Proceedings of *the* **New Zealand** *Grassland Association 47: 233-242 (1986)*

ALTERNATIVE SULPHUR FERTILISERS IN NEW ZEALAND

CC. BOSWELL and B. SWANNEY
Invermay Agricultural Research Centre,
MAF, Mosgiel.

Abstract

Interest in high analysis sulphur (S) fertilisers is centred on elemental S(S°) which is generally mixed with other materials for safety reasons and to improve effectiveness. Central to the effectiveness of S° fertilisers is the rate of oxidation to sulphate-S (SO_4-S) for plant uptake. Oxidation rates increase as particle fineness increases. The distribution of S° particle sizes in mixtures therefore affects the effectiveness of the fertiliser in any environment. Rates of oxidation vary between environments and thus different S° particle size distributions suit different environments.

Currently the choice of alternative commercial available S° fertilisers is restricted to screened 'agricultural's" and mixtures of S° with superphosphate. Of these, molten mixed S superphosphate is the most suitable material for most environments but especially where S oxidation is slow.

Commercial production of alternative S° fertiliser mixtures in New Zealand is imminent. Mixtures of S° and sodium bentonite offer the possibility of preparing fertilisers to suit different environments. Granulated ground S° mixed with bentonite clay can be expected to release SO"-S more slowly but this has advantages where leaching of sulphate is likely.

Production of SO_4-S from two Improved Canadian S°/bentonite materials is expected to be similar to or slower than that from granulated ground S".

Two other Imported products, S impregnated urea (20% S, 36% N) and 'Thiovit' (85% S) contain finely divided and ultra finely divided S° respectively. They are rapidly and very rapidly oxidised to sulphate and may have specialised uses in cropping and horticultural enterprises.

Keywords: Sulphur fertilisers, elemental sulphur, sulphur/sodium bentonite, plant sulphate, oxidation rates.

INTRODUCTION

New Zealand soils are low in phosphorus (P) and sulphur (S). Superphosphate contains similar amounts of P and S (9% P, 11% S) and for 100 years the S requirements of New Zealand pastures have been met by single superphosphate applied to meet plant P requirements. The escalating costs of superphosphate and transport and application costs, have triggered a move to high analysis P fertilisers such as ammonium phosphates, triple superphosphate and reactive phosphate rock (PR) and PR partially acidulated with phosphoric acid. All of these contain little or no S (Table 1). This has highlighted the future need to supplement the high analysis P fertilisers with S fertilisers — preferably high analysis S fertilisers.

Sulphur is either applied as sulphate (SO_4-S) as in superphosphate, or as elemental sulphur (S°) as in screened S. Plants take up S as SO_4-S and thus SO_4-S fertilisers are immediately available to plants on dissolution, but their S concentrations are moderately low (Table 1). S° would be the ideal concentrated S fertiliser if it were readily oxidised to the SO_4-S form. The rate of oxidation is the key to the effectiveness of S° fertilisers. This oxidation rate is directly proportional to the surface area of the S° particles and so increases as the fineness of particles increases. However, S° is not a good conductor of electricity and electrostatic charges tend to build up. Discharges in mixtures of fine S° and air may cause explosions. Safety is a major consideration in both the use of screened 'agricultural' S° and in the production of alternative S° fertilisers. For example, New Zealand Civil Aviation safety guidelines limit both the proportion of fine particles (20% < 150 microns diameter) in screened 'agricultural' S°, and the amount of S° which can be added in mixtures with other fertilisers (22.5%), for aerial application.

TABLE 1: Sulphur and Phosphorus Contents of a Selection of Fertilisers.

	% s	% SO^4-S	% Total S	% P
High Analysis P Fertilisers				
Triple superphosphate	—	2	2	20
Mono-ammonium phosphate (MAP)	—	2-3	2-3	20
Di-ammonium phosphate (DAP)	—	2-3	2-3	20
Reactive rock phosphate				13
Partially acidulated rock phosphate:				
(i) with phosphoric acid	—	—		13
(ii) with sulphuric acid		6-7	6-7	13
'Standard' S Fertilisers				
Single superphosphate		11	11	9
Ammonium sulphate	—	24	24	
Gypsum		18	18	
Sulphur superphosphate	9	9	18	9
Sulphur superphosphate extra	18	9	27	7
Screened 'agricultural' sulphur	100		100	
Alternative S° Fertilisers				
Sulphur/sodium bentonite (DSIR)	75-85		75-85	
Sulphur/bentonite[1] (imported Product A)	90		90	
Granulated ground S	90		90	
Sulphur impregnated urea	20		20	
'Thiovit'	85		85	

[1] Original trial shipment later product included 85% S".

