, he was renowned among his peers as one who challenged the status quo and sought more in-depth understanding. He continued this search under the guidance of Frank Crofts (Crofts was awarded the inaugural Donald medal in 1984) with PhD studies that focused on the supply-demand relationship of sulfur in fodder oats fertilized with nitrogen.

Following the completion of his PhD, Graeme's international career commenced early with a post-doctoral fellowship to the Department of Soil Science at the University of Guelph, Ontario, Canada. This work used autoradiography to explore mechanistic aspects of nitrogen and phosphorus nutrition of corn. Upon returning to Australia in 1970, he commenced his career-long association with the University of New England, with a position as a Research Fellow funded by the Australian Meat Research Committee. Here he conducted a series of large-scale field experiments to assist in developing improved fertilizer management strategies in pastures on the Northern Tablelands of NSW. This led to seminal work in phosphorus and sulfur cycling, again using radioisotopes as tracers. This work was often conducted in collaboration with colleagues in the CSIRO Division of Animal Production.

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Following on the success of these studies, Graeme was appointed as Senior Lecturer in the Department of Agronomy and Soil Science at the University of New England where he developed courses in plant nutrition for Rural Science undergraduates. He also commenced teaching and research activities in agronomy, nutrient cycling and animal production in Indonesia. This involvement in international science at the plant-soil interface was to become his passion and that of many of his students and colleagues over the ensuing decades.

During his early involvement in Indonesia, he was a visiting Lecturer at the Hasanuddin University and consultant to the International Rice Research Institute (IRRI) and the International Fertilizer Development Centre (IFDC). Whilst there, he developed a sulfur research program which recognized sulfur deficiency as a major limitation to rice production; this led to significant changes in the national fertilizer strategies used in Indonesia. This involvement in international research and teaching resulted in the establishment of the Australian Indonesian Forage Project funded by the Australian International Development Assistance Bureau (AIDAB). As project manager, Graeme was responsible for the training program which saw the upgrading of research facilities and staff training for the Agronomy Section of the Animal Husbandry Research Institute, Bogor and the Gowa Research Station in South Sulawesi, Indonesia.

Graeme continued this work with support from the Australian Centre for International Agricultural Research (ACIAR); he also managed, in conjunction with committed team members, a number of forage projects for ACIAR in Australia, Indonesia, Malaysia, China and Pakistan. One of those began an eight-year investigation of the rehabilitation of eroded red soils in southern-central China. Other ACIAR research projects have included investigations of phosphorus and sulfur cycling and of soil organic matter dynamics in rain-fed cropping systems in Australia, the Pacific Islands, Indonesia, Laos, Malaysia, the Philippines and Thailand.

Often in association with these ACIAR projects, Graeme undertook research programs on nutrient management in pasture and cropping systems in temperate Australia. His work in Australia has been well supported by the Research and Development Corporations and by industry, particularly the grains, meat, cotton and wool industries and Incitec Pty Ltd. In recognition of these achievements, he and his team were awarded the 1995 University of New England Vice Chancellor's Team Research Award.

By understanding the transformations between organic and inorganic forms of sulphur in soil, he and his colleagues were able to develop the KCI-40 sulfur soil test, which is used in all major soil testing laboratories in Australia. Close collaboration between his research team, NSW Agriculture and Incitec Ltd. led to the rapid adoption of the KCI-40 S soil test by Australian farmers.

An economic impact study undertaken by ACIL Consulting in 1998 estimated that the combined sulfur research effort, incorporating the sulfur soil test, led to additional profits to canola growers in NSW of \$A2.4m in 1998 alone and that this aspect of the research had a benefit-cost ratio of 3.4:1.

In 2000, the International Fertiliser Association (IFA) recognised his work on sulfur with the prestigious International Crop Nutrition Award for outstanding research contributing to the efficient use of mineral fertilisers and for the effective communication of the findings to the agricultural community. The Award is judged by an International panel on the basis of originality and practical application of the research. Emphasis is given to a comprehensive approach to the improvement of soil fertility, crop yield and economic viability, leading to an increase in the efficiency of use of mineral fertilisers. The assessments take account not only of the quality of the research but also of the communication of the results, the attention paid to environmental issues, and to the International relevance of the work.

His understanding of the relationships between organic and inorganic carbon (C) and nutrient cycles led to his team developing methodologies that separated soil carbon into pools of varying lability, relating these pools to functions such as aggregate stability and leading to the definition of a Carbon Management Index which has been widely applied.

Through various secondment and consulting roles, Graeme has assisted a large number of Research and Development organizations in the management of their research portfolios including the Food and Agriculture Organisation (FAO), the International Atomic Energy Agency (IAEA), ACIAR, Australian International Development Assistance Bureau (AIDAB), Australian Meat Corporation, the Dairy Research and Development Corporation and the Wool Research and Development Corporation.

