

## Source Identification of Sulfur in Uncultivated Surface Soils from Four Chinese Provinces



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### ABSTRACT

The analysis of stable isotopes of sulfur ( $\delta^{34}\text{S}$ ) is a useful tool for identifying sources of sulfur in soils. Concentrations and sulfur (S) isotopes of water-soluble sulfate (WSS), adsorbed sulfate (AS), residual sulfur (RS), and total sulfur (TS) in uncultivated surface soils of four Chinese provinces were systematically analyzed for identifying sources of S in the soils. Green and healthy mosses (*Haplodadium microphyllum*) were sampled as bioindicators. The mean WSS concentration ( $27.8 \pm 23.4 \text{ mg kg}^{-1}$ ) in the surface soils was lower than those of AS ( $101.4 \pm 57.0 \text{ mg kg}^{-1}$ ) and RS ( $381.5 \pm 256.7 \text{ mg kg}^{-1}$ ). The mean  $\delta^{34}\text{S}$  values of WSS and AS were very similar (about 2.0‰), lower than those of RS (8.0‰) and TS (6.1‰). A significant linear correlation was found between the  $\delta^{34}\text{S}$  values of AS and WWS ( $y = 1.0002x - 0.0557$ ,  $P < 0.0001$ ), indicating that sulfate adsorption in the soils did not markedly fractionate S. All S species in the soils of Guizhou Province were characterized by the lowest  $\delta^{34}\text{S}$  values, consistent with the most  $^{34}\text{S}$ -depleted rainwater sulfate reported at Guiyang of Guizhou Province. The  $\delta^{34}\text{S}$  values of sulfate in mosses and rainwater previously reported were significantly linearly correlated with those of both WWS and AS in surface soils, suggesting that atmospheric S input was an important source for soil WSS and AS. However, there were no significant correlations between isotopic composition of rainwater sulfate and RS or TS. The slopes of all these significant linear correlations (soil/rainwater or soil/moss isotopic ratio) were 0.4–0.6, indicating that inorganic sulfate in the surface soils should be a result of mixing of deposited atmospheric sulfate with a more  $^{34}\text{S}$ -depleted sulfate component possibly from mineralization of RS.

**Key Words:** adsorbed sulfate, atmospheric input, bioindicators, isotopic composition, moss, residual sulfur, water-soluble sulfate

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### INTRODUCTION

Due to increased  $\text{SO}_2$  emissions primarily from burning fossil fuels, atmospheric sulfur deposition increased in many countries (Husar *et al.*, 1991). Consequently, much consideration has been given to the influence of atmospheric deposition on sulfur biogeochemical cycles in soils (*e.g.*, Richter *et al.*, 1983). It has been known that deposited sulfur (S) from the atmosphere could be an important component of soil S cycling (Gebauer *et al.*, 1994).

Usually sulfate in uncultivated soils mainly comes from mineral weathering, atmospheric deposition, and decomposition of organic sulfur. The sulfate in soils plays an important role in the S geochemical cycling because it can be incorporated into organic S, adsorbed and desorbed by soil particles, leached into the deep soils or groundwater, and reduced to sulfide or  $\text{H}_2\text{S}$  (Harward and Reisenauer, 1966). Elevated inputs of sulfate will facilitate the transport of potentially toxic

acidic cations like  $\text{H}^+$  and  $\text{Al}^{n+}$  from soil to surface water (Van Breemen *et al.*, 1984). Understanding soil sulfate dynamics is therefore a prerequisite for assessing the role of inorganic sulfate in acidification of soils and surface waters.

The analysis of stable isotopes of sulfur ( $\delta^{34}\text{S}$ ) is a useful tool for studying the S biogeochemical cycles in soils (Novák *et al.*, 1996; Alewell and Novák, 2001). Most studies on soil S isotopes were focused on total S (*e.g.*, Novák *et al.*, 1996; Stack and Rock, 2011). There are relatively few studies on stable isotopes of soil inorganic sulfate up to now (Hinckley *et al.*, 2008).

Sulfur isotope selectivity has been examined for some soil processes. Although biologically mediated transformations select for the lighter isotope (Kaplan and Rittenberg, 1964), the isotope discrimination during sulfate assimilation by plants only leads to an average depletion of  $^{34}\text{S}$  by 1%–2‰ in the organic S, compared with the sulfate source (Trust and Fry, 1992;

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Novák *et al.*, 2001). A study conducted by Monaghan *et al.* (1999) showed that the isotope ratios of the whole wheat shoots, which had been supplied with only one S source, were very close to the  $\delta^{34}\text{S}$  values of the sources, with a maximum deviation of 0.6‰. Our recent study (Xiao *et al.*, 2011) also found that the average  $\delta^{34}\text{S}$  values of both soil S ( $-3.7\text{‰} \pm 1.0\text{‰}$ ) and rainwater sulfate ( $-3.1\text{‰} \pm 2.7\text{‰}$ ) were similar to that of foliar S in three plant species ( $-3.1\text{‰} \pm 1.9\text{‰}$ ).

Isotopic fractionation associated with sorption-desorption of sulfate in soils has been investigated. For instance, Nriagu (1974) found that adsorption resulted in a large fractionation from 12‰ to 25‰ in laboratory experiments with organic-rich lake sediments. However, Cortecchi (1978) believed that no detectable isotopic fractionation was associated with retention of sulfate by organic-poor red marine clay. Some field studies and laboratory studies also indicated negligible S isotope effects associated with soil sorption of sulfate (Fuller *et al.*, 1986; Van Stempvoort *et al.*, 1990).