New S° fertilisers include mixtures of S° with other materials which may act as carriers, and are designed to reduce the explosive hazards by incorporating S° in hard stable prills. On wetting these prills readily break down to finely divided S° particles.

Among the new S° fertilisers are S°/sodium bentonite fertilisers developed in New Zealand by the Industrial Processing Division of DSIR for the express purpose of meeting plant S requirements while being safe to handle. The addition of sodium bentonite to S° has a two fold effect on reducing explosive hazards. Firstly the prills are hard and stable and therefore largely dust-free. Secondly the addition of the bentonite improves the conductivity of the material and reduces the likelihood of discharges. S°/bentonite is formed into prills which consist of a matrix of S° through which the sodium bentonite clay is evenly dispersed. On wetting the clay expands to 14 times its volume and assists in the fracture of the S° into fine particles. Mixtures of S° and bentonite (often less expansive calcium bentonite) have been available in North America for at least 20 years but have attracted little attention in New Zealand. Two Canadian companies, which have taken New Zealand advice in using sodium bentonite and/or increasing the bentonite content of the mixture, are currently seeking a market for the new materials.

Another S° fertiliser developed in New Zealand is granulated ground S". Dry S° is ground and granulated with about 10% sodium bentonite clay mined in Canterbury. The grinding process is not generally favoured because of the attendant explosive hazards. To date imported S° (almost 100% pure), mainly used for the manufacture of sulphuric acid for superphosphate production, has been used in the New Zealand products. However, the renewed interest of mining New Zealand deposits of S at Lake Rotokaua near Taupo may result in local S being used. Although the deposits contain 10-20% S mixed with pumice, the material can be refined to 70% S which could be used as a source of S° for either of the locally developed types of products.

METHODS

S° fertilisers were subjected to both laboratory and field evaluations, Laboratory studies involved measurement of S content, rate of prill dispersion when immersed in water, and distribution of S° particle sizes following dispersion (by sieve analysis), Standard methods for these have been developed at Invermay and details are available from the authors. Both the rate of dispersion of prills and the size of S° particles govern the rate at which SO^4-S is likely to become available to plants. An indication of the rate of SO^4-S production in field conditions was measured from either phosphate-extractable soil SO^4-S or plant SO^4-S levels, or both. Results reported are mainly from small plot (8 m^2) experiments at Invermay (coastal Otago; annual rainfall 690mm, mean annual temperature 10.2°C) or near Omarama (inland Waitaki Basin; annual rainfall 530mm, mean annual temperature 9.3°C). At Invermay pastures were based on ryegrass and white clover but also contained about 30% crested dogstail, browntop and sweet vernal. Pastures at Omarama were based on Wairau lucerne, sometimes in association with red, white and alsike clovers. In one study four S fertilisers were compared in an unimproved hard tussock pasture after lucerne establishment had failed.

S° fertilisers were compared with a standard SO^4-S fertiliser (usually gypsum) applied either at a common rate of S, or over a range of rates representing a response curve to applied sulphate.

In addition to different S° fertilisers, background information on the relationships between S° particle size and SO^4-S production were obtained by applying a common rate of S° (50kg S°/ha) in a range of particle size sieve fractions. Results for similar studies at Westland (Williams et al. 1984) and Waikato (W.Saunders pers. comm.) sites enable comparisons of S° oxidation rates in different environments to be made.