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In 2000-01, Graeme spent a year as a Visiting Fellow at the IAEA where he wrote "Guidelines for the use of sulfur isotopes in soil, plant and water studies". This was followed in 2003 by authoring and editing "Plant Nutrition for Food Security - A Guideline for Integrated Nutrient Management" for the FAO in Rome.

Since retiring in 2002, Graeme has continued as an Honorary Fellow and most recently an Adjunct Professor at the University of New England. He continues a hectic international schedule as special advisor on agronomy for Shell Canada's sulfur enhanced fertiliser program in South America and South-East Asia.

Between 2008 and 2010, Graeme has contributed generously to enhancing research capacity in south-east Asia through periods spent as a volunteer for the Crawford Fund on a mentoring program at the Soils and Plant Nutrition Department of the Cambodian Agricultural Research and Development Institute (CARDI). In this role, he has trained research and laboratory staff, helped to develop experimental protocols and assisted with the writing of scientific papers. This volunteer work continues with recent excursions to Cambodia training the next generation of agricultural students.

In 2010 he was appointed as Special Advisor to Shell Canada to help develop a range of sulfur enhanced fertilisers based on his research. In 2014 he assisted Qinpan Fertilisers to develop a S enhanced triple superphosphate which is now being sold to Australian farmers.

Graeme has been a long-term member of a range of professional societies including the Australian Society of Agronomy, the American Society of Agronomy, the Soil Science Society of America and the International Union of Soil Science. He continues to be an active member in these societies by contributing papers to the regular conferences and stepping in as President of the Australian Society of Agronomy to successfully lead the organisation of the 2012 conference held in Armidale.

Graeme has been prolific in publishing. He has authored or co-authored over 200 peer-reviewed journal papers, in excess of 150 national and international conference proceedings, several books and book chapters, institutional publications and industry literature. He has also played a major role in training the next generation of agricultural scientists. Throughout his career, he has supervised 40 PhD and 20 Masters students to completion. In addition there have been scores of Rural Science students inspired by Graeme's teaching as well as Diploma students and many visiting scientists. These students and visiting scientists have come from Australia and Southeast Asia in particular, but also from East Asia, West Asia, South Asia, Africa, the Pacific and Europe. Many of them are now leaders in their own research, development, and business fields or are training the next generation of agricultural scientists.

Graeme has always challenged and been challenged in his research and teaching career and all who have been part of these interactions are richer for the experience. Some of the key outcomes of Graeme's productive career, in conjunction with the various teams he led, have resulted in significant advances in the fields of: (i) plant nutrition- sulfur fertilization, sulfur soil tests, sulfur fertilizers, phosphorus and sulfur interactions, plant nutrient dynamics in crops and pastures; (ii) forage science – forage and pasture management and livestock feeding systems and; (iii) soil organic matter dynamics – labile soil carbon pools, decomposition of plant residues. These achievements are documented in the scientific literature, but most importantly the work Graeme has pioneered is in practice in many aspects of agriculture in Australia and the developing world.

Graeme has made a major contribution to establishing Australia's reputation for excellence in agronomic research. The award of the Donald medal would be a fitting recognition of his outstanding work at home and overseas. For his long and distinguished career as a research scientist, teacher and mentor, Professor Graeme J. Blair is as an eminent Australian agriculturalist deserving of the 2015 Australian Society of Agronomy Inc. C.M. Donald Medal.

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Development of a soil sulfur test and sulfur enhanced fertilisers from the soil up

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Abstract

A series of field and glasshouse studies, mostly utilizing ^{35}S , have been undertaken to study S pools and transfer rates in soil. These studies highlighted the role of ester sulfates in supplying S to the solution SO_4^{2-} pool, which supplies S to plants. This knowledge was used to assess the suitability of a range of soil extracts to predict the S supplying capacity of the soil. A test using 0.26 M KCl heated at 40°C for 3 hours was found to be most suitable and this has been adopted in most accredited soil test laboratories in Australia.

Similarly, a series of detailed studies on elemental S oxidation have been undertaken and the knowledge obtained from these have been used to develop a range of elemental S coated and S incorporated fertilisers. By working closely with commercial fertiliser manufacturers a range of S enhanced DAP, MAP and TSP fertilisers are now available, which commonly contain 8-12% S with 1/3 sulfate and 2/3 fine particle sized elemental S incorporated in the granule. These fertilisers have been tested extensively in a wide range of environments and crop and pasture systems.

Key Words

sulphur, fertilizer, soil test, sulphur oxidation,

Introduction

Up until the 1950s little attention was paid to sulfur (S) as a plant nutrient mainly because it had been applied to soil in incidental inputs in rainfall and volcanic emissions and as a component of nitrogen, phosphorus and potassium fertilisers. Prior to that time experimentation concentrated on superphosphate responses, with the emphasis on phosphorus.