The use of stable isotopes in source identification of rainwater sulfate has increased rapidly because the isotopic values of S sources are often distinct (*e.g.*, Xiao and Liu, 2002). As a plant species sensitive to the atmospheric S, mosses have been believed to hold source-specific information that can serve as a fingerprint to identify S sources (Nriagu and Glooschenko, 1992). It has been demonstrated that little isotopic fractionation accompanies S assimilation by mosses as they acquire S from the atmosphere and their roots serve mainly for attachment, and they have no cuticles to block atmospheric inputs (Winner *et al.*, 1978; Trust and Fry, 1992; Bragazza *et al.*, 2005). It has further been shown by Liu *et al.* (2009) that the  $\delta^{34}\text{S}$  values of epilithic mosses ( $-4.2\text{‰} \pm 0.9\text{‰}$ ) are similar to the  $\delta^{34}\text{SO}_4^{2-}$

values of rainwater ( $-4.9\text{‰} \pm 2.8\text{‰}$ ) collected in the same study area. In our recently published study (Xiao *et al.*, 2009), we also found that moss  $\delta^{34}\text{S}$  values were comparable to those of rainwater sulfate at two Chinese cities in 2006.

This study was conducted 1) to investigate the distribution of different S species in uncultivated surface soils and variations of their S isotopes in four provinces of China; 2) to identify S sources by comparing isotopes of different S species in soils with those of rainwater sulfate or mosses; and 3) to check the isotopic fractionation associated with sorption-desorption of sulfate by comparing S isotopes between water-soluble sulfate and adsorbed sulfate.

## MATERIALS AND METHODS

### *Study sites and sample collection*

Three southern Chinese provinces (Fujian, Jiangxi, and Guizhou) and one northern Chinese province (Hebei) were chosen in this study because there are available data of rainwater  $\delta^{34}\text{S}$  values reported and, most important, much different sulfur isotopes of atmospheric deposition were found in the four provinces (Table I). This is because S isotopic values of northern Chinese coals are much more positive than those of southern Chinese coals, and among the three southern Chinese provinces, those of Guizhou coals are the most negative, followed by those of Jiangxi coals (Xiao and Liu, 2011).

Uncultivated surface soils (0–20 cm) were collected from the four provinces. Eight sites (Nanchang, Fengcheng, Anyi, Lushan, Chongren, Yingtan, Jingde-zhen, and Dexing) were selected in Jiangxi Province and one site in other three provinces, Xiamen in Fu-

TABLE I  
Description of the selected sites in four provinces of China

Province	Annual precipitation	Dominant S source ( $\delta^{34}\text{S}$ )	Atmospheric S deposition <sup>a)</sup>	Rainwater			No. of samples
				Sampling site	$\text{SO}_4^{2-}$	$\delta^{34}\text{S}$	
	mm		$\text{kg S hm}^{-2} \text{ year}^{-1}$		$\text{mg L}^{-1}$	‰	
Fujian	1 350	Coal (2.2‰)	12.7	Xiamen	2.82 <sup>b)</sup>	4.4±6.4 <sup>c)</sup>	13
Jiangxi	1 550	Coal (-3.1‰)	33.8	Nanchang	6.54±5.14 <sup>d)</sup>	0.4±2.3 <sup>d)</sup>	72
Guizhou	1 179	Coal (-7.5‰)	83.6	Guiyang	21.27±25.14 <sup>e)</sup>	-4.9±2.6 <sup>e)</sup>	15
Hebei	530	Coal (12.1‰)	26.8	Qinghuangdao	15.17 <sup>f)</sup>	7.9±1.6 <sup>g)</sup>	14

a) Calculated by annual precipitation and sulfate concentrations.

b) Cited from Yu *et al.* (1998).

c) Mean±standard deviation, cited from Yao *et al.* (1997).

d) Mean±standard deviation, cited from Xiao *et al.* (2011).

e) Mean±standard deviation, cited from Xiao and Liu (2002).

f) Cited from Xu and Han (2009).

g) Mean±standard deviation, cited from Hong *et al.* (1994).

jian, Guiyang in Guizhou, Qinghuangdao in Hebei. The sampling sites selected were located in open habitats like heaths or clearings of forested areas and at least 500 m away from main roads and at least 100 m away from other roads or houses. Each sample was collected by mixing at least 5–10 subsamples taken from an area of 1 m<sup>2</sup> and 10–20 samples were collected at each sampling site. The soil samples were air-dried, ground in an agate mortar to pass 200-mesh sieves, and stored in a desiccator for further sample analysis. Sampling site description is given in Table I.

In Jiangxi Province, there are no available S isotope data at most of the sampling sites. So moss materials (*Haplocladium microphyllum*) at all studied sites were collected in order to obtain atmospheric S isotope data (Xiao *et al.*, 2009) at the same place where we sampled surface soils. All mosses were obtained from natural rocks without canopies or overhanging vegetation ensuring no influences from throughfall S compounds. Moss sampling was performed only at those sites above ground level to avoid surface water splashes. Sites possibly disturbed by domestic animals or other point sources were also avoided. We collected 5–10 subsamples at each site and combined them into one representative sample (about wet weight of 10 g). Only green and healthy parts of the mosses were taken, avoiding yellow or dark sections.

#### Chemical analysis

Water-soluble sulfate (WSS) and adsorbed sulfate (AS) in soils were extracted with two commonly used extractants, Milli-Q water and 0.01 mol L<sup>-1</sup> Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>, respectively (Autry *et al.*, 1990; Zhao and McGrath, 1994). WSS was extracted first, followed by AS. The extraction procedures of the two sulfate species were the same as follows. A 1:5 soil to solution mixture was shaken for 1–2 h at room temperature and centrifuged at 8000 × *g* for 10 min. The supernatant was then passed through a 0.22-μm Whatman filter member. The filtered extracts were stored at 4 °C prior to further chemical and isotopic analysis. All extractions were performed in duplicate.

Following the method of Liu *et al.* (2007), moss samples were gently rinsed with 1.5 mol L<sup>-1</sup> HCl solution, and then sonicated and washed with deionized water for several times. All moss samples were dried in a vacuum oven at 70 °C and re-dried after being ground separately in liquid nitrogen into fine powders using a mortar and pestle. Then, the moss samples were oxidized in a Parr bomb to convert all forms of S present to sulfate (Murillo *et al.*, 1993). To assure complete conversion, hydrogen peroxide was added to

all washings.

