SOIL SULFUR POOLS UTILISED BY PLANTS AND MEASURED BY CHEMICAL EXTRACTANTS

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PREFACE

I certify that the substance of this thesis has not already been submitted for any degree and is not currently being submitted for any other degree or qualification.

I certify that any help received in preparing this thesis, and all sources used, have been acknowledged in this thesis.

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ABSTRACT

Soil sulfur (S) testing has met with variable success and there is no agreement as to which extractant best defines the S suppling capacity of soils. This study aimed to develop a soil S test that includes a measure of the sulfate in solution, an estimate of adsorbed sulfate which is available for plant uptake and an estimate of potentially mineralisable organic S which is available for plant uptake. Three separate experiments were undertaken in which a range of extractants were evaluated to predict S status and to investigate the sources of S for plants and the soil pools extracted by the various extractants.

The first series of experiments consisted of a field calibration study, a field verification study, and a pot study using ^{35}S labelled soil. The calibration study was undertaken on soil samples taken from the 0-7.5 cm horizon of soils from 18 field trials on the Northwest Slopes of New South Wales. The extractants used were water 0.01 M monocalcium phosphate (MCP), 0.5 M $NaHCO_3$, 0.25 M KCl heated for 3 h at 100, 80, 40 or 25°C (KCl-100, -80, -40, -25), and at 25°C for 16 h (KCl-16hr). The ability of eight soil S tests to estimate S availability was examined. The concentration of S extracted increased in the order KCl-25°C < MCP = KCl-40 = KCl-16 hr < H_2O < KCl-80°C < KCl-100°C < $NaHCO_3$. The 0.25 M KCl heated at 40°C (KCl-40) extraction method gave the best relationship between extractable S and the % maximum dry matter yield of pasture with an r^2 value of 0.73. A r^2 value of only 0.47 was recorded with the MCP extract.

The verification study was undertaken on soil samples from the 30 pasture trials throughout southern Australia. These soil samples were collected at 0-7.5 cm depth for the sites within New South Wales and 0-10 cm for the other States. The MCP and KCl-40 methods were used in the verification study with the KCl-40 extractant remaining superior.

In the pot study, a ^{35}S labelled Aquic Haplustalf soil was used in a pot experiment with rice. The use of ^{35}S allowed calculation of the specific activity (SA) of the soil S pools and the plant S. The ratio of the SA of the plant to the SA of the soil extractants, termed the specific activity ratio (SAR), was used to indicate whether the plant was accessing S from similar pool/s as removed by the extractants. Six extraction methods were evaluated in this study. These were water, MCP, $NaHCO_3$, KCl-100, KCl-80 and KCl-40. The fraction of S removed by the various extractants, from unfertilised and fertilised soil, was evaluated by measuring the amount of HI-reducible S removed by the extractants. The lowest concentration of S was found in the H_2O and MCP extracts, whilst the $NaHCO_3$ extractant had the highest S concentration. The amount of S removed from the HI-S fraction was highest in the $NaHCO_3$ extract. The amount of S removed from the HI-reducible S did not differ significantly between the water KCl-40 and MCP extractants in either the unfertilised or

fertilised soils. The data on specific activity ratio (SAR), in both non-flooded and flooded soils, showed that the lowest SAR value was recorded in the KCl-40 treatment and this was closest to 1, indicating that the KCl-40 extract and the plant were drawing S from similar pools.

A second experiment was conducted in a glasshouse with ryegrass (*Lolium perenne* L.). The experiment was a factorial design consisting of 2 soils (an Aquic Haplustalf of granitic origin and an Ultic Haplustalf of basaltic origin) and 2 rates of S fertiliser (0 and 17.7 mg kg^{-1} soil, equivalent to 0 and 30 kg S ha^{-1}), with 3 replicates. The reverse dilution ^{35}S labelling technique was used. Ryegrass was harvested at 50 days and the dry matter yield and S content of the ryegrass tops and roots were measured. Soil samples from the entire pot were analysed for S and ^{35}S. The four test extractants were MCP, KCl-40, KCl-100 and Bray-1. Soils were first extracted with one of the four extractants, centrifuged and the supernatant was filtered, and S in the supernatant was measured by ICP. A 10 mL sample of each supernatant was treated with activated charcoal, and SO_4^{2-}-S determined by turbidimetry. The soil remaining after the first extraction was used to determine the HI-S remaining and also re-extracted with MCP; the S contained in these fractions was determined by ICP-AES. This sequence of extractions allowed the estimation of the following soil S pools: a) SO_4-S, b) HI-reducible S, c) the loss of HI-S, d) Soluble organic S, e) Mineralised sulfate and f) Original sulfate.