Reports in 1915 and 1926 from the Glen Innis Research Station in New South Wales mention responses to potassium sulfate and gypsum (Blair and Nicholson, 1975). The soils on which these experiments were conducted were subsequently shown to be non-responsive to potassium and calcium hence this may be the first recorded response to S in Australia. The first published experimental evidence was by Anderson and Spencer (1950) on soils from the Southern Tablelands of New South Wales.

Plant metabolism depends on S and a deficiency of this nutrient will cause basic metabolic impairment, which will not only reduce crop and pasture yield but also the quality of produce (Duke and Reisenauer, 1986). Deficiency symptoms of S in plants includes a yellowing of the younger leaves as a result of a low chlorophyll production and S non-mobility (Yoshida and Chaudhry, 1979) and a marked reduction in plant height and tiller number in cereals (Blair et al. 1979).

The awareness of S deficiency is increasing and areas of S deficiency are being recognised in previously S sufficient areas of the World.

There are many reasons of increasing S deficiency but the most important I have listed in Blair et al. (1978) as follows:

- i) the increasing use of high analysis, low S containing fertilisers;
- ii) the increase in yields obtained as a result of other technological advances;
- iii) the decreasing use of S containing pesticides and fungicides;
- iv) environmental control of sulfur dioxide emissions in industrial areas and fuels; and,
- i) a greater number of experiments conducted where S is studied as a nutrient in its own right.

The S cycle

The S cycling literature has been extensively reviewed; for example Till (1975) and Blair (1986). The S cycle has similarities to both N and P cycles. The role of organic sources in supplying sulfate to plants is similar to both the N and P cycles and the adsorption reactions are similar to P reactions although the strength of sulfate adsorption is considerably less than for phosphate.

A diagram of the S cycle is shown in Figure 1. Uptake by plants is from the "available SO_4^{2-} " pool, which also supplies SO_4^{2-} to, and receives SO_4^{2-} from, some of the other components in the soil-plant-animal cycle at a range of rates. In addition, there are various other environmental input and loss processes which can make significant differences to the S balance of the whole system.

The plant will continue taking up SO_4^{2-} from the available pool and, in its simplest case the fertiliser can be considered as another source of SO_4^{2-} that becomes available at some rate and the plants compete with the other processes for it. Under normal circumstances as soon as the fertiliser S enters the system it becomes indistinguishable from that already in the cycle.

Work on S cycling related to pasture improvement in temperate conditions has been conducted by Till and May (1970) using radiotracers. In these studies, ^{35}S applied in fertiliser could still be detected two years after the initial application, indicating a long residual effectiveness. This radiotracer work emphasized the role of organic matter as the major temporary storage pool for added fertiliser in the system and provided a basis for a simple model and simulation studies, which showed the importance of process rates within the cycle (May et al. 1973).

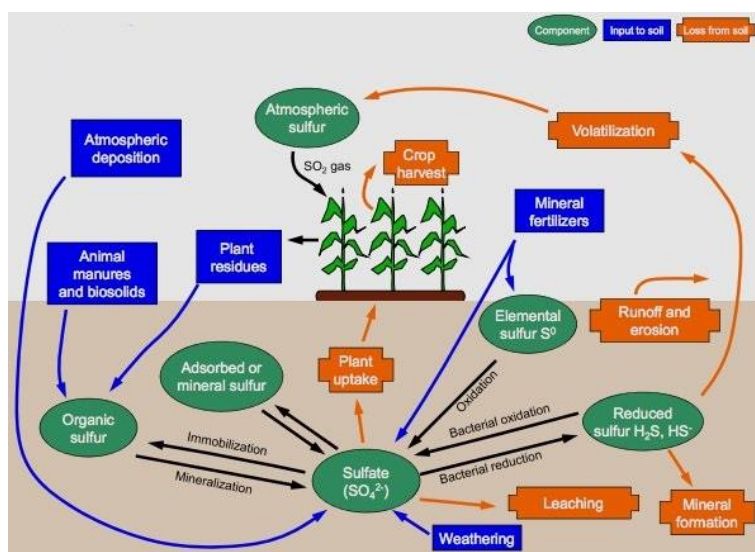


Figure 1. S pools and pathways in Agricultural systems

Source: https://upload.wikimedia.org/wikipedia/en/7/71/SulfurCycle_copy.jpg

Sulfur Soil testing

Soil testing to determine the S status of agricultural systems has met with variable success. The poor ability of the widely used mono-calcium phosphate extractant to identify S responsive soils is highlighted by the data from India in Figure 2.