Sulfate was recovered from soil extracts and moss washings by precipitating as BaSO<sub>4</sub> with enough 2 mol L<sup>-1</sup> BaCl<sub>2</sub> solution. After precipitated for 24 hours, the mixture was filtered through a 0.22-μm acetate membrane filter. The precipitates (BaSO<sub>4</sub>) on the filters from soils or mosses were collected and carefully rinsed with enough Milli-Q water to remove Cl<sup>-</sup>, and then transferred into crucibles with the filters and combusted at 800 °C for 40 min in the air. The composition of white powder in the crucible was analyzed using X-ray diffractometry. The results showed > 99% BaSO<sub>4</sub> in the powder.

In this study, we only analyzed the concentrations of water-soluble and adsorbed S in the forms of sulfate. Measurements of the concentrations of water-soluble and adsorbed sulfate extracts were conducted on a DIONEX ICS-90 ion chromatography (Dionex, Sunnyvale, USA) with a detection limit of 0.01 mg L<sup>-1</sup>. Total S concentrations of soils and mosses were determined by a PE2400II elemental analyzer (Perkin-Elmer Co., Norwalk, USA) with an analytical precision of 1%. Concentrations of residual S in soils were obtained by subtracting water-soluble and adsorbed S from total S.

#### Isotopic analysis

Thermal decomposition of BaSO<sub>4</sub> (Yanagisawa and Sakai, 1983) was conducted to prepare SO<sub>2</sub> for S isotopic analysis in a Finnigan MAT-252 mass spectrometer. The standard deviation for the δ<sup>34</sup>S analysis of the barium sulfate standard NBS-127 was lower than 0.2‰ (*n* = 5).

In the light of isotope mass balance, the δ<sup>34</sup>S values of residual sulfur (RS) in the soils were calculated as follows: δ<sup>34</sup>S<sub>TS</sub> × C<sub>TS</sub> = δ<sup>34</sup>S<sub>WS</sub> × C<sub>WS</sub> + δ<sup>34</sup>S<sub>AS</sub> × C<sub>AS</sub> + δ<sup>34</sup>S<sub>RS</sub> × C<sub>RS</sub>, where C<sub>TS</sub>, C<sub>WS</sub>, and C<sub>AS</sub> represent the concentrations of total sulfur (TS), water-soluble sulfate, and adsorbed sulfate, respectively.

#### Statistical analysis

Statistical analysis was conducted using the SPSS 11.5 statistical program (SPSS Science, Chicago, USA), and graphs were mainly created with SigmaPlot 2000 software (SPSS Science, Chicago, USA). Correlations were tested for significance by using a one-way analysis of variance (ANOVA) procedure. *P* < 0.05 was considered significant.

## RESULTS

#### Sulfur concentrations in uncultivated surface soil

Concentrations of TS in the uncultivated surface

soils varied in a wide range from 189 to 794 mg kg<sup>-1</sup>, being the lowest at Anyi (Jiangxi Province) and the highest at Yingtan (Jiangxi Province) (Fig. 1). The WSS concentrations in the surface soils averaged 27.8 mg kg<sup>-1</sup>, much lower than those of AS (101 mg kg<sup>-1</sup>) and RS (381 mg kg<sup>-1</sup>). The WSS/TS ratio in the northern Chinese province (Qinghuangdao in Hebei Province) (11.7%) was significantly higher than those in the southern Chinese provinces. Among the eight sites in Jiangxi Province, the lowest WSS/TS ratio occurred at Anyi (1.6%). The highest AS/TS ratio in the surface soil (27.0%) was found at Guiyang in Guizhou Province, while the mean ratio at Qinghuangdao (Hebei Province) was only 14.6%. Residual S was the most dominant soil S species at almost all these studied sites except for Anyi. At Yingtan, the RS/TS ratio was 88.1%, about twice that at Anyi (44.9%). The RS/TS ratio at Qinghuangdao was 73.9%, slightly higher than the mean ratio of the three southern Chinese provinces (69.5%).

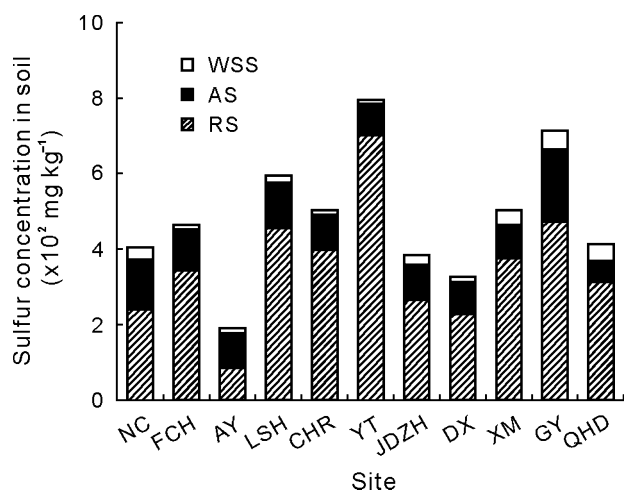


Fig. 1 Concentrations of total sulfur (TS), water-soluble sulfate (WSS), adsorbed sulfate (AS), and residual sulfur (RS) in uncultivated surface soils from three southern Chinese provinces (Fujian, Jiangxi, and Guizhou) and one northern Chinese province (Hebei). TS = WSS + AS + RS. NC = Nanchang in Jiangxi; FCH = Fengcheng in Jiangxi; AY = Anyi in Jiangxi; LSH = Lushan in Jiangxi; CHR = Chongren in Jiangxi; YT = Yingtan in Jiangxi; JDZH = Jingdezhen in Jiangxi; DX = Dexing in Jiangxi; XM = Xiamen in Fujian; GY = Guiyang in Guizhou; QHD = Qinghuangdao in Hebei.

