



Sulfur isotopic signatures in rainwater and moss *Haplocladium microphyllum* indicating atmospheric sulfur sources in Nanchang City (SE China)

Hua-Yun Xiao*, Ren-Guo Zhu, Bi-Na Lin, Cong-Qiang Liu

State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

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ABSTRACT

Sulfur source identification previously reported has been based on sulfur isotopic ratios in either rainwater or mosses. The $\delta^{34}\text{S}$ values of rainwater sulfate and the epilithic moss *Haplocladium microphyllum* in Nanchang region (China) were determined for comparisons and used to delineate atmospheric sulfur sources. At the urban and rural sites, similar mean $\delta^{34}\text{S}$ values were observed between rainwater sulfate (+1.6‰ and -0.2‰, respectively) and epilithic mosses (+1.7‰ and +0.6‰, respectively), suggesting that mosses acquire $\delta^{34}\text{S}$ values similar to those found for rainwater sulfate. This has further demonstrated that moss $\delta^{34}\text{S}$ signatures hold valuable source-specific information as rainwater $\delta^{34}\text{S}$ values do. The $\delta^{34}\text{S}$ values of both rainwater sulfate and epilithic mosses indicated that atmospheric sulfur in Nanchang region was mainly associated with coal combustion. The lower $\delta^{34}\text{S}$ values at the rural site can be explained by higher contribution of local coals (lower $\delta^{34}\text{S}$ values relative to those of north Chinese coals) and biogenic sulfur.

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1. Introduction

Sulfur in the atmosphere occurs in a variety of gaseous, liquid and solid chemical forms. In remote regions, natural sources such as biogenic emissions in the form of dimethyl sulfide (DMS) and H_2S , volcanic SO_2 , and sea salt sulfate are the dominant origins of atmospheric sulfur compounds (Nriagu et al., 1987; Yang et al., 1996; Shooter, 1999). Major inputs in heavily industrialized areas are anthropogenic SO_2 mainly due to the combustion of fossil fuels in the form of coals (Kellogg et al., 1972; Li et al., 1999; Mukai et al., 2001). SO_2 plays an important role in the development of acid rain. Deposition of acid compounds from the atmosphere has increased in some Chinese areas during recent decades (e.g. Lü and Tian, 2007). High sulfur deposition has resulted in sulfur accumulation in forest soils, which will further acidify surface waters (Duan et al., 2000).

Since numerous potential sources likely exist, it is vital to be able to distinguish them from each other in a given area in order to assess their relative impacts. The atmospheric sulfur isotope ratio ($\delta^{34}\text{S}$) may hold source-specific information that can serve as a fingerprint to identify sulfur sources. The $\delta^{34}\text{S}$ values of anthropogenic emissions in industrial and consumer processes generally show a wide range depending on the nature of the source (coal, oil, or natural gas): petroleum natural gas, -20 to +30‰; coal, -35 to +30‰ (Nielsen, 1978). The $\delta^{34}\text{S}$ values of Chinese coals at different localities also show wide variations, while specific individual coal deposits are relatively

uniform in isotopic ratios (Hong et al., 1993). Flue gas desulfurization affects the isotopic composition of the emitted SO_2 and particulates. For instance, Derda et al. (2007) showed that during desulfurization process (wet limestone method), sulfur in the outlet gases has lower $\delta^{34}\text{S}$ values ($-4.03 \pm 0.03\%$) and the by-product from this process (gypsum: $\pm 2.29 \pm 0.03\%$) has higher $\delta^{34}\text{S}$ values than the SO_2 at the inlet ($\pm 1.56 \pm 0.03\%$).

The $\delta^{34}\text{S}$ average of sea spray sources is around +21‰ (Rees et al., 1978) while most of the biogenic emissions are isotopically lighter (-10 to -2‰; Liu et al., 1996; Panettiera et al., 2000; Zhang et al., 2010). Moreover, atmospheric isotopic signatures can tell us about mixing processes, oxidation processes, transport pathways and deposition of sulfur in the environment (Ohizumi et al., 1997; Leung et al., 2001; Xiao and Liu, 2002; Pruet et al., 2004; Sinha et al., 2008). Atmospheric oxidation of SO_2 occurs by both heterogeneous and homogeneous paths. Homogeneous oxidation of SO_2 results in isotopically lighter sulfate S (Tanaka et al., 1994), in contrast to heterogeneous oxidation which results in isotopically heavier sulfate S (Eriksen, 1972).

