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## A NEW METHOD FOR THE DETERMINATION OF THE $^{34}\text{S}/^{32}\text{S}$ RATIO OF WATER-SOLUBLE SULPHUR IN SOIL

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A new method for the determination of the  $^{34}\text{S}/^{32}\text{S}$  ratio of water-extractable sulphate in soil is described. Soils are extracted directly with deionized water, which is evaporated down. The remaining residue is then rehydrated and transferred to tin cups containing an adsorbent and mixed with an oxygen donor ( $\text{V}_2\text{O}_5$ ). Samples are then analysed using a continuous flow isotope ratio mass spectrometer. The new method requires around 10 g soil per determination, compared to much larger amounts (up to kilograms) of soil required for the previous methods. Sample preparation and subsequent analysis is quick and efficient. The method is demonstrated using a number of soils collected from around the world to provide a range of determined  $\delta^{34}\text{S}$  values. The  $\delta^{34}\text{S}$  values of water-extractable sulphur were broadly similar to those of the soil total sulphur.

*Keywords:*  $^{34}\text{S}$ ; S isotope ratio; Sulphur; Sulphate; Isotope ratio mass spectrometry; Soil

### INTRODUCTION

The application of stable isotope measurements in geochemical and environmental studies is a well-established technique, particularly in relation to the C, N and S cycles. Sulphur has four stable isotopes ( $^{32}\text{S}$ ,  $^{33}\text{S}$ ,  $^{34}\text{S}$  and  $^{36}\text{S}$ ), of which  $^{32}\text{S}$  (95.0%) and  $^{34}\text{S}$  (4.2%) are the most abundant. Usually, the abundance of the latter two isotopes are measured in isotope studies, with the ratio of  $^{34}\text{S}/^{32}\text{S}$  of a sample expressed as the per mil (‰) deviation from that in the Canyon Diablo meteorite (CDT) in  $\delta$  notation [1]:

$$\delta^{34}\text{S} (\text{‰}) = \left( \frac{^{34}\text{S}/^{32}\text{S}_{\text{sample}}}{^{34}\text{S}/^{32}\text{S}_{\text{CDT}}} - 1 \right) \times 1000.$$

$\delta^{34}\text{S}$  values found in nature vary mostly within the range from  $-40$  to  $+40\text{‰}$  [2]. The stable S isotope ratio has been used extensively to identify sources and the fates of S in the environment [e.g. 3–10]. If the S isotope ratios from different sources are

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known, it is possible to apportion the contributions of S from these sources to a receptor. For example, Zhao *et al.* [6,10] observed a strong negative correlation between  $\delta^{34}\text{S}$  values of plant and soil samples from long-term (> 140 years) experiments at Rothamsted, UK, and the national  $\text{SO}_2$  emissions. They estimated that approximately 30–40% of the total S in the topsoil has been derived from anthropogenic sources. Another application of the stable isotope  $^{34}\text{S}$  is to use it as a tracer. Gypsum naturally enriched in  $^{34}\text{S}$  has been used to follow the fate of S applied to soils [11], and the recent commercial availability of highly enriched forms of  $^{34}\text{S}$  has led to tracer studies in plants and soil [12].

Determination of the  $^{34}\text{S}/^{32}\text{S}$  ratio has previously been performed by isotope ratio mass spectrometry using an off-line method. This method requires a complex sample preparation before samples may be analysed. Typically, total or a fraction of S is extracted and converted to sulphate, before being precipitated with  $\text{BaCl}_2$ . The  $\text{BaSO}_4$  produced is reduced  $\text{SO}_2$  through thermal decomposition with a mixture of  $\text{Cu}_2\text{O}$  and  $\text{SiO}_2$  [13] or  $\text{V}_2\text{O}_5$  and  $\text{SiO}_2$  [14].  $\text{SO}_2$  produced is then condensed in a stainless steel trap immersed in liquid nitrogen and used for the determination of the isotope ratio, using dual-inlet mass spectrometry. Not only is this preparation very lengthy and prone to errors [15], but it also requires relatively large amounts (3–7 mg) of S, due to the number of chemical processes involved. More recently, an on-line method has been developed whereby samples are oxidised to  $\text{SO}_2$  in an elemental analyser that is coupled to an isotope ratio mass spectrometer (IRMS) [16,17]. Combining vanadium pentoxide ( $\text{V}_2\text{O}_5$ ) with the samples enhances oxidation, and the S content required in samples is reduced to approximately  $10\ \mu\text{g}$  [17]. The on-line method greatly simplifies the procedure for the determination of S isotope ratio, and increases the analytical throughput.