A number of reasons for this have been outlined in reviews by Freney (1986). The nature of the S cycle in soil, which includes four main pools, contributes to this poor performance.

These pools contain:

- sulfate in the soil solution which is the source of S for plants and which can move in the soil water and/or be adsorbed.

- adsorbed sulfate, which is bonded weakly to positively charged colloid surfaces. In highly weathered soils not all of this S may be accessible to plant roots
- ester sulfates, which are a group of compounds containing a C-O-S linkage. The content of these compounds in the soil can be determined by digestion with hydriodic acid (HI). They are important because the C-O-S bond can be split on drying to release plant available SO_4^{2-} .
- carbon bonded S has a strong C-S bond which is difficult to break. This pool of S provides the long term supply to plants and is therefore less important to soil test results.

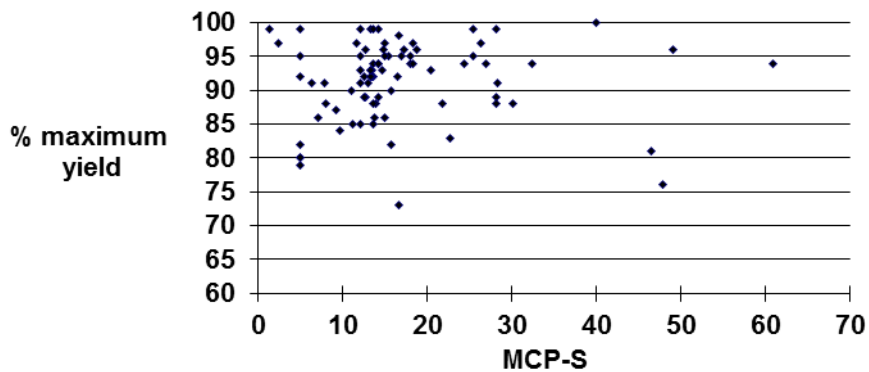


Figure 2. Relationship between mono-calcium phosphate (MCP) extractable S and % maximum yield in field trials in India conducted by The Sulfur Institute.

Plants take up their sulfate from the soil solution pool, which receives S from both the adsorbed and organic S pools. The organic S pool contains two major sub-pools, namely ester sulfates and carbon bonded S. Soil extractants used to determine the S status have most commonly involved a measurement of the sulfate in the soil solution plus adsorbed S. Amongst the extractants used, calcium dihydrogen orthophosphate containing 500 $\mu\text{g P/mL}$ has been the most common.

Blair (1979) tabulated data from the world literature on critical levels of soil S. In doing this he partitioned the extractants into those which extract readily soluble sulfate, readily soluble plus portions of adsorbed sulfate, readily soluble, adsorbed and a proportion of organic sulfate. Within each of these groups, variable critical levels have been proposed. Generally, correlations between extractable S, using these types of extractants, and plant response have been poor. As for other nutrients local calibration of a soil test is critical if sensible predictions are to be made of S status.

Simulation modelling of agricultural systems (McCaskill and Blair 1988) indicates that fluxes of S from the organic pool play a major role in supplying S to agricultural plants, particularly in pasture systems where organic matter levels are high.

The importance of the ester sulfate pool is highlighted by the data of Blair et al. (1994) (Figure 3). In this experiment, where ^{35}S was used, the ryegrass plants acquired SO_4^{2-} from the MCP-S extractable pool and the HI-S (ester sulfate) pool and at 98 days in phase 1. When the plants and sulfate S were removed from the soil and new plants established in phase 2 the HI-S (ester sulfate) pool provided S to the plant and to the MCP-S pool.

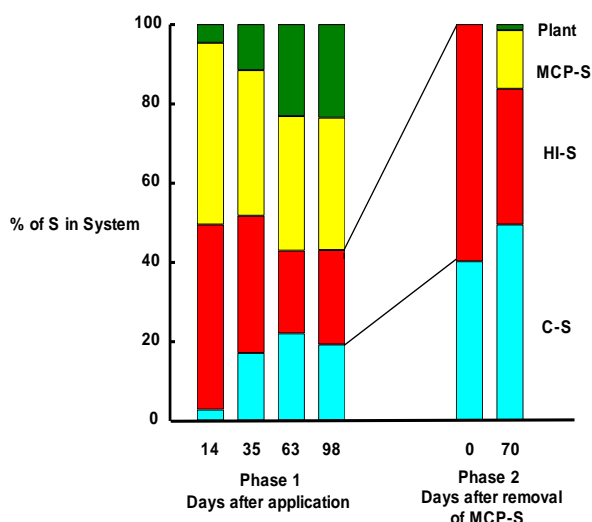


Figure 3. The pools of soil S accessed by ryegrass in a pot experiment showing the importance of HI-S (ester sulfates) in supplying sulfate to the plant available pool. Blair et al. (1994).