#### Sulfur isotopes in uncultivated surface soil

The  $\delta^{34}\text{S}$  values of TS in the uncultivated surface soils ranged from  $-9.4\text{‰}$  to  $11.6\text{‰}$ , being the lowest in Guizhou Province ( $2.1\text{‰}$ ) (Fig. 2). Total S in surface soils in Hebei Province showed a mean  $\delta^{34}\text{S}$  value of  $7.0\text{‰}$ , close to that in Fujian Province ( $7.0\text{‰}$ ), lower than that in Jiangxi Province ( $8.1\text{‰}$ ) while slightly higher than the mean value of the three southern Chi-

nese provinces ( $6.5\text{‰}$ ). In Jiangxi Province, the  $\delta^{34}\text{S}$  mean value was the highest at Anyi ( $9.9\text{‰}$ ), followed by Chongren ( $9.8\text{‰}$ ), and the lowest at Nanchang ( $6.0\text{‰}$ ) (Fig. 3).

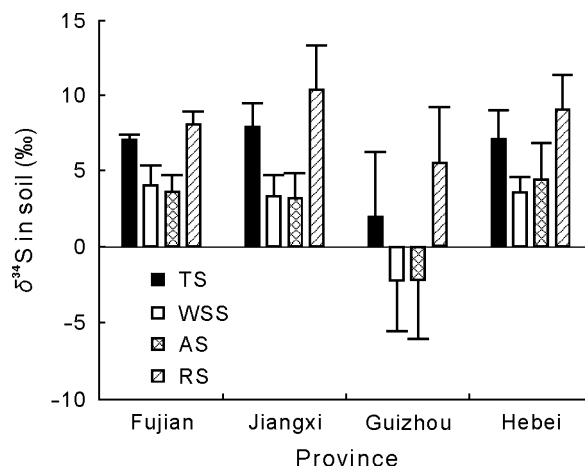


Fig. 2  $\delta^{34}\text{S}$  values of total sulfur (TS), water-soluble sulfate (WSS), adsorbed sulfate (AS), and residual sulfur (RS) in uncultivated surface soils from three southern Chinese provinces (Fujian, Jiangxi, and Guizhou) and one northern Chinese province (Hebei). Values are means with standard deviations shown by vertical bars.

In the four provinces, the mean  $\delta^{34}\text{S}$  values of both WSS and AS were very similar (about  $2.0\text{‰}$ ), much lower than those of RS ( $8.0\text{‰}$ ) and TS ( $6.1\text{‰}$ ) (Fig. 2).  $\delta^{34}\text{S}$  values of both WSS and AS were the lowest in Guizhou Province ( $-2.2\text{‰}$  and  $-2.2\text{‰}$ , respectively). In Jiangxi Province, the lowest  $\delta^{34}\text{S}$  values of both WSS and AS were observed at Nanchang ( $1.4\text{‰}$  and  $1.1\text{‰}$ , respectively) (Fig. 3). Similar  $\delta^{34}\text{S}$  values were found between WSS ( $-6.3\text{‰}$  to  $9.9\text{‰}$ ) and AS ( $-7.1\text{‰}$  to  $8.7\text{‰}$ ) in Jiangxi Province (Fig. 3). The significant linear relationship between the  $\delta^{34}\text{S}$  values of WSS and AS ( $P < 0.0001$ ) showed an intercept of  $-0.0557\text{‰}$  and a slope of  $1.0002$  for all the surface soils (Fig. 4).

At almost all sampling sites in Jiangxi Province and the other three provinces, RS was the most  $^{34}\text{S}$ -enriched among the three S forms in the uncultivated surface soils (Figs. 2 and 3). The highest  $\delta^{34}\text{S}$  value of RS appeared in Jiangxi Province ( $10.4\text{‰}$ ) and the lowest in Guizhou Province ( $5.5\text{‰}$ ) (Fig. 2). The lowest  $\delta^{34}\text{S}$  value of RS in Jiangxi Province surface soils was found at Fengcheng ( $8.2\text{‰}$ ) (Fig. 3).

#### Sulfur isotopes in moss

In Jiangxi Province, the moss samples from Jingdezhen were the most  $^{34}\text{S}$ -enriched ( $7.1\text{‰}$ ) while those from Fengcheng were the most  $^{34}\text{S}$ -depleted ( $-3.3\text{‰}$ ) (Fig. 3). The mean  $\delta^{34}\text{S}$  value of mosses in the

