



Sulphur fractionation in calcareous soils and bioavailability to plants

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Abstract

Sulphur fractionation and availability to plants are poorly understood in calcareous soils. Sixty-four calcareous soils containing varying amounts of CaCO₃ were collected from ten provinces in China and their S fractions determined. Organic S was the predominant fraction of S, accounting for on average 77% of the soil total S. The amounts of adsorbed sulphate were found to be negligible. 1 M HCl extracted substantially more sulphate than either 0.01 M CaCl₂ or 0.016 M KH₂PO₄, indicating the existence of water-insoluble but acid-soluble sulphate, probably in the form of sulphate co-precipitated with CaCO₃. The concentrations of water-insoluble sulphate correlated positively with the contents of CaCO₃ and accounted for 0.03–40.3% (mean 11.7%) of soil total S. To test the bioavailability of water-insoluble sulphate, a sulphate-CaCO₃ co-precipitate labelled with ³⁵S was prepared and added to a calcareous soil in a pot experiment with either NH₄⁺ or NO₃⁻ as the N source. In 29 days, wheat plants took up 10.6% and 3.0% of the ³⁵S added to the soil in the NH₄⁺ and NO₃⁻ treatments, respectively. At the end of the pot experiment, the decrease of water-insoluble, acid-soluble, sulphate was more apparent in the NH₄⁺ than in the NO₃⁻ treatment. The results indicate that sulphate co-precipitated with CaCO₃ in calcareous soils may become partly available for plant uptake, depending on rhizosphere pH, if the field precipitate is similar to the laboratory prepared sample studied.

Introduction

Sulphur (S) deficiency in crops has become increasingly widespread world-wide (Blair, 2002; Zhao et al., 2002). This is due to a combination of factors such as reduced atmospheric inputs of S, increased crop yields, and a shift in the use of S-containing fertilisers to S-free or low S fertilisers. During late 1960s and early 1970s when SO₂ emissions peaked, deposition of S from the atmosphere reached 70 kg S ha⁻¹ or more in the UK (McGrath et al., 2002). However, current inputs of S from atmospheric deposition are less than 10 kg S ha⁻¹ in most areas of western Europe, which is smaller than the amounts of S required by most crops (McGrath et al., 2002). In areas with low inputs of S from the atmosphere or fertilisers, soil S supply becomes more critical for crop S nutrition.

It is therefore important that the factors controlling the bioavailability of S in soil are well understood in order to predict the occurrence of S deficiency and to recommend appropriate S fertilisation.

Sulphate is the form of S that is taken up by plant roots, although the sulphate fraction generally accounts for less than 5% of the total S in soil. Sulphate is present in soil in either water-soluble or adsorbed form; the latter depends on soil characteristics such as the contents of iron oxide/hydroxide and pH (Curtin and Syers, 1990; Syers et al., 1987). Various methods have been proposed to evaluate the amounts of soil S available for plant uptake (Anderson et al., 1992; Blair et al., 1991; Ensminger, 1954; Goh and Pamidi, 2003; Scott, 1981; Watkinson and Kear, 1996; Zhao and McGrath, 1994). Most of the methods for soil S testing involve extraction of soil with a weak salt solution, e.g. CaCl₂, KCl, Ca(H₂PO₄)₂ or KH₂PO₄. Phosphate-containing ex-

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Table 1. Range, mean and median values of basic soil properties in 64 calcareous soils from China

	Organic C (g kg ⁻¹)	CaCO ₃ (g kg ⁻¹)	Total N (g kg ⁻¹)	pH (in water)	Total S (mg kg ⁻¹)	Soil organic S (mg kg ⁻¹)
Minimum	0.6	0.8	0.31	7.25	63.5	58.8
Maximum	64.0	137.7	4.31	8.70	831.4	565.6
Mean	14.8	51.5	1.40	8.09	291.5	215.1
Median	11.2	42.0	1.17	8.12	253.2	187.8