The concentration of S in the various extractants, as measured by ICP and turbidimetry increased in the order Bray<MCP<KCl-40<KCl-100 in the Uralla granitic soil. By contrast, the concentration of S in these same pools increased in the order Bray<KCl-40<MCP<KCl-100 in the Walcha basaltic soil. A difference in the S concentration between the MCP and KCl-40 extracts was recorded between the two soils due to the relative size of the adsorbed S and ester-S pools in these soils. In the Uralla soil, which had a lower capacity to adsorb sulfate than the Walcha soil, the KCl-40 extract removed the solution and adsorbed sulfate pool and some portion of labile HI-reducible S pool, while the MCP extracted the soil solution and adsorbed sulfate pool and a lower proportion of the labile HI-S pool than from the Walcha soil. The recovery of ^{35}S in these fractions for these two extracts confirmed this result.

Most of the ^{35}S added was recovered in the sulfate pool, with less that 10% of the ^{35}S recovered in the non-sulfate pool. Data on the specific activity (SA) of the ICP-S fraction of the four test extractants showed that the highest SA was recorded in the sulfate pool in both soils, indicating that the ^{35}S in the sulfate pool was more highly labelled than the ^{35}S in the other pools. The data on the specific activity ratio (SAR) showed that the SAR was lower in the sulfate pool than that in the other pools in both soils and S treatments prior to planting. Within the ICP-S and sulfate pools, the KCl-40 extract had the SAR closest to 1 in the treatment with no added S. This again indicated that the KCl-40 was removing S from similar pools to the plant and that the plant was utilising S from the soil solution and adsorbed sulfate pools and some portion of the highly labile HI-S pool. The SAR of the ICP-S and sulfate pools in the +S treatment was greater than 1 in all extractants prior to planting in both the Uralla and Walcha soils. None of the extractants were capable of assessing the soil S pools used by the plant in the +S treatment because of the greater dilution of ^{35}S resulting from the addition of S fertiliser.

The third experiment examined the ability of S extractants to predict S supply to crops with differing S demand rates and growth periods and was conducted at the same time as the ryegrass experiment. Radish (*Raphanus sativus* L.) and corn (*Zea may* L.) were grown and harvested at 23 days and 50 days respectively. The results of this experiment showed that the application of S fertiliser increased the yield, S uptake and S concentration of radish and corn in both the Uralla and Walcha soils. The amount of S extracted by the extractants followed a similar pattern to that in the ryegrass experiment. Data on the specific activity ratio (SAR) showed that all extractants had a higher SAR in the +S than in the -S treatment in both crops and soils before planting, due to the dilution of ^{35}S in this pool by sulfate from the S fertiliser. Conversely, the SAR was higher for all extractants in the -S than in the +S treatment after cropping. The SAR for the KCl-40 extract determined before planting was closest to 1 in both crops in the -S treatment in both soils and generally closest to 1 in the +S treatment after cropping which confirmed the earlier finding. The KCl-40 extraction was observed to underestimate the size of the available S pool taken up by radish in the Walcha soil. In contrast, it tended to overestimate the S pool taken up by ryegrass in the Uralla soil. The KCl-100 extract also had a high correlation between the estimated amount of S lost from the extracted pools and S uptake by all crops. However, the KCl-100 extract generally overestimated S uptake by all crops. The MCP and Bray extracts had a high SAR (higher than 1) and a low correlation between the estimated amount of S lost from the soil S pools and S uptake by all crops. These two extractants tended to underestimate S supply. This experiment showed that the KCl-40 extract generally performed well for all crops and soils tested.

The series of experiments have demonstrated that by understanding the pool size and turnover rates of soil S pools it has been possible to develop an appropriate soil extractant to predict soil S supply.

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