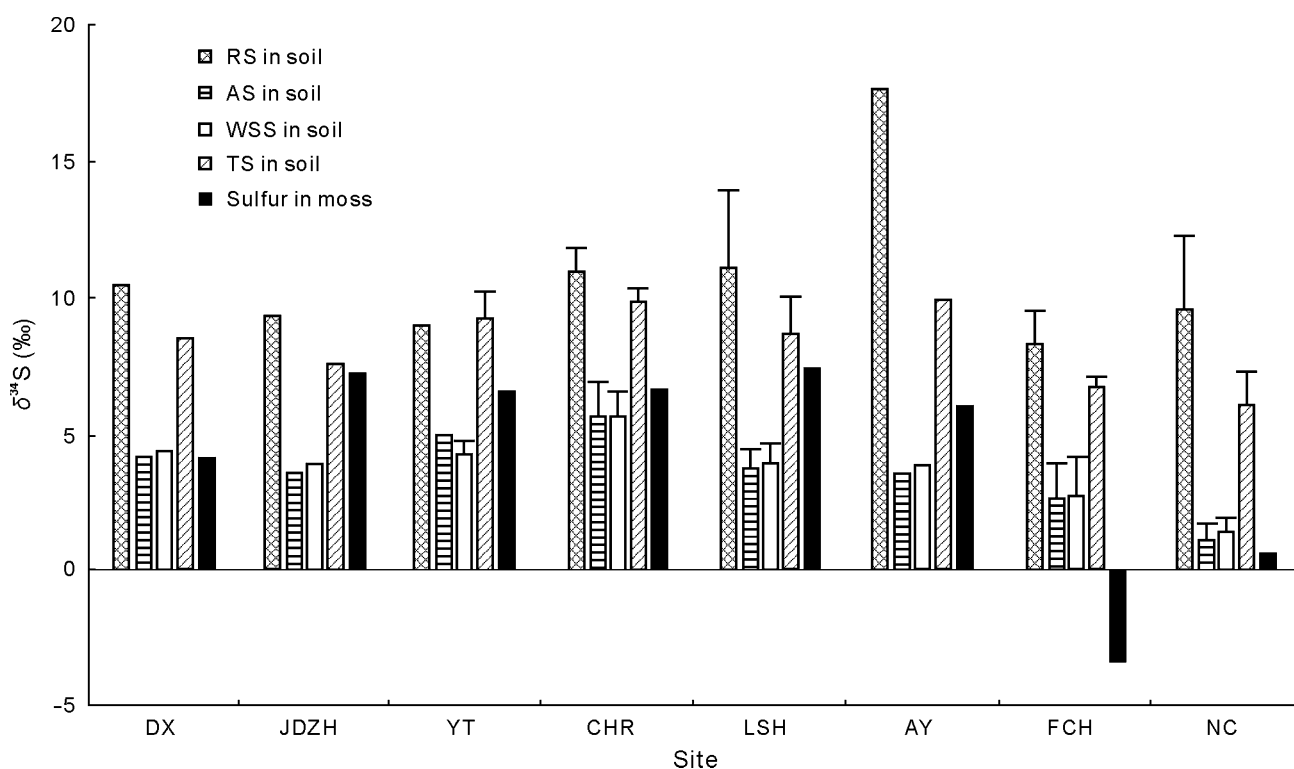


Fig. 3  $\delta^{34}\text{S}$  values of total sulfur (TS), water-soluble sulfate (WSS), adsorbed sulfate (AS), and residual sulfur (RS) in uncultivated surface soils and mosses from nine selected sites of Jiangxi Province. DX = Dexing; JDZH = Jingdezhen; YT = Yingtan; CHR = Chongren; LSH = Lushan; AY = Anyi; FCH = Fengcheng; NC = Nanchang. Values are means with standard deviations shown by vertical bars.

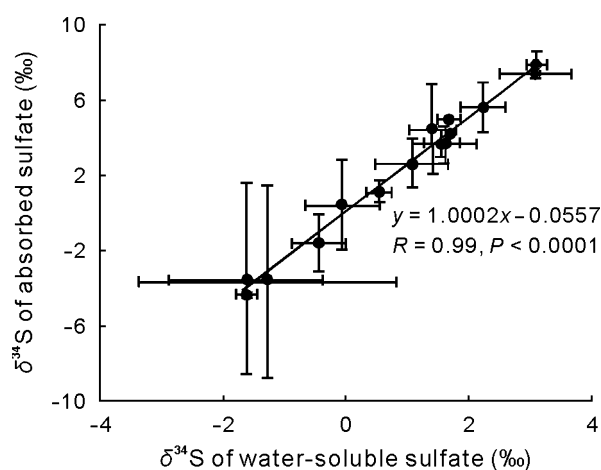


Fig. 4 Correlation between the  $\delta^{34}\text{S}$  values of water-soluble and adsorbed sulfate in uncultivated surface soils from three southern Chinese provinces (Fujian, Jiangxi, and Guizhou) and one northern Chinese province (Hebei). Values are means with standard deviations shown by bars.

province was 4.4‰. At Guiyang in Guizhou Province, mosses showed lower  $\delta^{34}\text{S}$  values, with a mean of  $-0.4\text{‰}$  (data not shown).

#### *Correlations among S concentrations and isotopes in uncultivated surface soil*

The results of correlation analysis among the S con-

centrations and isotopes in the uncultivated surface soils are given in Table II. For correlations between the concentrations, the highest correlation coefficient existed between TS and RS ( $R = 0.97$ ,  $P < 0.001$ ). A weak correlation was also found between TS and WWS or TS and AS, but no concentration correlations of RS with WWS or AS were observed. The isotope correlation analysis results showed that TS was highly correlated with WWS, AS, and RS ( $R = 0.77 - 0.84$ ,  $P < 0.001$ ). The highest isotope correlation coefficient was observed between WWS and AS ( $R = 0.99$ ,  $P < 0.001$ ), indicating that S isotopes of WWS were in some kind of equilibrium with those of AS.

Moderately high negative correlations existed between concentrations and isotopes for TS, WWS, AS, and RS ( $R = -0.55 - 0.67$ ,  $P < 0.001$ ). Concentrations of both TS and WWS also showed moderately high negative correlations with isotopic values of other S forms ( $R = -0.44 - 0.63$ ,  $P < 0.001$ ).

#### *Sulfur isotopic comparison of soils, rainwater and mosses*

The isotopic relationships of soil S species with rainwater sulfate were analyzed as shown in Fig. 5. The  $\delta^{34}\text{S}$  values of rainwater sulfate were found to be significantly linearly correlated with those of both WWS

TABLE II

Matrix of correlation coefficients ( $R$ ) between the sulfur concentrations and  $\delta^{34}\text{S}$  values in uncultivated surface soils from three southern Chinese provinces (Fujian, Jiangxi, and Guizhou) and one northern Chinese province (Hebei)

Item	Concentration				$\delta^{34}\text{S}$ value			
	Total sulfur	Water-soluble sulfate	Adsorbed sulfate	Residual sulfur	Total sulfur	Water-soluble sulfate	Adsorbed sulfate	Residual sulfur
Concentration	Total sulfur	1						
	Water-soluble sulfate	0.39*	1					
	Adsorbed sulfate	0.42*	0.25	1				
	Residual sulfur	0.97***	0.24	0.22	1			
$\delta^{34}\text{S}$ value	Total sulfur	-0.67***	-0.68***	-0.55*	-0.32	1		
	Water-soluble sulfate	-0.44***	-0.61***	-0.51**	-0.22 <sup>ns</sup>	0.78***	1	
	Adsorbed sulfate	-0.47***	-0.63***	-0.57***	-0.21 <sup>ns</sup>	0.77***	0.99***	1
	Residual sulfur	-0.62***	-0.62***	-0.30	-0.56**	0.84***	0.43*	0.43*

\*, \*\*, \*\*\*Significant at the 0.05, 0.01, and 0.001 levels of probability, respectively.

