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**AN INVESTIGATION OF SOME FACTORS INFLUENCING THE RATE  
OF OXIDATION OF ELEMENTAL SULPHUR FERTILIZERS**

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the requirements for the degree of  
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## ABSTRACT

Methodologies for measuring the particle size of  $S^0$  in pure and compound fertilizers (sulphurized superphosphates (SSP), reactive phosphate rocks (RPR) and partially acidulated phosphate rock (PAPR)) and for determining the rate at which  $S^0$  in these materials oxidises in soils were evaluated and improved. Sample dispersion in 10% HCl followed by wet sieving was the most successful method for sizing  $S^0$  in SSP, RPR and PAPR based fertilizers.  $S^0$ /bentonite fertilizers, however, were more easily dispersed in water than in acid.

Acetone extraction (40 g:200 ml acetone, using a 16 h shaking period) and determination of  $S^0$  in the extract proved to be a suitable method for measuring amounts of  $S^0$  in finely ground fertilizers and soils at concentrations above  $5 \mu\text{g S g}^{-1}$  soil and below  $200 \mu\text{g S ml}^{-1}$  acetone.

The rate of  $S^0$  oxidation in soil was determined by regularly measuring residual amounts of  $S^0$ . The influence of soil type and fertilizer history on the potential of soils to oxidise  $S^0$  was examined in incubation studies. On average, soils that had previously received  $S^0$  applications had higher initial rhodanese enzyme activities (RA) and higher  $S^0$  oxidation rates but there was no simple relationship between fertilizer history or RA and initial  $S^0$  oxidation rate.

Different sources of  $S^0$ , namely Rotokawa  $S^0$  (geothermal  $S^0$ ), dark  $S^0$ , Damman  $S^0$ , and agricultural grade  $S^0$  had similar oxidation rates per unit surface area. Granules or prills oxidised slowly in incubated soil because they did not disintegrate when placed in soil and had small specific surface area.

On average, the oxidation rate of  $S^0$  was increased when mixed or granulated with reactive phosphate rocks and incorporated in soil but this effect was not consistently reproducible. Further incubations of  $S^0$  in the presence of various combinations,  $\text{CaHPO}_4$ ,  $\text{CaCl}_2$  and  $\text{CaCO}_3$ , demonstrated that the presence of  $\text{CaHPO}_4$  and  $\text{CaCO}_3$  could elevate  $S^0$  oxidation rates.

Granulation of RPR and PAPR with  $S^0$  did not significantly increase ( $p > 0.05$ ) the oxidation rate of  $S^0$  surface applied to undisturbed pasture soils (glasshouse and field

trials). Under surface application conditions granulated  $S^0$  had similar oxidation rates to finely divided  $S^0$  forms.

An iterative computer program was developed to calculate specific oxidation rates ( $K$ ,  $\mu\text{g } S^0 \text{ cm}^{-2} \text{ day}^{-1}$ ) from the amounts of acetone extractable  $S^0$  remaining in soils at different times. On average,  $K$  for  $<150 \text{ } S^0 \text{ }\mu\text{m}$  was significantly lower ( $p < 0.05$ ) when surface applied to undisturbed soil cores than when incorporated into incubated soils.

Specific oxidation rates of different particle sizes ( $<150$ ,  $150\text{-}250$  and  $250\text{-}500 \text{ }\mu\text{m}$ ) of surface applied  $S^0$  were similar (ranging from  $11\text{-}19 \text{ }\mu\text{g } S^0 \text{ cm}^{-2} \text{ day}^{-1}$ ) but were different ( $P < 0.05$ ) for the two soil types used in glasshouse trials (means of  $17$  and  $13 \text{ }\mu\text{g } S^0 \text{ cm}^{-2} \text{ day}^{-1}$  for Ramiha and Tokomaru soil, respectively). Corrections for the effects of soil moisture on oxidation rates provided evidence that all  $S^0$  could have similar maximum potential  $K$  values ( $K_{\text{max}} = 18 \text{ }\mu\text{g } S \text{ cm}^{-2} \text{ day}^{-1}$ ) in both soils. This suggested, with other evidence from the literature, that  $S^0$  oxidation in soil could be effectively modelled by knowing  $S^0$  particle size and the effects of soil moisture and temperature on  $S^0$  oxidation.

A  $S^0$  oxidation simulation model was constructed using a value for  $K_{\text{max}}$  determined in the glasshouse trials. Within experimental error, the simulation model predicted  $S^0$  oxidation in field soil well (explaining between  $76$  and  $97\%$  of data variance at  $3$  field sites) and provides a useful basis for designing future research projects.

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