tractants are used to extract both water-soluble and adsorbed sulphate, whereas Cl-based extractants extract mainly water-soluble sulphate. A small portion of organic S may also be extracted, which can become available to plants through rapid mineralisation (Blair et al., 1991; Goh and Pamidi, 2003; Watkinson and Kear, 1996; Zhao and McGrath, 1994). However, in calcareous soils, sulphate may also be present in the insoluble form due to co-precipitation with CaCO₃. It has been shown that the sulphate co-precipitated with CaCO₃ accounted for up to for 93% of the total S in some Australian calcareous soils (Williams and Steinbergs, 1962), and up to 42% of the total S in some Canadian soils (Roberts and Bettany, 1985). Despite the quantitative significance of insoluble sulphate in calcareous soils, there has been little research on the bioavailability of the sulphate in this fraction to plants. An early study by Williams and Steinbergs (1964) showed that insoluble SO₄ could be released from the CaCO₃ co-precipitate by reaction of the CaCO₃ with exchangeable H⁺ in soil. This suggests that soil pH, in particular rhizosphere pH, would control the bioavailability of insoluble sulphate in calcareous soils.

The objectives of this study were to determine the size of the insoluble sulphate pool in a range of calcareous soils, and to assess the bioavailability of SO₄²⁻ co-precipitated with CaCO₃ to plants in a calcareous soil as influenced by the source of N supplied to the crop. Two sources of N, NH₄⁺ and NO₃⁻, were included in order to manipulate soil and rhizosphere pH (Marschner, 1995).

Materials and methods

Soils used and sulphur fractionation

Sixty four calcareous soils were collected from ten provinces of China. These soils were developed from the parent materials: loess ($n = 40$), limestone ($n =$

16) or calcareous purple sandstone ($n = 8$). The land management was either arable or grassland. Table 1 shows the ranges and means of organic C, total N, total S, CaCO₃ and pH in the soils. Soils were air-dried and passed through a 2-mm sieve before analysis. For the analysis of total C, N and S, soils were ground to < 0.15 mm. Total C and total N were determined using a LECO CNS-2000 Elemental Combustion Analyzer (LECO Corporation, Michigan, USA). Total S was determined using an inductively coupled plasma atomic emission spectrometer (ICP-AES; Fisons ARL simultaneous multichannel model 3400) after soil was digested with HClO₄/HNO₃ (Zhao et al., 1994). Soil organic S was calculated from the difference between soil total S and the sum of soluble and insoluble sulphate; the latter were determined with the methods described below. The CaCO₃ content was determined using a water-filled calcimeter (Eijkelkamp, South Africa). Organic C was calculated from the difference between total and inorganic C. Soil pH was measured with a glass electrode in a suspension of 1: 2.5 of soil to water.

Three extractants were used to extract different fractions of soil S: 0.01 M CaCl₂, 0.016 M KH₂PO₄ and 1 M HCl. All extractions were carried out under the same conditions, i.e. 1:5 soil to solution ratio, shaking for 1 h at room temperature (20 ± 2 °C), centrifugation at 8000 *g* for 10 min and filtration through Whatman No. 42 filter paper. Total and inorganic S (sulphate) in the CaCl₂ and KH₂PO₄ extracts were determined using ICP-AES and ion chromatography (Dionex DX 500, Dionex Corporation, Sunnyvale, California, USA), respectively, and the difference between the total and sulphate-S was taken as a measurement of organic S extracted by the two extractants (Zhao and McGrath, 1994). Inorganic S in the 1 M HCl extracts could not be measured directly by ion chromatography because of the strong acidity. In order to remove soluble organic matter and the associated organic S from the 1 M HCl extracts, 100 mg S-free activated charcoal was added to 10 mL of the HCl ex-

tracts and shaken for 15 min (Wu et al., 1994). The extract was then centrifuged at 8000 g for 10 min and filtered through Whatman No. 42 filter paper. Sulphur concentrations in the 1 M HCl extract before and after the charcoal treatment were determined by ICP-AES, using the wavelength of 180.73 nm. Quantification of S at this wavelength was found to be subject to a small interference of Ca in the solution, which resulted in an overestimation of S. This interference became significant only when the concentration of Ca in the extract exceeded 1000 mg L^{-1} , which was common in the 1 M HCl extracts of calcareous soils. The interference of Ca on S determination was removed by the use of a correction factor derived from running a series of Ca standards. Organic S extracted by 1 M HCl was calculated from the difference in the S concentration between before and after the charcoal treatment.