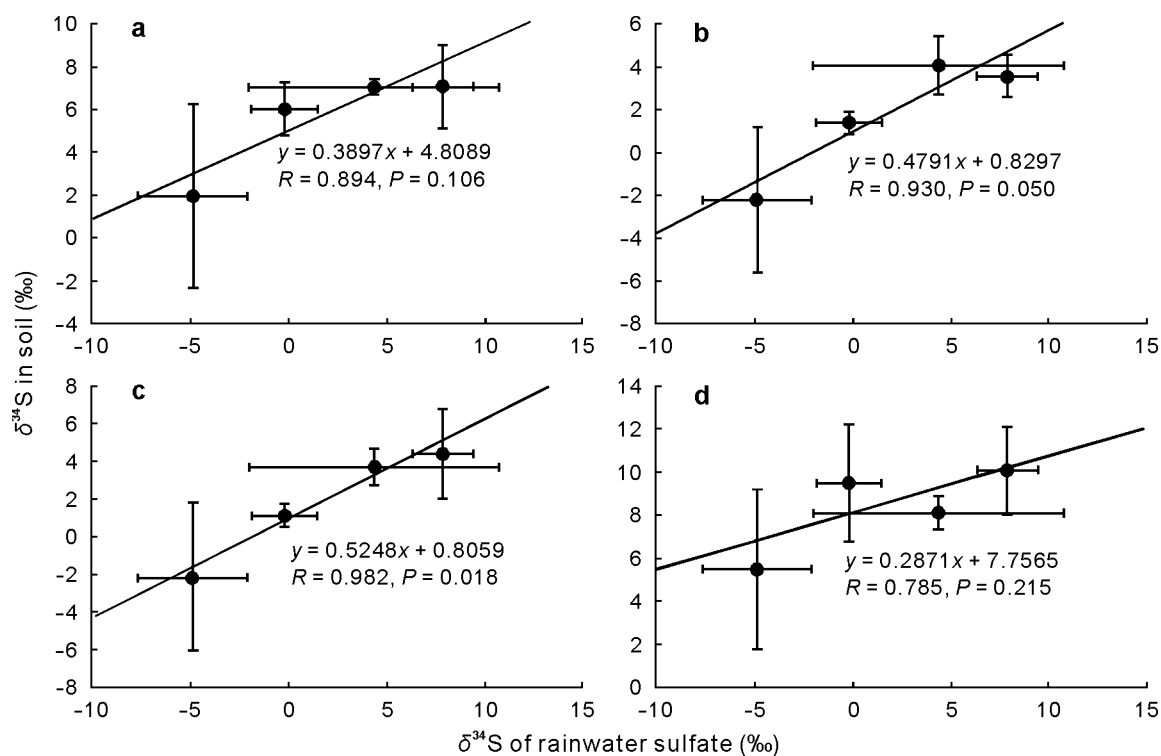


Fig. 5 Relationships of the  $\delta^{34}\text{S}$  values of rainwater sulfate with those of total sulfur (a), water-soluble sulfate (b), adsorbed sulfate (c), and residual sulfur (d) in uncultivated surface soils from three southern Chinese provinces (Fujian, Jiangxi, and Guizhou) and one northern Chinese province (Hebei). Values are means with standard deviations shown by bars.

( $R = 0.930$ ,  $P = 0.05$ ) (Fig. 5b) and AS ( $R = 0.982$ ,  $P = 0.018$ ) (Fig. 5c) in the surface soils. This suggested that rainwater sulfate was an important source for soil WSS and AS. The slopes of both the linear correlations (soil/rainwater isotopic ratio) were about 0.5, indicating the existence of a  $^{34}\text{S}$ -depleted sulfate source. There were no significant correlations between isotopic values of rainwater sulfate and TS (Fig. 5a) or RS (Fig. 5d).

Owing to the very limited S isotopic data of rainwater sulfate in Jiangxi Province, we could not study the isotopic correlations between rainwater sulfate and

soil S for all the studied sites. However, we can analyze the isotopic correlations between mosses and soil S for all the studied sites, as shown in Fig. 6. Similar to that with rainwater sulfate, WSS and AS in the surface soils were significantly isotopically correlated with mosses (Fig. 6b, c). The soil/moss isotopic ratio of about 0.6 was obtained according to the correlation, close to that between soil S and rainwater sulfate. We did not find significantly isotopic correlations between mosses and RS ( $P > 0.05$ ) (Fig. 6d), but significant S isotopic correlation between mosses and TS existed ( $P = 0.0047$ ) (Fig. 6a).