In the pot experiment of Blair et al. (1994) the loss of S from the MCP-S and gains to the plant, HI-S and C-S pools in the first 63 days (Table 1) shows how rapidly S fluxes occur in soils after the addition of $^{35}\text{SO}_4^{2-}$. The incorporation rate of $^{35}\text{SO}_4$ into the HI-S and C-S pools was considerably higher than that found in New Zealand by Goh and Gregg (1982), who found that from 17 to 40% of added sulfate was present in organic forms within 34 to 75 days. The finding that only the HI-S pool had a negative transfer rate (loss of S from pool) in the 0-70 day period of phase 2 (Table 1) supports the finding of Freney et al. (1971). They found that most of the available S removed by plants over a 9-month period came from the ester sulfate fraction although there were changes in all soil fractions.

Table 1. Net transfer rate of ^{35}S in plant and soil pools in Phase 1 and Phase 2 of the experiment of Blair et al. (1994).

S Pool	Net transfer rate (%/day)	
	0-63 days	0-70 days
Plant	+0.36	+0.07
MCP-S	-1.05	+0.20
HI-S	+0.33	-0.38
C-S	+0.35	+0.02

An evaluation of a range of soil S tests has been undertaken by researchers at the University of New England, Australia. Blair et al (1991) compared H_2O , $0.01\text{M Ca}(\text{H}_2\text{PO}_4)_2$ (MCP), NaHCO_3 and KCl-40 in a series of field and glasshouse studies. In the KCl-40 procedure the soil is extracted with 0.25 M KCl at a temperature of $40\text{ }^\circ\text{C}$ for 3 hours and the inorganic and organic S in the extract measured. The various soil S pools being utilised by plants has been evaluated by Chaitep et al. (1994) in an experiment with flooded and non-flooded rice grown in a glasshouse. In this evaluation plants were grown in soil which had been incubated for 3 weeks with ^{35}S . This allowed equilibration of the radioactive tracer with the various soil pools. Flooded and non-flooded rice was then grown to maturity in the glasshouse and the ^{35}S and total S in the above-ground biomass determined. The ratio of ^{35}S / total S is termed the specific radioactivity and this ratio in the plant is compared with the specific radioactivity in the soil extract (termed the specific radioactivity ratio, SRR). When this ratio equals 1 it indicates that the plant is removing S from the same or similar soil S pools as the extractant. The data in Table 2 shows that the SRR value is closest to 1 for the KCl-40 extract among the extractants evaluated indicating that this extractant was removing S from similar pools as the plant.

Table 2. Specific Radioactivity Ratio (SRR) between plants and extracted S for a range of chemical extractants.

Extractant	System	
	Non-flooded	Flooded
H ₂ O	0.88	0.85
MCP	0.83	0.79
KCl-40	0.92	0.92
NaHCO ₃	0.27	0.19

Research by Chinoim et al.(1997) has shown that the KCl-40 extract generally removes more S from the ester sulfate pool (shown as loss from HI-S in Figure 4) than MCP. In the data from a granite soil shown in Figure 4 the amount of S extracted from the sulfate and organic S pools was also greater than with MCP, but this is not always so. Because MCP removes more S from the adsorbed sulfate pool than KCl-40 the MCP value is always higher than KCl-40 in soils high in S and with a high S adsorption capacity.

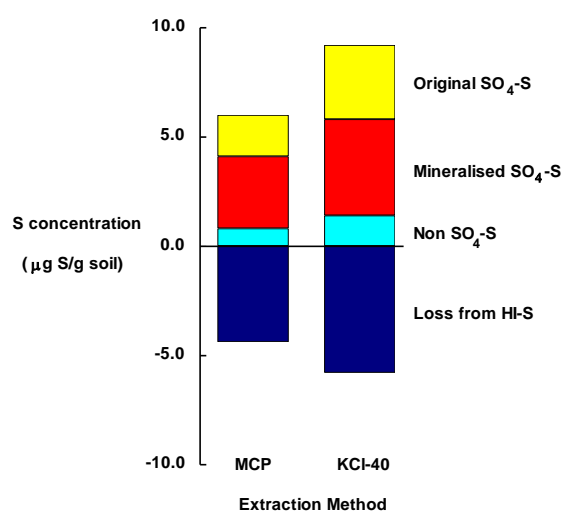


Figure 4. Sources of S removed by KCl-40 and MCP from a granite soil and S transformations that take place during extraction (Chinoim et al. 1997).