In acid rain regions where more intensive study has occurred, rainwater sulfate sources are better understood through sulfur isotopic signatures. Considerable previous studies on rainwater sulfur isotopes have suggested that coal burning makes a significant contribution to rainwater sulfate in most southern Chinese cities (Xiao and Liu, 2002; Zhang et al., 2010). In addition to the well-established coal source for rainwater sulfate, previous works have indicated an important contribution of biogenic sulfur (BS) in some urban regions (Zhang et al., 1995; Yao et al., 2003; Zhang et al., 2010; Liu, 2007). For instance, Zhang et al. (1995) reported that coal

* Corresponding author.

E-mail address: xiaohuayun@vip.skleg.cn (H.-Y. Xiao).

combustion and BS contributed about 43% and 46%, respectively, to rainwater sulfate in Guangzhou area based on isotopic mass balance. Yao et al. (2003) found that sulfur isotopic values of rainwater sulfate were higher in winter than in summer in Hengyang and attributed it to higher contribution of BS in summer.

In addition to those in atmospheric samples, measurements of sulfur isotopic ratios in mosses have been exploited in the study of atmospheric sulfur pollution (Nriagu and Glooschenko, 1992; Bottrell and Novak, 1997; Novák et al., 2001a,b; Xiao et al., 2009; Migaszewski et al., 2010). We also used moss sulfur isotopic ratios to indicate atmospheric sulfur sources in some southern Chinese mountainous areas (Xiao et al., 2008).

At present, almost all previous studies were focused on sulfur isotopic ratios in either rainwater (e.g. Panettiarea et al., 2000; Xiao and Liu, 2002) or mosses (e.g. Xiao et al., 2008, 2009). To our knowledge, source identification based on sulfur isotopic ratios in both rainwater and mosses has not been reported previously. So, the aims of this work were firstly, to compare the $\delta^{34}\text{S}$ values of rainwater sulfate and epilithic mosses in Nanchang region and, secondly, to identify sulfur sources in the atmosphere using sulfur isotopes in rainwater and mosses.

2. Materials and methods

2.1. Study area description

In Nanchang region (S China) acid rain has been observed since the 1980s. The SO_2 emission rates slightly increased as a result of the expansion of coal consumptions from 2000 to 2006 (Fig. 1). Although ambient SO_2 concentration averaged only $56 \mu\text{g}/\text{m}^3$ in the city, almost all of the rainwater was found at $\text{pH}<5$ in 2006 (Nanchang Environmental Protection Bureau, 2007). The major sulfur pollution source is Nanchang Power Plant (NPP) which is located in the north direction and about 2 km away from the north campus of Nanchang University (NNU). Due to shortage of local coals, coals from northern China are introduced for combustion in NPP. The predominant wind direction is southerly in summer and northerly in winter in the Nanchang region.

One site in the urban area (NNU) and one site in the rural area (QH) were chosen for rainwater collection, both of which lie in Nanchang University (Fig. 2). Besides the above two sites, one site in a clean area (ML) was also chosen for moss sampling for comparisons. Both local coals ($\delta^{34}\text{S}$: $-5.8 \pm 1.7\%$) and northern Chinese coals ($\delta^{34}\text{S}$: $+9.7 \pm 5.2\%$) were combusted in the city (Xiao et al., 2009). The sampling site in the Meiling forest (ML) is >20 km away from the urban area.

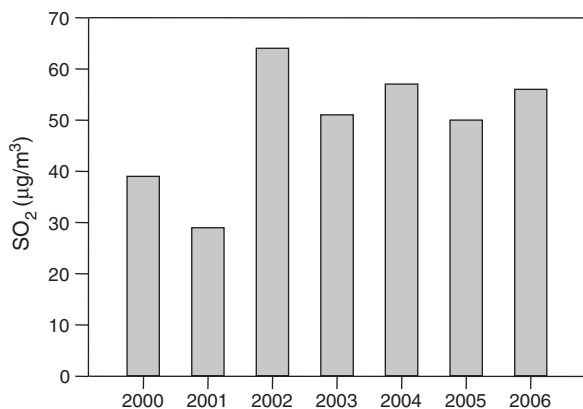


Fig. 1. Temporal changes of ambient SO_2 from 2000 to 2006 in Nanchang City.