In studies of soil S cycling, it is often necessary to determine  $\delta^{34}\text{S}$  of not only total S, but also different fractions of S, particularly sulphate. Sulphate is the form of S that is taken up by plants and is also prone to leaching. Sulphate may be adsorbed by positively charged surfaces, particularly iron and aluminium oxides/hydroxides. Adsorption of sulphate increases with a decrease in soil pH, but is negligible above pH 6.5 [18]. As well as water, various chemical extractants have been employed to extract  $\text{SO}_4^{2-}$  from soil [19]. In many soils, phosphate-based extractants recover similar levels of  $\text{SO}_4^{2-}$  to extraction with water [20], but they are likely to be more efficient at recovering adsorbed  $\text{SO}_4^{2-}$  in low pH soils. However, the determination of the  $^{34}\text{S}/^{32}\text{S}$  ratio of  $\text{SO}_4^{2-}\text{-S}$  continues to employ a  $\text{BaCl}_2$  precipitation step [1].  $\text{SO}_4^{2-}\text{-S}$  usually represents < 10% of the total S in soil, with concentrations typically varying from 1 to 20 mg of S per kilogram of soil. Therefore, to produce sufficient amounts of  $\text{BaSO}_4$  precipitate (containing > 3 mg of S) for the determination of the S isotope ratio in  $\text{SO}_4^{2-}$ , 0.15–3 kg of soil would be required. The need for replicated analysis means that even more soil is required, which is not possible in many experiments. Clearly, a new method is needed that is simple and uses much smaller amounts of soil. This paper proposes a simplification in the determination of the  $^{34}\text{S}/^{32}\text{S}$  ratio of water-soluble S by direct determination.

## EXPERIMENTAL

Seven soils from three distinct locations were used in this study. Three soil samples were collected in 2000 from the Broadbalk Classical Experiments at Rothamsted: an arable

TABLE I Characteristics of soils used in the study

<i>Location</i>	<i>Land Use</i>	<i>pH (H<sub>2</sub>O)</i>	<i>Total C (%)</i>	<i>Total N (%)</i>	<i>Total S (μg g<sup>-1</sup>)</i>
Pitcaple, Scotland	Grassland	4.77	4.95	0.39	651.6
Inschfield, Scotland	Arable	6.73	4.46	0.39	582.4
Broadbalk, England	Grassland	6.64	4.06	0.34	531.0
Broadbalk, England	Arable	8.37	0.96	0.10	154.0
Broadbalk, England	Arable farmyard manure applied	7.77	3.33	0.31	544.5
Christchurch, New Zealand	Grassland	5.68	3.45	0.27	338.1
Christchurch, New Zealand	Arable	5.81	2.65	0.22	282.2

control plot ('Broadbalk arable'), a plot receiving farmyard manure applications ('Broadbalk FYM') and a grassland section of Broadbalk ('Broadbalk grassland'). Grassland and arable soils were also collected from sites in north-east Scotland ('Scottish Grassland', 'Scottish Arable') and the Crop and Food Research Centre, Christchurch, New Zealand ('New Zealand Grassland', 'New Zealand Arable'). Characteristics of the soils are listed in Table I.

All soils were air dried and ground to <2 mm prior to analysis. Subsamples used for total  $\delta^{34}\text{S}$  determinations were ground to <0.25 mm using an agate ball mill. Total S was determined by aqua regia digestion followed by analysis using inductively coupled plasma atomic emission spectrometry [21]. Soil pH was determined using a glass electrode, with soil in a 1:2.5 solution with deionized H<sub>2</sub>O. Total C and N were measured using a LECO CNS 2000 analyser (Leco Instruments, Stockport, UK).

### $\delta^{34}\text{S}$ Determination of Total Soil S

Total  $\delta^{34}\text{S}$  of soil samples was determined using a continuous-flow isotope ratio mass spectrometer (20-20 IRMS, Europa Scientific Ltd, Crewe, UK), coupled to an elemental analyser (ANCA-SL sample converter). The instrumental setup and analytical conditions have been described in details previously [22]. Approximately 20 mg of soil (<0.25 mm) was weighed into a tin cup containing 20 mg of V<sub>2</sub>O<sub>5</sub>. All determinations were made in triplicate. Analysis of reference materials IAEA S-1, S-2 and S-3 (Ag<sub>2</sub>S) and NBS 127 (BaSO<sub>4</sub>) produced mean values of -0.3, 21.8, -32.5 and 20.5‰, respectively. The results concurred with their respective certified values of -0.3, 21.6, -32.1 and 20.3‰. Analytical precision (standard deviation of five repeats) of IAEA S-1 and an in-house ammonium sulphate standard was  $\pm 0.31$  and  $\pm 0.25\%$ , respectively.