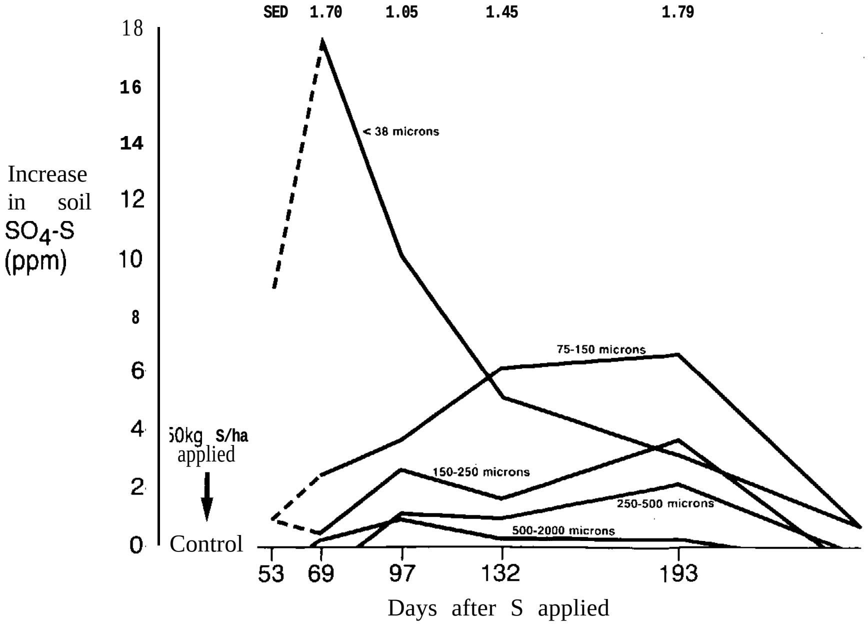

FIGURE 1: Effects of S° Particle Size on Increases in Soil SO'-S Levels with Time (Invermay Site, Spring Application).

RESULTS AND DISCUSSION

Relationships Between S° Particle Size and Oxidation Rates

The effects on soil SO^4-S concentrations of different sized particles of agricultural S° applied to pasture at lnvermay are shown in Figure 1. Finest particles (< 38 microns) were oxidised to SO^4-S more rapidly than larger particles but their effect was short-lived compared with larger sized particles. Progressively larger S° particles produced lower and later peaks in soil SO^4-S. There was very limited elevation of soil SO^4-S with particles between 250 and 500 microns and negligible increase from particles greater than 500 microns.

In semi arid Central Otago (annual rainfall 340mm; mean annual temperature 10.6°C) Ludecke (1965) showed that finely divided S° particles (< 150 microns) or alternatively SO^4-S fertilisers were necessary to produce maximum responses to S fertiliser. Data from the Waitaki Basin (McIntosh and Sinclair 1983, Boswell unpublished) support these findings.

In warmer, moist or wet environments (e.g. Westland, > 2000mm rainfall, mean annual temperature 13.4°C; and Waikato, 1200mm annual rainfall, mean annual temperature 13.3°C) S° particles at least 150-250 microns are rapidly oxidised within a few weeks of application (Williams et al. 1984, W. Saunders pers. comm.). Thus the relationships between S° particle size and rates of oxidation vary between environments. Those from the cool (Invermay) and/or dry (Waitaki Basin) areas represent slowest oxidation rates and therefore our field results can be expected to emphasise the finely divided S° fraction of fertilisers. In contrast, in Northland (1250-2500mm annual rainfall, mean annual temperature 13.3-15.5°C) more emphasis is likely to be placed on coarser S° fertilisers since we could expect rapid oxidation of particles < 250 microns and moderate rates of oxidation of particles up to 500 microns.

Screened Agricultural S° and S Superphosphate — the Currently Available High Analysis S Fertilisers

Screened agricultural S° is obtained by screening the imported S° already described. It contains a proportion of fine S° (i.e. 20% < 150 microns), but the majority of it is slowly oxidised. In fact, at lnvermay there was little effect of SO^4-S production from particles > 250 microns during the two years following application (Boswell and Swanney 1984). The potential oxidation of screened S° in warm environments could be expected to be about 25% of S applied within one year of application (i.e. assuming oxidation of all particles < 250 microns within 12 months (Williams et al. 1984) — see Table 2).