Pot experiment

This experiment was carried out to investigate the bioavailability of sulphate which was co-precipitated with $CaCO_3$. The sulphate- $CaCO_3$ co-precipitate was prepared according to the method described by Williams and Steinbergs (1962), and labelled with radioactive $^{35}SO_4^{2-}$. 19.25 g $Ca(OH)_2$ (analytical reagent grade) was dissolved in 5000 mL deionised water to form a $Ca(OH)_2$ saturated solution. CO_2 (99.9%) was passed through the $Ca(OH)_2$ saturated solution for 24 h to form $CaCO_3$. A subsample of 500 mL was then taken, and 10 mL K_2SO_4 solution containing 250 mg S L^{-1} and 450 kBq $^{35}SO_4^{2-}$ was added while being stirred continuously. The solution was boiled for 5 min to precipitate $CaCO_3$, and left to stand for 6 h, before being filtered through a Whatman No. 42 filter paper. The insoluble sulphate- $CaCO_3$ co-precipitate was washed with deionised water until the concentration of SO_4^{2-} in the leachate was below the detection limit of the turbidity test with 1 M $BaCl_2$. This compound was dried at 60 °C for 15 h. Analysis showed that it contained 41% Ca, 326 mg kg^{-1} S and a radioactivity of 28.6 kBq g^{-1} . Water extractable SO_4^{2-} in the compound was 5.4 mg S kg^{-1} and water extractable radioactivity 0.38 kBq g^{-1} , accounting for 1.7 and 1.4% of the total S and total radioactivity, respectively.

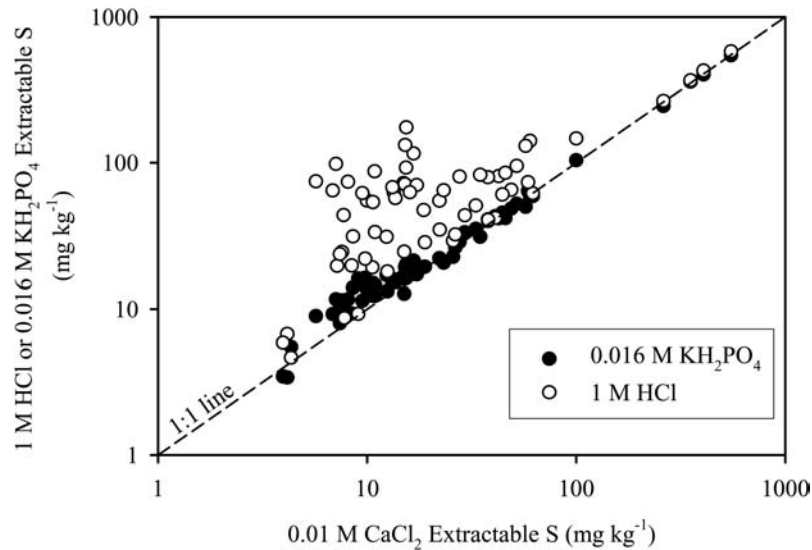
Wheat (*Triticum aestivum* cv. Hereward) was grown in a pot experiment using a calcareous soil collected from an arable field in Dorset, southern England. The soil was air-dried and sieved to < 2 mm. The soil was a clay loam, and contained 13.4 g kg^{-1}