### $\delta^{34}\text{S}$ Determination of Water-soluble S in Soil

Ten grams of air-dried soil (<2 mm) were shaken with 20 mL deionized H<sub>2</sub>O in a 50-mL polyethylene centrifuge tube for 1 h on a rotary shaker at 200 rpm. Samples were then centrifuged at 1500 g for 10 min and the supernatant filtered (Whatman no. 42) into 25-mL boiling tubes. A 2-mL aliquot of the filtrate was removed for determination of SO<sub>4</sub><sup>2-</sup> by ion chromatography (Dionex, Camberley, UK). Boiling tubes were placed in a heating block set to 110°C and left until their contents had evaporated. Once the tubes had cooled, the dry residue at the bottom of the tube was redissolved in 60 μL deionized H<sub>2</sub>O and mixed on a whirlimixer. Two 20 μL aliquots of the solution

produced were then transferred using a precision syringe to tin cups containing 20 mg of  $V_2O_5$  and a small amount of the inert absorbent Chromosorb<sup>®</sup> (Europa Scientific). Five extractions were made from each soil, with subsequent mass-spectrometry determination of each extraction in duplicate. The  $\delta^{34}S$  value was determined as described above. The in-house ammonium sulphate standard with a known  $\delta^{34}S$  ( $-1.1\text{‰}$ ) was used to determine the variability of  $\delta^{34}S$  measurements as affected by the amount of S in the sample, using a range of 1.5–30  $\mu\text{g}$ .

To test the effectiveness of extracting soil  $SO_4^{2-}$  with  $H_2O$ , a comparative extraction was made using 0.016 M  $KH_2PO_4$ . Five 10-g sub-samples were extracted for 1 h in 50 mL of 0.016 M  $KH_2PO_4$ . After filtering (Whatman no. 42), samples were analysed for  $SO_4^{2-}$  by ion chromatography.

## RESULTS AND DISCUSSION

Figure 1 shows the effect of varying the amount of S in each sample on the determination of  $\delta^{34}S$ . The deviation of the measured  $\delta^{34}S$  from the value of the ammonium sulphate standard was  $<0.3\text{‰}$  for samples containing 3–30  $\mu\text{g}$  of S. The deviation was substantially greater (0.8 $\text{‰}$ ) for the sample having only 1.5  $\mu\text{g}$  of S. The standard error was also larger for the 1.5- $\mu\text{g}$  S sample. The results indicate that the amount of S in each sample should be at least 3  $\mu\text{g}$ , or preferably 10–30  $\mu\text{g}$  for a better reproducibility. Previously, Eriksen [15] reported that the amount of S in each sample should match that of the calibration standard, otherwise deviation would occur as a result of different  $SO_2$  pressures. This requirement would render the on-line measurement of S isotope ratio very time-consuming. However, our results indicate a wide working range of the amount of S in each sample, which means that exact matching of samples and standards is not necessary, as long as the amount of S is within the working range. Similarly, Giesemann *et al.* [17] found very good reproducibility for the determination of  $\delta^{34}S$  within the range of 10–100  $\mu\text{g}$  of S per sample using an on-line IRMS system.

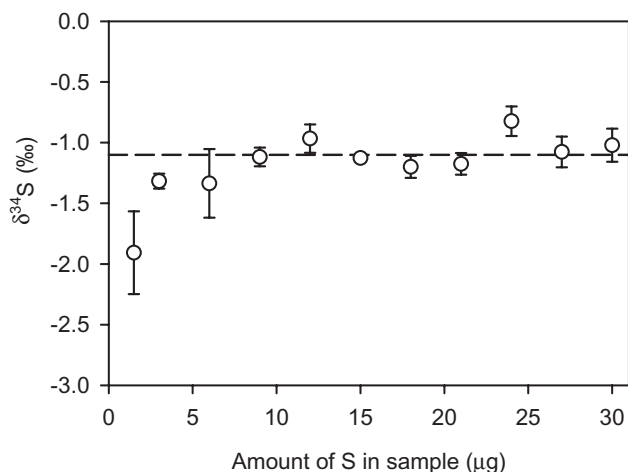


FIGURE 1 Efficiency test of the mass spectrometer. The  $\delta^{34}S$  value of the ammonium sulphate standard is indicated by the horizontal dashed line at  $\pm 1.1\text{‰}$ . Vertical bars indicate standard error of the mean ( $n=3$ ).