Common mixtures of S° and superphosphate contain 9 or 18% of S° in fertilisers known as ‘S superphosphate’ and ‘S superphosphate extra’ respectively. S superphosphate can be prepared either by mixing screened agricultural S° with manufactured superphosphate (dry mixed S superphosphate), or by adding molten S to the superphosphate during the manufacturing process. Molten mixed sulphur superphosphates (MMSS) are the most effective high analysis S fertilisers currently available in New Zealand (Sinclair and Boswell 1983). Whereas the distribution of S° particles from dry mix S superphosphate are the same as for the screened S (Table 2), S° particles in MMSS are moderately finely divided (Table 2). MMSS supplied both readily available SO^4-S (from dissolution of the superphosphate fraction of the mixture) and prolonged SO^4-S production from the oxidation of the S”. It has proven useful in environments ranging from the Waitaki Basin (McIntosh and Sinclair 1983) with about 600mm of rain/annum, to Haast (Sinclair and Boswell 1983) with a rainfall of 5000mm/annum.

In the non leaching Waitaki Basin environment MMSS proved less effective than superphosphate applied at the same rate; while screened S° was about half as effective as superphosphate for legume establishment (McIntosh and Sinclair 1983).

TABLE 2: Summary of Dispersion Rates of Prills and S° Particle Size Distributions from Alternative S° Fertilisers.

	Time for 80% dispersion of prills (minutes)	S° particle size — microns[1] % of particles < nominated size				
		38	75	150	250	500
S°/sodium bentonite (DSIR)						
85% S°	1000	5	22	73	95	98
80% S°	35	8	35	87	98	100
75% S°	10	20	61	96	99	100
70% S°	7	35	89	99	99	100
Imported S°/bentonite						
Product A 90% S	5760	2	5	11	22	34
Product A 85% S	4320	8	15	40	70	90
Product B 90% S		3	7	24	47	84
Granulated ground S° prills 90% S°	1'	6	15	42	71	99
S impregnated urea	20[2]	5	36	96	100	100
'Thiovit'	1[2]	100[3]				
Molten mixed S superphosphate	n a.	11	30	70	91	97
Screened agricultural S°	n.a.	4	9	13	26	40

[1] Mean values of fertilisers used in Otago experiments 1980-85.
[2] Estimated by visual assessment.
[3] Manufacturers consider all particles to be in the range 5-8 microns n.a Not applicable.

TABLE 3: Comparison of the Effects of S Fertilisers (Including S° Extracted from MMSS) on Lucerne Cover (%) and Vigour (Scored O-10) in the Waitaki Basin.

Rates of S applied kg/ha[1]	SO_4-S fertiliser (gypsum, ammonium sulphate)		MMSS		S° extracted from MMSS		Screened S°		LSD
	%	vigour	%	vigour	%	vigour	%	vigour	
15	30	5.8	12	5.8	17	5.7	6	3.2	
30	52	8.8	65	7.7	35	6.5	31	5.2	29.2%
60	72	8.8	78	8.8	12	8.2	16	7.7	(2.72)[2]
120	83	9.2	92	9.7	53	8.8	29	8.3	
mean	59	8.3	62	8.0	29	7.3	20	6.1	14.6% (1.36)
Control (nil S)	6	3.1							

[1] Single spring application.
[2] LSD values in brackets are for vigour scores.

The differences between SO_4-S fertilisers and MMSS applied as maintenance fertiliser disappeared in the third year after S application in trials in the Waitaki Basin (Boswell, unpublished).

S° separated from MMSS and alternative S fertilisers were compared in a further trial in the Waitaki Basin on oversown lucerne pasture. The results of visual assessments of plant cover and vigour at lucerne flowering in the fourth year after S application are shown in Table 3. The MMSS was comparable with SO^4-S fertilisers in the non leaching environment. However, much of the MMSS effect was due to its SO^4-S content. The oxidation of finer S° in MMSS relative to screened S° tended to improve lucerne cover and vigour although significant differences were not recorded. Plant cover was more affected by form of S fertiliser than plant vigour. This suggests that a ready supply of SO^4-S was required to assist lucerne establishment but slowly available SO^4-S fertilisers subsequently produced sufficient SO^4-S to supply the relatively scarce plants in the S° fertiliser treatments.

New S° Fertilisers Developed in New Zealand

S°/sodium bentonite mixtures consist of molten S° mixed with an expanding clay, sodium bentonite, and cooled in oil into prills. On wetting the clay expands and the S° in the prill shatters to finely divided S°. The fineness of S° particles increases as the bentonite content increases (Table 2).