In the development of the KCl-40 method Blair et al. (1991) found a coefficient of determination (r^2) of 0.74 between extractable S and percent of maximum yield on a range of 18 pasture soils collected from Northern New South Wales, Australia (

Table 3). In a supplementary study, where radioactive S had been added to rice soils, it was found that the KCl extract removes a portion of the HI reducible ester sulfates, which are believed to be rapidly turning over in soil systems. It is hypothesised that the greater accuracy of this test results from the extraction of soil sulfate, adsorbed S and a portion of the actively turning over organic S components in the soil.

Table 3. Coefficient of determination (r^2) between extractable S and percent of maximum yield for a range of extractants on a range of 18 pasture soils collected from Northern New South Wales, Australia.

Extractant	r^2
H ₂ O	0.47
MCP	0.48
KCl-40	0.74
NaHCO ₃	0.15
Total S	0.03

A schematic of the various pools accessed by plants, and removed by a range of extractants, is shown in Figure 5.

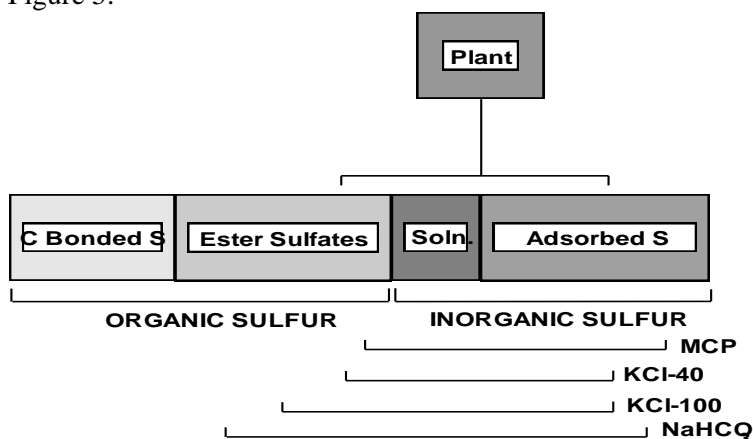


Figure 5. Schematic of the S pools accessed by plants and removed by a range of extractants.

The ability of S soil tests to indicate responsive and non-responsive sites was examined by evaluating the number of times the soil test, measured at the start of the experimental year, was above the critical level (6.5 $\mu\text{g/g}$ for KCl-40, Blair et al. 1991), and 10 $\mu\text{g/g}$ for MCP (Incitec) and the response to S in that year was statistically non-significant (i.e. a correct prediction of a non-responsive site) or statistically significant (i.e. a correct prediction of a responsive site). In the first instance the soil test prediction was correct more often with the KCl-40 extract than with MCP. The KCl-40 extract was also more often correct in predicting responsive sites in 2 out of 3 years for which data was available.

Several sites were notable in the poor performance of the soil tests and these were those where extractable S was present below the sampling depth (e.g. Site Q1, Malanda, S23, Nangwarry Figure 6). Probert and Jones (1977) observed a similar situation in their North Queensland studies and used a weighted profile mean to overcome the problem.

The KCl-40 procedure has now been adopted by most accredited soil test laboratories in Australia.

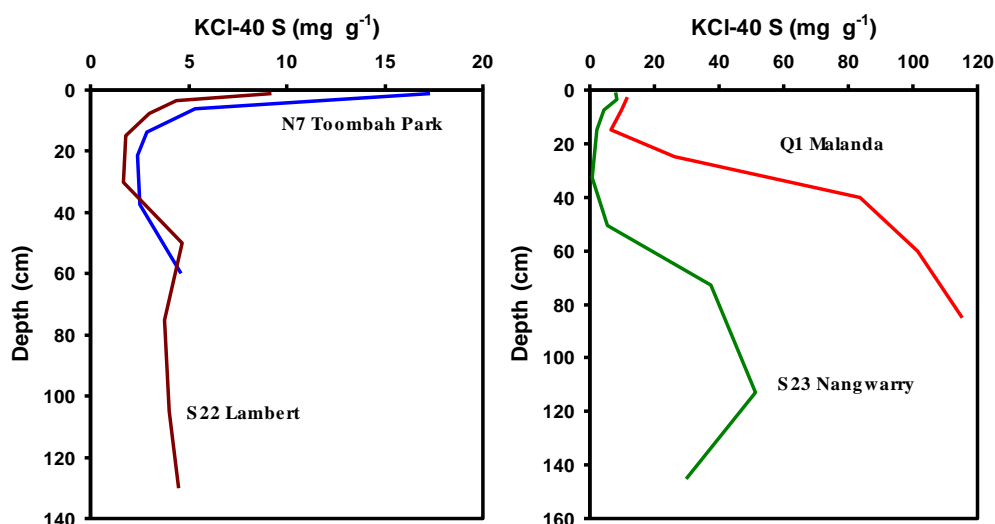


Figure 6. KCl-40 extractable S in profiles of four soils from Australia.