organic C, 511 g kg^{-1} $CaCO_3$, 0.53 g kg^{-1} total S and 7.6 mg kg^{-1} KH_2PO_4 -extractable S. The soil pH (in water) was 7.8. Portions of 250 g air-dried soil were weighed into 12 cm plastic pots. Four treatments were included: with or without the addition of the ^{35}S labelled co-precipitate of sulphate- $CaCO_3$, in combination with two forms of N fertilisers (NO_3^- -N or NH_4^+ -N). Each treatment was replicated in 4 pots. In the treatment with the addition of sulphate- $CaCO_3$, 0.1 g ^{35}S labelled sulphate- $CaCO_3$ was added to the soil in each pot and mixed thoroughly, equivalent to an addition of 0.13 mg S kg^{-1} soil. A solution of NH_4Cl or $NaNO_3$ containing 40 mg N was added to each pot and mixed thoroughly. All pots received a basal dressing of 25 mg P and 31.5 mg K as KH_2PO_4 , 2.5 mg Mn as $MnCl_2$, 0.25 mg Cu as $CuCl_2 \cdot 2H_2O$, 0.5 mg Zn as $ZnCl_2$, 12.5 mg Mg as $MgCl_2 \cdot 6H_2O$; and 0.25 mg B as H_3BO_3 . These were added to the soil as solution and mixed thoroughly. Soil moisture content was brought up to 60% of the water holding capacity (WHC) with deionised water. Fifteen seeds of winter wheat were sown to each pot, and thinned to six seedlings after germination. Soil moisture content was maintained at approximately 60% WHC by frequently weighing and adding water during the experiment. All pots were arranged randomly inside a controlled environment growth room, with the following conditions: day/night duration 14 h/10 h, light intensity 350 $\mu mol m^{-2} s^{-1}$, day/night temperature 20 °C/16 °C and relative humidity 60–70%. Twenty nine days after germination, plants were harvested by cutting the shoots at the soil surface. Roots were separated from the soil, and washed. Shoots and roots were rinsed with deionised water, and dried at 80 °C for 24 h before the dry weights were measured. A subsample of fresh soil was taken from each pot for the determination of extractable S and pH.

Plant materials were ground with mortar and pestle. Plant samples (0.1–0.5 g) were weighed into a 250 mL conical flask, and digested with 15 mL of concentrated HNO_3 at 100 °C to near dryness. After cooling, 5 mL of H_2O_2 were added to each flask to help decompose organic matter. The digestion procedure was repeated once again to obtain a clear digest solution. The digest was made up to 10 mL with deionised water. Total S in the digest was determined by ICP-AES. An aliquot of the digest was used for the determination of the radioactivity of ^{35}S using a liquid scintillation counter (Packard Tri-Carb 2500TR, CT, USA).

Table 2. Range, mean and median values of extractable S in 64 calcareous soils from China

	1 M HCl Extractable S (mg kg ⁻¹)			0.016 M KH ₂ PO ₄ Extractable S (mg kg ⁻¹)			0.01 M CaCl ₂ Extractable S (mg kg ⁻¹)		
	Total S	SO ₄ -S	Organic S	Total S	SO ₄ -S	Organic S	Total S	SO ₄ -S	Organic S
Minimum	4.7	3.7	0.5	3.4	3.2	0.1	4.0	3.6	0.1
Maximum	580.6	580.0	27.6	545.9	533.7	51.4	550.0	495.6	54.5
Mean	81.1	72.4	9.8	46.8	42.8	4.8	45.7	38.8	7.0
Median	61.9	51.4	7.7	17.1	14.3	3.2	15.4	12.8	3.2

Figure 1. Relationships between 1 M HCl, 0.016 M KH₂PO₄ and 0.01 M CaCl₂ extractable S in 64 calcareous soils.

Soil was extracted with 0.01 M CaCl₂ and 1 M HCl as described above. SO₄-S in the 0.01 M CaCl₂ extracts was determined by ion chromatography, and in the 1 M HCl extracts by ICP-AES after removing dissolved organic matter by activated carbon. Soil pH was measured in 1:2.5 soil to water suspension.

Analysis of variance was performed using Genstat 5 statistical software (Numerical Algorithms Group 1998). Least significant difference was used to compare treatment means.