Field studies have shown that the rate of oxidation of the dispersed S° increases as the fineness of S° particles increase (i.e. as sodium bentonite content increases -Fig. 2). By altering the bentonite content of the mixtures it is possible to vary the oxidation rate and thus the rate of SO^4-S production.

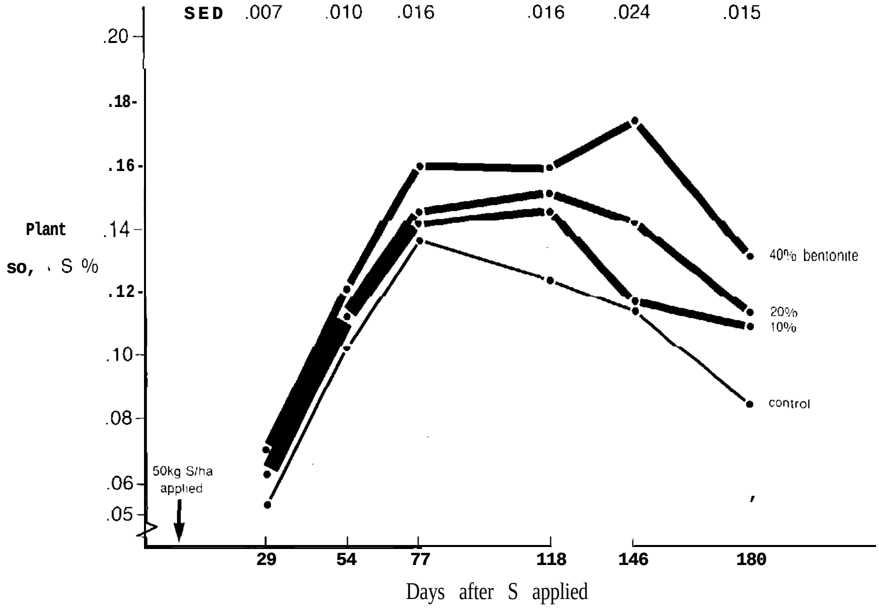

FIGURE 2: Effects of Bentonite Contents of S°/Sodium Bentonite Mixture on Plant SO^4-S Levels (Invermay Site, Spring Application).

There is negligible electrostatic buildup in S°/sodium bentonite mixtures with at least 15% bentonite (W. Owers, pers. comm.). This bentonite content is likely to be the minimum used in New Zealand fertilisers. Although the 15% bentonite mixture contains the largest particles among the S°/sodium bentonite mixtures listed in Table 2, the S° particles are comparable with those in MMSS. Based on particle size distribution, 15% bentonite mixtures are recommended for use in environments where S° oxidation is rapid or for strongly leaching environments. In dry (e.g. inland

Otago) and/or cool (e.g. coastal Otago) environments mixtures containing 20.25% bentonite are recommended.

S°/sodium bentonite prills mix well with other granulated fertilisers. In 1983, the manufacturing costs were estimated to be $55/tonne (Evason and Owers 1983). Allowing for 25% inflation 1985 costs could be expected to be approximately $69/tonne.

The effectiveness of imported Canadian S°/bentonite products has to be predicted from preliminary laboratory analyses of experimental batch samples (Table 2) since field data are not available. At best they most closely compare with granulated ground S° and would appear to be more suited to North Island conditions than Otago/Southland.

Granulated ground sulphur fertiliser is produced from granulating a mixture of 90% ground screened agricultural S° and 10% sodium bentonite clay. On dispersion of the prills in water the S° particles released are the same as those mixed into the prills during granulation.

The S° particle size distribution depends on the degree of grinding, but that recorded in experimental batches was intermediate between screened agricultural S° and MMSS (on average 42% of S° particles were < 150 microns — Table 2).

As could be expected this allows a moderately slow but sustained release of SO_4-S. From Otago experience the best use to date has been in dry inland (non leaching) environments where a slow steady release has benefitted the production of indigenous legumes such as haresfoot trefoil *(Trifolium arvense L.)* on unimproved pastures (Boswell, unpublished), and also improved legumes (overdrilled) in Central Otago producing at moderate levels (D.Brash pers. comm.). However, granulated ground S° also has potential as a slow release fertiliser for moist warm areas and strongly leaching environments.