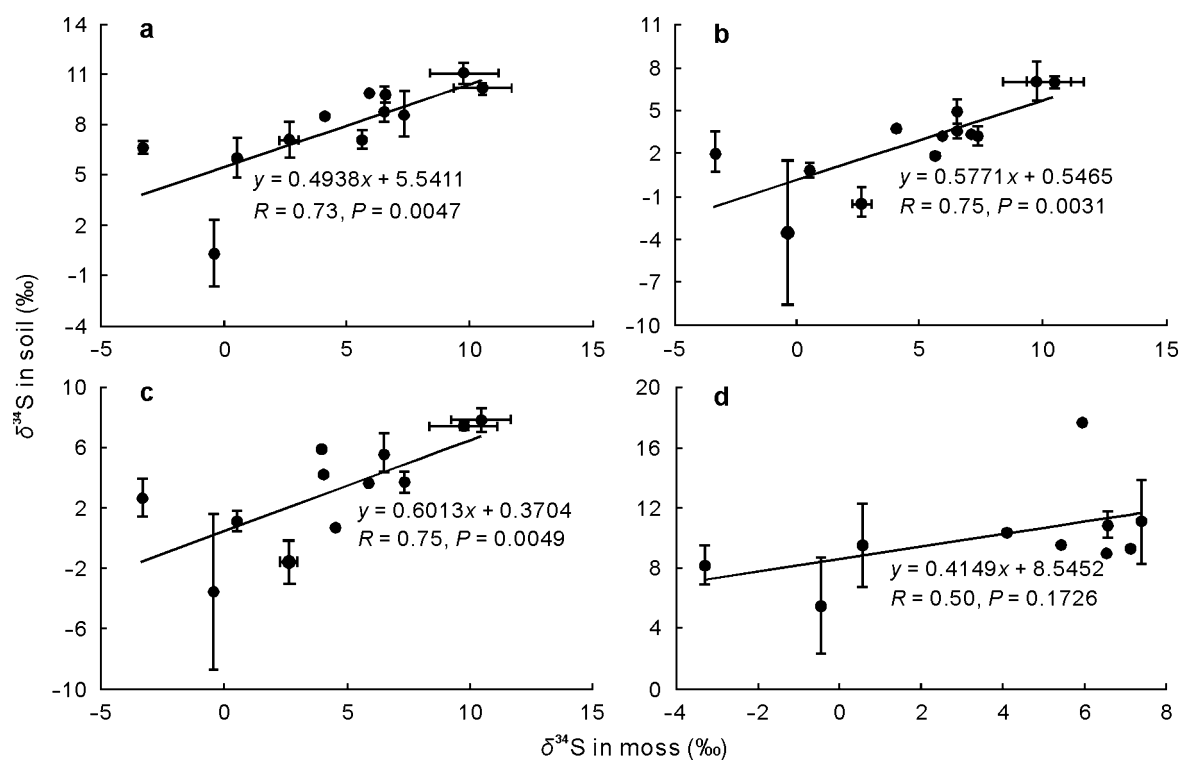


Fig. 6 Relationships of the  $\delta^{34}\text{S}$  values of mosses with those of total sulfur (a), water-soluble sulfate (b), adsorbed sulfate (c), and residual sulfur (d) in uncultivated surface soils from three southern Chinese provinces (Fujian, Jiangxi, and Guizhou) and one northern Chinese province (Hebei). Values are means with standard deviations shown by bars.

## DISCUSSION

Precipitation is an important factor controlling S distribution and leaching losses (Hinckley *et al.*, 2008). The significantly higher (WSS+AS)/TS ratio in the northern Chinese province (Hebei Province) than in the southern Chinese provinces may be due to more WSS and AS retention in the soils in the northern Chinese area, where precipitation is lower (Table I). Similar results in Chinese soils were also found by other researchers (Liu *et al.*, 1990; Sun *et al.*, 1997).

The higher WSS+AS concentrations observed in Guizhou Province relative to other provinces (Fig. 1) may be associated with higher atmospheric S deposition in the province (Table I). Alewell and Novák (2001) argued that adsorbed inorganic sulfate becomes an important soil S species in forested systems if soils receive high S deposition rates. Gustafsson (1996) observed elevated concentrations of water-extractable sulfate in Norwegian and Finnish soils situated close to high  $\text{SO}_2$ -emission smelters. In the Kola Peninsula, increased concentrations and a higher proportion of water-extractable sulfate were found in the most polluted B- and C-horizons (Kashulina and Reimann, 2001). The much higher wet deposition of sulfate in Guizhou Province than in other provinces

as listed in Table I was likely the explanation for the higher (WSS+AS)/TS ratio that was found at Guiyang (Fig. 1).

Alewell and Novák (2001) reported that the  $\delta^{34}\text{S}$  values of inorganic sulfate in the top 5 cm soils were very similar to those of TS and the organic S at the upland site Coulissenhieb and at the fen site Schlöppnerbrunnen in Germany. Our study in all the four provinces, however, agrees well with those of Chae and Krouse (1987), Schoenau and Bettany (1989), and Mayer *et al.* (1995a, b) in that the sum of organic S forms was isotopically heavier than inorganic sulfate (Fig. 1) due to preferential release of  $^{32}\text{S}$  during mineralization (Norman *et al.*, 2002). Although a higher  $\delta^{34}\text{S}$  value of inorganic sulfate at Coulissenhieb (about 4‰) than at Schlöppnerbrunnen (about -1‰) was believed to be related with soil type (Alewell and Novák, 2001), the significant isotopic difference in sulfate between Guizhou Province and the other 3 provinces (Fig. 1) should mainly be caused by a much more  $^{34}\text{S}$ -depleted atmospheric sulfate input in the former (Table I).

The significant linear relationship between the  $\delta^{34}\text{S}$  values of WWS and AS ( $P < 0.0001$ ) gave an intercept of  $-0.0557\text{‰}$  and a slope of 1.0002 (Fig. 4), indicative of a high similarity in  $\delta^{34}\text{S}$  values between WWS and

AS in the uncultivated surface soils (Figs. 2 and 3). This supports the findings of Fuller *et al.* (1986), who reported that sulfate adsorption in soils does not markedly fractionate S. Both field and laboratory data provided by Van Stempvoort *et al.* (1990) also showed that there is no significant isotope fractionation of sulfate during sorption and that field soil sorption enriches dissolved sulfate in  $^{34}\text{S}$  by approximately  $1\% \pm 1\%$  in upland forest Podzols while laboratory sorption of sulfate by prepared goethite gives a mean fractionation factor of 0.3% between adsorbed and dissolved sulfate.