Results and discussion

Extractable S and S fractions in calcareous soils

The 64 soils collected in China varied widely in the concentrations of organic C, total N, and CaCO₃ (Table 1). Soil pH was in the range 7.3 and 8.7. Soil total and organic S ranged from 64 to 831 mg kg⁻¹, and from 59 to 566 mg kg⁻¹, respectively (Table 1). Organic S accounted for 23.7–98.8% (mean 77.0%)

of the total S in the 64 calcareous soils. Both 0.01 M CaCl₂ and 0.016 M KH₂PO₄ extracted very similar amounts of S (Table 2 and Figure 1), indicating that there was little adsorbed sulphate in the calcareous soils. This is not surprising because adsorption of sulphate usually occurs in acidic soils (Curtin and Syers, 1990). The amounts of 0.01 M CaCl₂ and 0.016 M KH₂PO₄ extractable S represented 1.3–70% (mean 12.2%) and 1.4–69% (mean 7.7%), respectively, of the soil total S. Both extractants extracted small amounts of soluble organic S, which on average accounted for 19 and 16% of the total extracted S for 0.01 M CaCl₂ and 0.016 M KH₂PO₄, respectively. Zhao and McGrath (1994) showed that soluble organic S accounted for approximately 30–60% of total S extracted with 0.016 M KH₂PO₄ in ten arable soils collected in Britain. The lower percentages of soluble organic S found in the present study may be because the total concentrations of S extracted by 0.01 M CaCl₂ and 0.016 M KH₂PO₄ were substantially larger than those of the British arable soils.