Development of new S containing fertilisers

Intensification of cropping systems using high-yielding varieties has accelerated S removal from the soil, which has resulted in more soils becoming S-deficient. Increased use of high-analysis S-free fertilisers such as MAP, DAP, TSP and urea has aggravated the S deficiency problem.

Many alternative sources of S fertiliser are available (Blair 2002). Fertiliser sulfate is immediately available to the crop (Friesen and Chien, 1986), but leaching losses may be significant from these fertilisers. Elemental S must undergo oxidation to plant available sulfate and both moisture and aeration are interrelated factors that affect the rate of oxidation of elemental S. Generally, elemental S is oxidised most rapidly at a moisture content of approximately field capacity (Moser and Olsen, 1953), which is the optimum soil moisture for plant growth (Burns, 1968), so the SO_4 is largely released in synchrony with plant demand.

Equations for incorporating the effects of soil temperature and moisture on S oxidation and plant S demand were developed from published data (McCaskill and Blair 1989) and these were incorporated into a simple model to predict sulfate supply from single superphosphate and elemental S. The model predicted that after 72 days 99% of the S in single superphosphate would have been released from the fertiliser granule. By contrast the release and oxidation of S from elemental S fortified single superphosphate (36% elemental S, 9% sulfate-S) was 54% after 1 year and only 23% from crushed agricultural grade elemental S.

Elemental S is an almost ideal fertiliser as it contains 100% nutrients, hence its inclusion into fertilisers such as DAP, MAP and TSP does not dilute the content of other nutrients in the fertiliser nearly as much as does the inclusion of sulfate.

Many studies have demonstrated that the rate of oxidation is proportional to the surface area of S exposed and hence inversely proportional to the particle size (Fox et al., 1964). Shedley et al. (1979) showed that S oxidation was complete from 50 μm particles 70 days after the commencement of his experiment and he also found that in the coarser particle size treatments the release of sulfate continued throughout the 1 year experimental period.

Sholeh et al. (1997) found marked differences in S oxidation between 50-150 and 150-250 μm particles in the presence of P but little difference when P was absent (Figure 7). This has important implications for incorporation of elemental S into fertilisers and indicates that P containing ones are the best candidates.

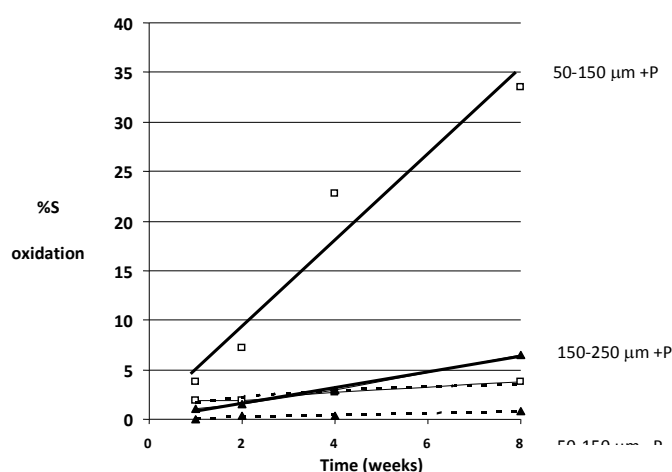


Figure 7. Effect of elemental S particle size and the presence of P on the % of elemental S oxidised over an 8 week period (Sholeh et al. 1997).

In studies undertaken at UNE (Kubelo, 2008) S oxidation rates were higher at 30°C than at 18°C over a range of particle sizes with the difference becoming less as particle size increased (Figure 8).

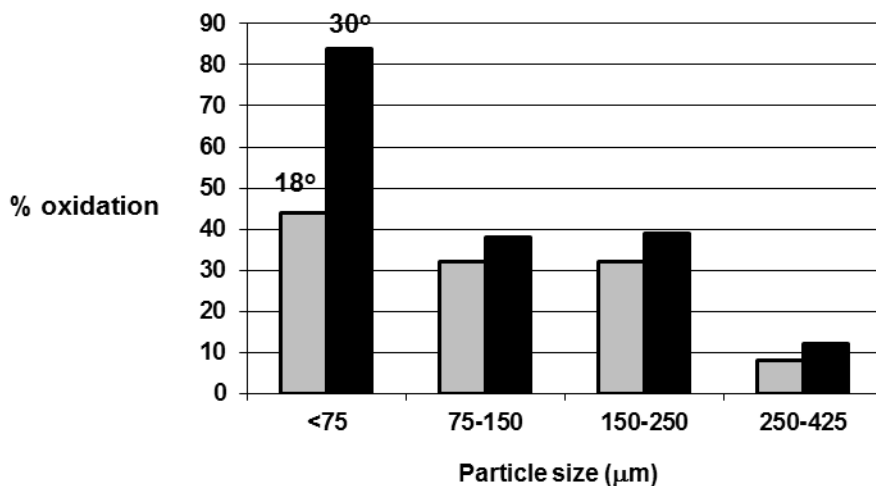


Figure 8. Effect of temperature and particle diameter on S oxidation at 6 weeks.