Biologic fractionation can lower the  $\delta^{34}\text{S}$  values of the sulfate deposited into the soils. In fifteen soil pits of northern Czech Republic, Novák *et al.* (2000) found isotopically systematically lighter soil S compared to  $^{34}\text{S}$  of atmospheric input. Their explanation for the isotopic difference was provided by a negative assimilation-related  $^{34}\text{S}$  shift. Novák *et al.* (2003) studied the stable isotopes of soils in five European forest ecosystems and found that assimilation favored the lighter isotope  $^{32}\text{S}$ . Krouse *et al.* (1992) compiled all available data on  $^{34}\text{S}$  ratios of coexisting sulfate and organic S in plants. Their conclusion is consistent with that of Novák *et al.* (2001) in that plant tissues prefer the light isotope  $^{32}\text{S}$  by 2%, with the resulting sulfate sulfur isotopically heavier. It was very reluctant in this study for the small assimilation-related discrimination to be used to explain the large isotopic differences between inorganic sulfate (WSS or AS) and RS (Fig. 2). In addition, as shown in Fig. 3, however, the lower  $\delta^{34}\text{S}$  values of sulfate should not be caused by assimilation-related discrimination because RS (primarily organic S, the product) was the most  $^{34}\text{S}$ -enriched while the WSS or AS (the resulting sulfate) was the most  $^{34}\text{S}$ -depleted.

The atmospheric sulfate input was, as discussed above, an important source of inorganic sulfate in the uncultivated surface soils. The result was also confirmed by the S isotope correlation between WSS (or AS) and rainwater sulfate (Fig. 5b, c). Similar results were also reported in other areas. For instance, at the Hubbard Brook Experimental Forest (HBEF) in the White Mts. of New Hampshire,  $\delta^{34}\text{S}$  values of adsorbed plus soluble sulfate averaged  $4.3\% \pm 3.4\%$  across all horizons (Fuller *et al.*, 1986), similar to the  $\delta^{34}\text{S}$  measurements of summer bulk precipitation and aerosols from HBEF (2.3% to 3.0% and 0.8% to 3.5%, respectively) (Saltzman *et al.*, 1983). Mayer *et al.* (1995a, b) also observed that the  $\delta^{34}\text{S}$  values of inorganic sulfate in five acid forest soils of southern Germany generally fall in the range of those of precipitation sulfate. Winner *et al.* (1978) found that the  $\delta^{34}\text{S}$  values

of soil S increased from  $-9\%$  at the beginning of transfer to a higher  $\text{SO}_2$ -stress site to  $25\%$ – $10\%$  5 months later. The findings were also evidenced by the relationships between isotopic values of soil sulfate and moss tissue S, as shown in Fig. 6b, c. Mosses usually show very similar S isotopic ratios to atmospheric S deposition (Nriagu and Glooschenko, 1992; Xiao *et al.*, 2009) because little isotopic fractionation accompanies S assimilation (Trust and Fry, 1992).

The isotopic values of soil TS was found to be correlated with those of moss tissue S in this study (Fig. 6a), suggesting that atmospheric S deposition was a controlling factor on variation of soil  $\delta^{34}\text{S}$ . However, no correlation was observed between isotopic values of soil TS and rainwater sulfate in this study (Fig. 5a), unlike those in Québec (Marty *et al.*, 2011) and in northern Ireland (Stack and Rock, 2011). The weak relationship between isotopic values of soil TS and rainwater sulfate in this study may be because of a different sampling time of soils and rainwater (Table I) and also because moss tissue S indicates total atmospheric S deposition (Liu *et al.*, 2009) while rainwater sulfate is only a portion of total deposition.

Previous investigations have shown that inorganic sulfate in surface soils can be derived from two major sources: deposited sulfate and mineralization of soil organic S because of the low or insignificant contribution of weathering of S-containing minerals such as gypsum (Houle and Carignan, 1995). Soil sulfate (WSS or AS)/moss isotopic ratio of 0.4–0.6 in this study (Fig. 6b, c) suggested that inorganic sulfate in the uncultivated surface soils was not purely derived from atmospheric input, and its  $\delta^{34}\text{S}$  should be a result of mixing of deposited atmospheric sulfate with a  $^{34}\text{S}$ -depleted sulfate component possibly from mineralization of RS because of preferential release of  $^{32}\text{S}$  from organic S during mineralization (Novák *et al.*, 1996).

## CONCLUSIONS

The four Chinese provinces selected in this study for identifying the sources of S species in uncultivated surface soils had much different S isotopes of atmospheric deposition. The WSS concentrations in the surface soils were lower than those of AS and RS. The mean  $\delta^{34}\text{S}$  values of WSS and AS were similar, lower than those of RS and TS. Lower precipitation helped retaining more WSS and AS in the northern Chinese province soils, while higher wet sulfate deposition resulted in the higher (WSS+AS)/TS ratios in the soil from Guizhou Province. The lowest  $\delta^{34}\text{S}$  values of all S species in the soil of Guizhou Province were consis-



tent with those of the most  $^{34}\text{S}$ -depleted rainwater sulfate at Guiyang. Small S isotope fractionation of sulfate during sorption in soils was confirmed by a significant linear correlation between the  $\delta^{34}\text{S}$  values of AS and WWS ( $y = 1.0002x - 0.0557$ ,  $P < 0.0001$ ). The  $\delta^{34}\text{S}$  values of sulfate in rainwater and moss were significantly linearly correlated with those of both WWS and AS in surface soils, but the slopes of all these significant linear correlations were 0.4–0.6, suggesting that inorganic sulfate in the surface soils should be a result of mixing of deposited atmospheric sulfate with a more  $^{34}\text{S}$ -depleted sulfate component possibly from mineralization of RS.

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