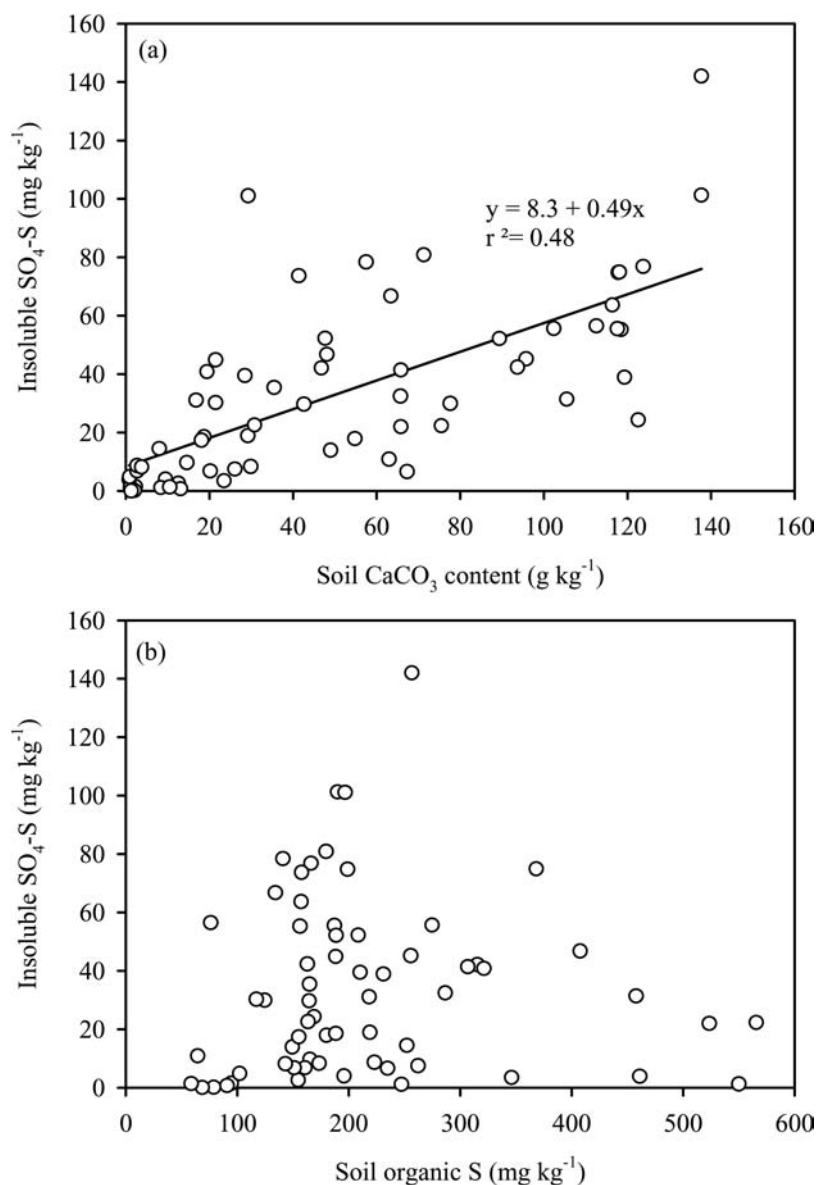


Figure 2. Relationships between water-insoluble, acid-soluble sulphate and the content of CaCO_3 (a) or soil organic S (b) in 64 calcareous soils.

Compared to CaCl_2 and KH_2PO_4 , 1 M HCl extracted significantly more S from the soils (Table 2 and Figure 1), accounting for 4.3–73% (mean 25%) of the soil total S. Because the amounts of soluble organic S extracted by 1 M HCl were broadly similar to the amounts extracted by either 0.01 M CaCl_2 or 0.016 M KH_2PO_4 (Table 2), the larger concentrations of HCl extractable S indicated the existence of water-insoluble but acid-soluble sulphate. This portion of sulphate is likely to be present as a co-precipitate with

CaCO_3 (Williams and Steinbergs, 1962). The water-insoluble sulphate, calculated from the difference of 1 M HCl and 0.01 M CaCl_2 extractable sulphate (Roberts and Bettany, 1985; Williams and Steinbergs, 1962), varied from 0.02 to 142 mg S kg^{-1} soil, accounting for 0.03–40.3% (mean 11.7%) of the soil total S. Furthermore, there was a highly significant correlation ($r = 0.69$, $P < 0.001$) between water-insoluble sulphate and CaCO_3 content (Figure 2a). In contrast, there was no correlation ($r = 0.016$,

Table 3. Effects of form of N and sulphate-CaCO₃ co-precipitate on plant growth, S uptake, specific activity of plant S, recovery of ³⁵S, and soil pH at the end of the pot experiment (mean ± SE)

Sulphate-CaCO ₃ co-precipitate	N form	Shoot dry weight (mg pot ⁻¹)	Root dry weight (mg pot ⁻¹)	Plant S uptake (mg pot ⁻¹)	Specific activity (Bq mg ⁻¹ S)	Recovery of ³⁵ S by plants (%)	Soil pH at the end of experiment
+	NH ₄ -N	725 ± 53a	462 ± 18a	2.33 ± 0.23a	121.6 ± 22.7a	10.6 ± 1.9a	7.92 ± 0.01b
	NO ₃ -N	735 ± 40a	487 ± 35a	2.37 ± 0.13a	34.3 ± 13.7b	3.0 ± 1.1b	8.37 ± 0.02a
-	NH ₄ -N	759 ± 54a	550 ± 55a	2.12 ± 0.23a	-	-	7.81 ± 0.01b
	NO ₃ -N	659 ± 16a	432 ± 16a	1.62 ± 0.07b	-	-	8.25 ± 0.03a

*Means in the same column followed by different letters indicate a significant difference at $P < 0.05$ according to LSD.

$P \gg 0.05$) between water-insoluble sulphate and soil organic S (Figure 2b), suggesting that the water-insoluble, acid-soluble, fraction is not a measurement of soil organic S that was hydrolysed by HCl. The results indicate that water-insoluble sulphate can be a significant form of S in calcareous soils. Previous reports showed that water-insoluble sulphate accounted for up to 42% of total S in some Canadian soils (Roberts and Bettany, 1985), and up to 93% of total S in some Australian soils (Williams and Steinbergs, 1962). In many other studies, however, this fraction of S has been largely ignored.