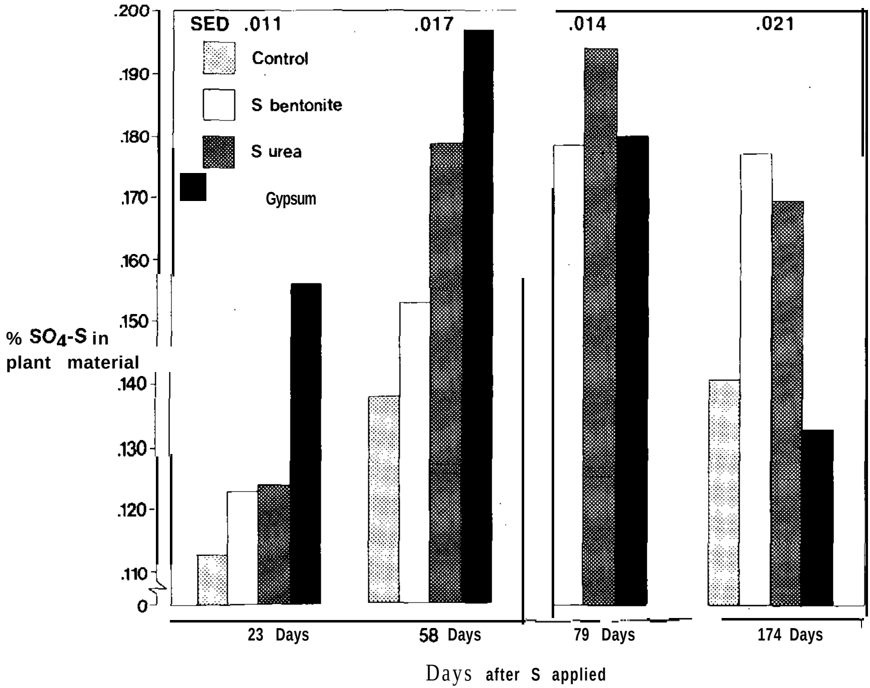

FIGURE 3: Effects of S-Impregnated Urea, S°/Sodium Bentonite and Gypsum on Plant SO_4-S Levels (Invermay Site, Spring Application).