The concentrations of water-soluble S in the soils used in this study ranged from 2.8 to 15.9  $\mu\text{g/g}$ , typically accounting for 2% of total soil S. To produce sufficient  $\text{BaSO}_4$  for an off-line determination of  $\delta^{34}\text{S}$  of water-soluble S in these soils, 188–1070 g of soil would be required. In contrast, the proposed new method used 10 g of soil for an extraction, which in turn produced enough extracted S for at least two separate determinations of  $\delta^{34}\text{S}$  with the on-line method. The amount of S in each tin cup was calculated to be between 9 and 54  $\mu\text{g}$  (Table II), sufficiently high for a reliable determination of  $\delta^{34}\text{S}$ .

The  $\delta^{34}\text{S}$  values of total and water-soluble S of the soils used in this study are shown in Fig. 2. For the water-soluble pool,  $\delta^{34}\text{S}$  ranged between 0.39 and 13.50‰, a range similar to the values obtained for total S. Standard errors associated with five replicated extractions and determination of  $\delta^{34}\text{S}$  of water-soluble S ranged from 0.09 to 0.60‰. These values are considered low, indicating that the proposed new method is reliable. Typically for the region [23], New Zealand soils were found to have high  $\delta^{34}\text{S}$  values,

TABLE II Sulphur content of soils examined and the amount of S used to determine  $\delta^{34}\text{S}$

Soil	$\mu\text{g/g } \text{SO}_4\text{-S}$		$\mu\text{g S in tin cup}$	
	Mean	SE <sup>a</sup>	Mean	SE
Scottish Grassland	3.1	0.07	10.4	0.24
Scottish Arable	5.9	0.07	19.8	0.25
Broadbalk Grassland	10.0	0.25	33.7	0.91
Broadbalk Arable	2.8	0.21	9.4	0.75
Broadbalk farmyard manure	5.6	0.14	18.5	0.30
New Zealand Grassland	4.4	0.18	14.8	0.65
New Zealand Arable	15.9	1.79	53.8	5.99

<sup>a</sup>SE: standard error of the mean;  $n = 5$ .

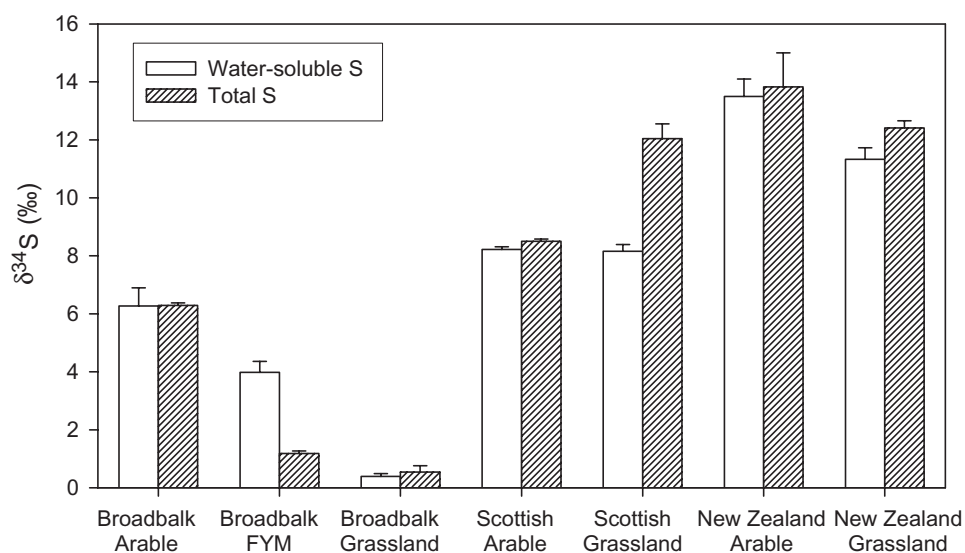


FIGURE 2  $\delta^{34}\text{S}$  of water-soluble and total S in the soils studied. Bars indicate standard error of the mean ( $n = 5$  and 3 for water-soluble S and total S, respectively). FYM: farmyard manure.