Bioavailability of water-insoluble sulphate in calcareous soils

In the pot experiment, neither the form of N nor the addition of sulphate-CaCO₃ co-precipitate affected the dry matter of shoots and roots of wheat significantly (Table 3). Analysis of variance showed that the addition of sulphate-CaCO₃ co-precipitate significantly increased plant S uptake ($P < 0.05$), whereas the form of N applied had no significant effect. However, in the treatment with the addition of sulphate-CaCO₃ co-precipitate, the amount of ³⁵S taken up by wheat plants was significantly ($P < 0.01$) greater in the NH₄⁺ treatment than in the NO₃⁻ treatment. This is reflected in a 3.5-fold higher specific radioactivity of ³⁵S in the NH₄⁺ treatment than in the NO₃⁻ treatment (Table 3). Plant uptake of ³⁵S accounted for 10.6 ± 1.9% and 3.0 ± 1.1% of the ³⁵S added to the soil in the sulphate-CaCO₃ co-precipitate of the NH₄⁺ and NO₃⁻ treatments, respectively. The higher recovery of ³⁵S by plants in the NH₄⁺ treatment can be explained by a lower soil pH (Table 3), which may subsequently enhance solubilisation of the sulphate-CaCO₃ co-precipitate. The difference in soil pH between the NH₄⁺ and NO₃⁻ treatments was 0.45 at the end of

the pot experiment. The pH decrease observed in the NH₄⁺ treatment was likely to be caused by the nitrification of NH₄⁺ in the soil. Furthermore, uptake of NH₄⁺ by roots can also lead to rhizosphere acidification, whereas uptake of NO₃⁻ may increase rhizosphere pH (Marschner, 1995). The results indicate that sulphate co-precipitated with CaCO₃, prepared under laboratory conditions, can become available to plants, particularly if rhizosphere pH decreases. One question that cannot be answered from the results of this study is whether the sulphate co-precipitated with CaCO₃ in field soils is as bioavailable as the sample prepared freshly in laboratory. Similar bioavailability would be expected if both field aged CaCO₃ and laboratory prepared CaCO₃ have similar solubility characteristics.

Changes in extractable sulphur fractions after plant growth

Compared to the initial values, both 1 M HCl total extractable S and insoluble sulphate in the soil decreased after plant growth (Table 4). The decrease was more noticeable in the NH₄⁺ treatment than in the NO₃⁻ treatment. The concentration of 0.01 M CaCl₂ extractable sulphate also decreased considerably after plant growth. In contrast, soluble organic S extracted by 1 M HCl increased markedly in the NH₄⁺ treatment after plant growth. The results indicate that the addition of NH₄⁺ to soil favoured solubilisation of the sulphate that was co-precipitated with CaCO₃, and the solubilised sulphate was partly transformed into soluble organic form.

Conclusions

Calcareous soils appear to differ from acid and neutral soils in that there are negligible amounts of adsorbed

Table 4. Changes in different fractions of extractable S after plant growth in the pot experiment (mg S kg⁻¹ soil, mean ± SE)

Sulphate-CaCO ₃ co-precipitate	Extractable soil S	Initial concentration before experiment	NH ₄ -N treatment	NO ₃ -N treatment
+	Total S extracted by 1 M HCl	80.8	72.3 ± 0.8	76.5 ± 2.6
	Insoluble SO ₄ -S extracted by 1 M HCl	68.4	49.1 ± 1.2	60.7 ± 5.6
	Organic S extracted by 1M HCl	6.97	17.3 ± 2.5	10.5 ± 4.3
	SO ₄ -S extracted by 0.01 M CaCl ₂	12.3	5.9 ± 0.8	5.3 ± 0.4
-	Total S extracted by 1 M HCl	80.8	75.2 ± 4.1	78.3 ± 2.7
	Insoluble SO ₄ -S extracted by 1 M HCl	68.4	50.6 ± 1.6	61.9 ± 4.1
	Organic S extracted by 1 M HCl	6.97	18.9 ± 4.6	6.8 ± 3.1
	SO ₄ -S extracted by 0.01 M CaCl ₂	12.3	5.7 ± 1.1	9.6 ± 1.4