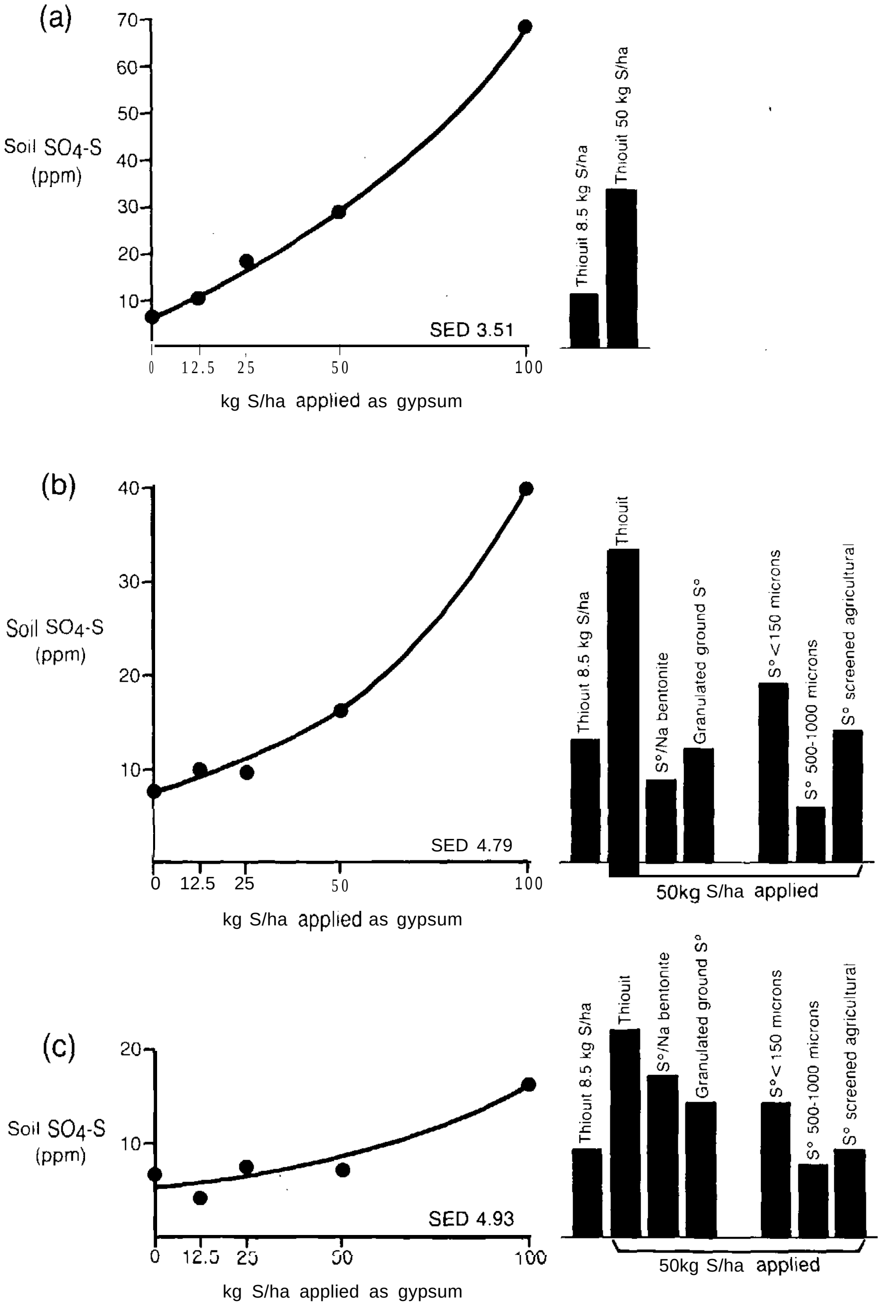

FIGURE 4: Comparison of 'Thiovit' S° Applied in December 1984 at 8.5 and 50kg S/ha with Gypsum (SO^{4}-S) and Other S Fertilisers on Soil SO^{4}-S Levels.

(a) Invermay Site 67 days after application.
(b) Omarama 91 days after application.
(c) Omarama 206 days after application.

Sulphur impregnated urea is made by prilling a molten homogenous mixture of S° and urea. It contains finely divided S° (Table 2) integrated into urea prills (20%S°, 36% N). The S° is released from the prills on wetting, when urea is dissolved, and some S° is rapidly oxidised to SO^4-S.

At Invermay peak concentration of plant SO^4-S occurred 50-70 days after fertiliser application (Fig. 3), although elevated SO^4-S levels in soil and plant tissue has persisted for at least 12 months. In warmer, moisture environments this rate of oxidation would be expected to be more rapid. It should for example offer only a slightly delayed release of SO^4-S in association with an immediate nitrogen supply for early spring production where both S and N are limiting.

'Thiovit' micronised wettable powder consists of ultra-finely divided S° particles (5-8 microns) mixed with 15% clay. It represents a specialist product which is applied as an emulsion in water. Originally it was used as a fungicide at a recommended rate of 10 kg/ha of mixture (8.5 kg S/ha), but has subsequently found favour as S° fertiliser for crops and even pastures in the United Kingdom — generally at the same rate of S.

It is very rapidly oxidised and limited Invermay experience indicates it quickly raises soil SO^4-S levels to a similar extent as gypsum SO^4-S does (Fig. 4a). About three months after fertiliser application at Omarama (Fig. 4b) 'Thiovit' produced greater soil SO^4-S levels than gypsum. Soil SO^4-S levels were maintained longer with'Thiovit' than gypsum (e.g. 206 days after fertiliser application Fig. 4c). From figures 4b and 4c it is clear that the huge difference between 'Thiovit' and the other alternative S° fertilisers diminished rapidly as the season progressed. No lucerne was harvested in the intervening period between the two sampling occasions. It is likely that some of the reduction in high soil SO^4-S levels occurred by transfer into standing plant tissue and into the soil organic matter.