probably as a result of the inputs of sea salt sulphate, which has an average  $\delta^{34}\text{S}$  of 21‰ [2]. Apart from the Scottish grassland soil and the soil from the Broadbalk farmyard manure plot, the other five soils showed similar  $\delta^{34}\text{S}$  value for the total and water-soluble S. Water-soluble S in the Scottish grassland soil was more depleted in  $^{34}\text{S}$  (by 4‰) than total S, whereas in the Broadbalk farmyard manure soil, water-soluble S was more enriched in  $^{34}\text{S}$  (by 3‰) than total S. Two main reasons may underlie any differences observed between water-soluble S and total soil S in their isotopic composition. First, the isotopic ratio of the water-soluble S pool is more likely to reflect that of the recent S inputs, e.g. atmospheric deposition, fertilizer or manure applications, which may be different from the isotopic ratio of the S that is derived from soil parent materials. Second, mineralization of organic S to sulphate may be associated with isotopic fractionation. Several studies have shown a depletion of  $^{34}\text{S}$  in sulphate compared to organic S [8,24,25].

The pH of the soils used in this study ranged from 4.77 to 8.37 (Table I). The effect of pH on the difference in the amount of  $\text{SO}_4^{2-}$ -S extracted by  $\text{KH}_2\text{PO}_4$  and water is shown in Fig. 3. The effect was negligible in six out of the seven soils, of which the lowest pH was 5.63. In a highly acidic soil (Scottish Grassland), water extracted significantly less  $\text{SO}_4^{2-}$  than  $\text{KH}_2\text{PO}_4$ , indicating the presence of a substantial amount of adsorbed  $\text{SO}_4^{2-}$ . However, for the purposes of determining isotope ratios, it has been shown that soil solution  $\text{SO}_4^{2-}$ , water-soluble  $\text{SO}_4^{2-}$ , and adsorbed  $\text{SO}_4^{2-}$  in the soil are in isotopic equilibrium without significant isotope fractionation [1]. Therefore, even partial extraction of the whole inorganic sulphate pool is likely to give a reliable  $\delta^{34}\text{S}$  value for this pool in the soil [1].

One particular advantage of the proposed method is that no salt is added during the extraction of soil  $\text{SO}_4^{2-}$ , which produces extracts with low concentrations of cations and anions. In our preliminary tests, we found that the reliability of the on-line mass spectrometry method deteriorated rapidly when samples extracted with either  $\text{CaCl}_2$  or  $\text{KH}_2\text{PO}_4$  were analysed, presumably due to the interference of the salt added or poisoning of the catalyst by chlorine produced during the initial combustion step.

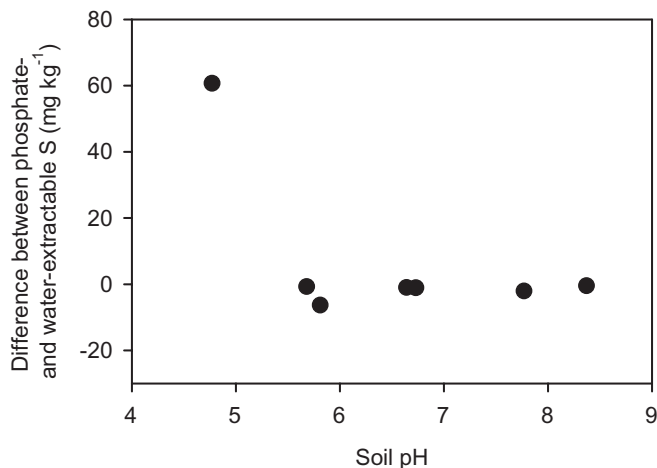


FIGURE 3 The effect of soil pH on the difference between phosphate- and water-extractable S.

The previous off-line method for  $\delta^{34}\text{S}\text{-SO}_4^{2-}$  determinations has often been criticized in the literature for being too time-consuming and impractical. The proposed new method considerably reduced the preparation time required for samples – typically 20 samples per hour – and produced consistent results when applied to large batches of samples. Since the samples contained very little residue and were largely inert, there was a negligible deterioration of the combustion tubes in the mass spectrometer, compared to whole plant or soil sample analysis. This allowed for 20–30 samples to be run consecutively on the mass spectrometer, further reducing the overall time required. Another advantage of this method is the comparatively small amount (~10 g) of soil required for analysis. Previously, amounts of soil of up to several kilograms would be required to obtain the 3–7 mg of S required for off-line sample preparation, which is not possible in many studies. In conclusion, compared with the extensive preparation required for off-line isotope ratio mass spectrometry, the method presented here is simpler, less time-consuming and inexpensive.

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