sulphate but significant amounts of water-insoluble sulphate. The concentrations of water-insoluble but acid-soluble sulphate correlated positively with the contents of CaCO₃, and accounted for 0.03–40.3% (mean 11.7%) of the total S in 64 calcareous soils tested. This fraction of sulphate probably occurs in the form of sulphate co-precipitated with CaCO₃ in the calcareous soils. In a pot experiment, wheat was able to take up ³⁵S labelled sulphate from the sulphate-CaCO₃ co-precipitate added to a calcareous soil, with the extent of utilisation being greater when NH₄⁺-N was supplied than when NO₃⁻-N was supplied. The results indicate that sulphate co-precipitated with CaCO₃ in calcareous soils may become partly available for plant uptake, depending on rhizosphere pH, if the field precipitate has a similar solubility to that of the laboratory prepared sample.

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References

- Anderson G, Lefroy R, Chinoim N and Blair G 1992 Soil sulphur testing. *Sulphur Agricult.* 16, 6–14.
- Blair G J 2002 Sulphur Fertilisers: A Global Perspective. Proceedings No. 498. International Fertiliser Society, York.
- Blair G J, Chinoim N, Lefroy R D B, Anderson G C and Crocker G J 1991 A soil sulfur test for pastures and crops. *Aust. J. Soil Res.* 29, 619–626.
- Curtin D and Syers J K 1990 Extractability and adsorption of sulphate in soils. *J. Soil Sci.* 41, 305–312.

- Ensminger L E 1954 Some factors affecting the adsorption of sulfate by Alabama soils. *Soil Sci. Soc. Amer. Proc.* 18, 259–264.
- Goh K M and Pamidi J 2003 Plant uptake of sulphur as related to changes in the HI-reducible and total sulphur fractions in soil. *Plant Soil* 250, 1–13.
- Marschner H 1995 Mineral Nutrition of Higher Plants. Academic Press, London.
- McGrath S P, Zhao F J and Blake-Kalff M M A 2002 History and Outlook for Sulphur Fertilisers in Europe. Proceedings No. 497. International Fertiliser Society, York, U.K.
- Numerical Algorithms Group 1998 Genstat 5 for Windows Release 4.1. NAG Ltd., Oxford, UK.
- Roberts T L and Bettany J R 1985 The influence of topography on the nature and distribution of soil sulphur across a narrow environmental gradient. *Can. J. Soil Sci.* 65, 419–434.
- Scott N M 1981 Evaluation of sulphate status of soils by plant and soil tests. *J. Sci Food Agric.* 32, 193–199.
- Syers K J, Skinner R J and Curtin D 1987 Soil and Fertiliser Sulphur in UK Agriculture. Proceedings No. 264. The Fertiliser Society, London.
- Watkinson J H and Kear M J 1996 Sulfate and mineralizable organic sulfur in pastoral soils of New Zealand. I. A quasi equilibrium between sulfate and mineralizable organic sulfur. *Aust. J. Soil Res.* 34, 385–403.
- Williams C H and Steinbergs A 1962 The evaluation of plant-available sulphur in soils. I. The chemical nature of sulphate in some Australian soils. *Plant Soil* 17, 279–294.
- Williams C H and Steinbergs A 1964 The evaluation of plant-available sulphur in soils. II. The availability of adsorbed and insoluble sulphates. *Plant Soil* 21, 50–62.
- Wu J, A.G. O D, He Z L and Syers J K 1994 Fumigation-extraction method for the measurement of soil microbial biomass-S. *Soil Biol. Biochem.* 26, 117–125.
- Zhao F and McGrath S P 1994 Extractable sulphate and organic sulphur in soils and their availability to plants. *Plant Soil* 164, 243–250.
- Zhao F, McGrath S P and Crosland A R 1994 Comparison of three wet digestion methods for the determination of plant sulphur by inductively coupled plasma atomic emission spectroscopy (ICP-AES). *Comm. Soil Sci. Plant Anal.* 25, 407–418.
- Zhao F J, McGrath S P, Blake-Kalff M M A, Link A and Tucker M 2002 Crop Responses to Sulphur Fertilisation in Europe. Proceedings No. 504. International Fertiliser Society, York.

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