Elemental S containing P based fertilisers were introduced to the Eastern Australia market in 1957 in the form of S fortified SSP. This was made by spraying molten elemental S into the den during manufacture. Freisen et al. (1987) compared the P and S release from partially acidulated rock phosphates and found that the presence of elemental S increased both P and S release from the fertiliser. Australian fertiliser manufacturers did not take up this technology as they had considerable investments in single superphosphate plants, which needed to be run at full capacity to be economical.

This basic research conducted by the University of New England (UNE) team has been used to develop a range of S coated fertilisers and in 1991 a patent was granted to UNE for a S coating process (Blair, 1991). Work continued for the next 15 years to refine the process and to develop a range of coated DAP, MAP, TSP and urea coated products (Blair et al. 1994, Dana et al. 1994, Yasmin et al. 2007). During this period Hi-Fert began marketing S coated products under the Goldphos name.

Shell 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). The design of the products to be produced was based on the UNE research and I was invited to become a Special Advisor on Agronomy and Soils to the “Thiogro Project”. Much of the process developmental work on Shell Thiogro was undertaken at the International Fertilizer Development Centre (IFDC) in Muscle Shoals, Alabama, USA where a reactive granulation process was developed using pre-neutralizers (PN), pipe cross reactors (PCR) and combination of PN and PCR units with S concentrations ranging up to 20% by weight.

In the Shell Thiogro S enhanced MAP and DAP processes, molten S is added to the ammonium phosphate slurries, along with small concentrations of proprietary additives to emulsify the hydrophobic elemental S into a hydrophilic ammonium phosphate slurry/melt. This results in phosphatic slurry containing discrete elemental S particles with an average size ranging from 20 to 60 microns. The reactor slurry is subsequently granulated in conventional rotary drum granulator. Commercial fertilizers made using this process commonly contain 10-12% S. Because of the risk of a delay in oxidation following application, 1/3 of the S is added as sulfate and 2/3 as elemental S.

A distinguishing feature of the Shell Thiogro process is that the elemental S is uniformly distributed throughout the fertiliser granule, which reduces the risk of potentially explosive S dust being generated as the fertiliser particles abrade during handling and ensures that the elemental S and P are in close proximity to promote S oxidation.

S oxidation from fine elemental S (S⁰) and from S incorporated into Shell Thiogro MAP has been studied extensively at UNE and results from one such study are presented in Table 4. The trial was conducted in a

temperature controlled glasshouse set to simulate subtropical conditions with day and night conditions fluctuating around 25 °C. The results showed that there was no significant difference in S recovery by the maize plants between fine elemental S (<48.1µm) mixed throughout the soil or from the 1/3 sulfate/ 2/3 elemental S contained within the Shell Thiogro MAP (12% S) when both were applied at the equivalent rate of 10 kg S/ha.

Table 4. Dry matter yield and S uptake by maize after 44 days.

Numbers within a column followed by the same letter are not significantly different (p<0.05).

Treatment	Dry Weight (g)	Total S uptake(mg/pot)	Recovered S (%)
Fine (<48.1µm) S°	4.72a	7.03a	25.6a
Shell Thiogro MAP12	4.50a	6.11ab	20.5a

A total of 138 replicated randomised block plot experiments have been conducted to evaluate Shell Thiogro. 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 in total.

Of the 136 experiments 84 were responsive (difference between minus S control and Shell Thiogro treatment significant at p=0.05 according to Duncan's Multiple Range Test) to S with a weighted mean yield increase to Shell Thiogro of 14%, compared with the zero S control. The comparison treatment consisted of a mixture of MAP and gypsum used to simulate an addition of single superphosphate (SSP). Nitrogen and all other nutrients were balanced between treatments so that S was the only variable. Shell Thiogro produced yield responses equal to SSP at 50 sites, responses exceeding SSP at 28 sites and responses inferior to SSP at 6 sites.

An S enhanced triple superphosphate TSPS fertiliser has been developed by Yunnan Lufeng Qinpan Phosphor Chemical Co., Ltd., China, which is based on the UNE research and it contains 8.5% S present as 1/3 sulfate and 2/3 elemental S within the fertiliser granule and this is now on sale in the New England Tablelands of NSW.

Conclusion

The sound basic research, which has had good long term financial backing from Australian Research Corporations, AusAid, ACIAR and Commercial interests and an enthusiastic group of post-graduate students and Research Fellows has led to the development of a robust S soil test and to a new generation of S containing fertilisers. Persistence pays!

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