On the basis of relative fertiliser S costs, the use of 'Thiovit'in New Zealand can be expected to be restricted to high value crops which require immediate short term supplies of SO^4-S and possibly where there is additional benefit from fungicidal effect. Its acceptance will be determined by how competitively it can be costed.

Changes in Circumstances Affecting New Zealand S Fertilisers

Apart from the agronomic properties of S fertilisers there are two other factors which will influence the choices of S fertilisers available to New Zealand farmers in the near future. The first concerns the redefinition of safety regulations concerning the handling of high analysis S° fertilisers. If regulations designed for safe aerial application of screened S”, were applied to newer safe prilled fertilisers they would defeat the purposes of developing the fertilisers. Dr Peter Rothbaum of Chemistry Division DSIR, who with Mr Bill Owers did the development work on S°/sodium bentonite prills, is drafting new guideline regulations. It is expected that the current restrictions will be lifted from prill materials which meet strength and conductivity standards. They will probably remain for screened agricultural S”.

The second factor is the extent to which New Zealand sulphur deposits will be commercially exploited. Feasibility studies for commercial mining and refining operations are being conducted. Although refined materials are likely to be only 70% S compared with almost pure imported S”, the S may still be useful for incorporation into either MMSS, molten S prepared S°/sodium bentonite prills, or without further grinding into granulated S prills. In addition the raw pumice contains 10-20% S° which, after grinding to pass a 6mm screen, has an S° particle size distribution somewhat finer than can be expected from screened S°. With increasing costs of importing and transporting S° the raw pumice material could be an alternative for screened agricultural S° in an area within 100-150km of its source at Rotokaua.

CONCLUSIONS

The comparative availability of SO^4-S from S° fertilisers is dependent on the S° particle size and the physical environment. Most rapid oxidation occurs with fine S° particles in warm moist conditions.

The efficacy of different fertilisers depends on the farming system. For horticulture or cropping systems only the most rapidly oxidised S° fertilisers could be considered possible alternatives to SO^4-S fertilisers. Pastures are likely to require a steadier, more prolonged supply of SO^4-S. Where leaching losses occur the choice of S° fertiliser should be a slow release material.

The oxidation characteristics of S° fertilisers either available in New Zealand or soon to become available, are summarised for two broad environmental groupings in Table 4.

TABLE 4: Expected Rates of Oxidation of S°.

(a) Cool Coastal Otago (e.g. Invermay), Dry Inland Southern South Island (e.g. Waitaki Basin, Central Otago)[1].

Very Slow	Slow	Moderate	Rapid
Screened S° Dry mixed super S° particles > 250 microns	Granulated ground S° Imported Canadian S°/bentonite	MMSS S°/Na-bentonite (15% bentonite)	Thiovit S impregnated urea S°/Na-bentonite (20-25% bentonite)

(b) Warm moist environments (Nelson, Westland, Waikato)[2].

Very Slow	Slow	Moderate	Rapid
S° particle > 500 microns	Screened S° Dry mixed super	Granulated ground S° S° particles < 250 microns Imported Canadian S° bentonite	Thiovit S impregnated urea S°/Na bentonite (15% bentonite) MMSS

[1] Boswell and Swanney (1984, unpublished)

[2] Williams et al. (1984), W. Saunders (pers. comm.).

Acknowledgments

Soil Testing Laboratory, Invermay, for soil SO^4-S measurements

References

Boswell, C.C.; Swanney, B. 1984. N.Z. *Soil* News 32: 198.
Evason, W.; Owers, W.R. 1983. *Proc.* 19th Tech. *Conf.* N.Z. *Fert. Manufrs'* Res. Ass. I: 353 365.
Ludecke, T.E. 1965. *Proc.* N.Z. *Grassld* Ass. 27: 129-137.
McIntosh, P.D.; Sinclair, A.G. 1983. Ibid 44: 172-178.
Sinclair, A.G.; Boswell, C.C. 1983. *Proc.* 19th Tech. *Conf.* N.Z. *Fert. Manufrs' Res Ass. 1:* 377-389.
Williams, P.H.; Trought, M.C.T.; Morgan, C.G.T. 1984. *MAF Agricultural* Research Division Annual *Report 1983/84* pp. 214-215