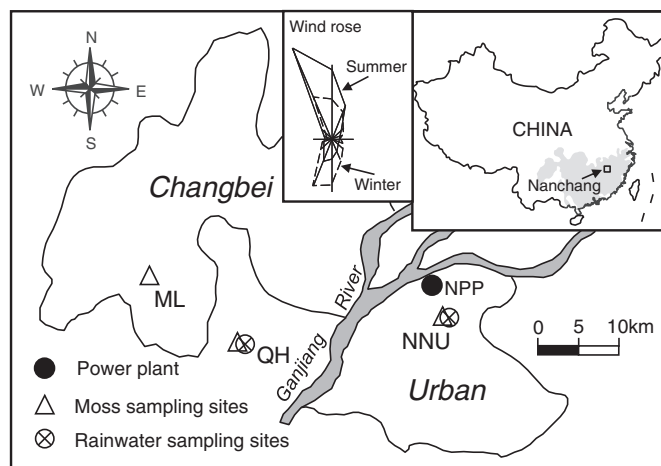


Fig. 2. Map of China showing the sampling sites of rainwater and mosses in Nanchang region. ML—Meiling forest; QH—Qianhu campus of Nanchang University; NNU—north campus of Nanchang University; NPP—Nanchang Power Plant. Wind rose of Nanchang region is also presented. The shaded regions represent areas where acid rain was measured ($\text{pH}<5$) in 2004 (revised from China Environmental Protection Bureau, 2005).

2.2. Sample collection methods

Rainwater samples were collected on building roofs of Nanchang University in the whole year of 2007. In order to collect enough water samples for isotope analysis, a sampler with a large polyethylene sheet ($1.5 \text{ m} \times 2 \text{ m}$) served as the collection device. Prior to use, the polyethylene sheet was cleaned with 2 N HCl solution and rinsed with Milli-Q water, and dried. Then a hole of 2 cm in diameter was punched in the center of the sheet. The polyethylene sheet was fastened 1.5 m upon the floor by a stainless bracket beforehand. Between rains, the polyethylene sheet was closed to avoid dry deposition and other contaminations. After collection, the samples were immediately filtered to exclude material greater than $0.45 \mu\text{m}$ using Whatman acetate membrane filters. A small aliquot of these filtered samples was stored in brown clean plastic bottles for chemical determination, while other aliquots were stored at 4°C for isotopic analysis after poisoned by $\text{HgCl}_2(\text{s})$.

The moss materials (*Haplocladium microphyllum*) at all studied sites were collected in the spring and summer of 2006–2007. Urban mosses were mainly collected around parks or hills. The sampling sites in the rural areas were selected to be located in open habitats like heaths or clearings and at least 500 m away from main roads and at least 100 m away from other roads or houses. All mosses were obtained from natural rocks without canopies or overhanging vegetation ensuring no influenced from throughfall sulfur compounds. 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. Only green, healthy samples were taken, avoiding yellow or dark samples.

2.3. Sample analytical methods

All rainwater samples were acidified at $\text{pH}<2$ with 2 mol/L HCl solution, then sulfate was recovered from rainwater by precipitating as BaSO_4 with enough 2 mol/L BaCl_2 solution. After precipitating for 24 h, the mixture was filtered through $0.22 \mu\text{m}$ acetate membrane filters.

Using the treatment method by Liu et al. (2007), moss samples were gently rinsed with 1.5 mol L^{-1} HCl solution, then sonicated and washed with deionized water for several times. All 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. Moss sulfur contents were measured by an elemental analyzer (Model PE-2400 II, USA) with an analytical precision of 1%.

Moss samples were oxidized in a Parr bomb to convert all forms of sulfur present to sulfate. To assure complete conversion, hydrogen peroxide was added to all washings. Sulfate was recovered from moss washings by precipitating as BaSO₄ with enough 2 mol/L BaCl₂ solution. After precipitating for 24 h, the mixture was filtered through a 0.22 μm acetate membrane filter.

The precipitates (BaSO₄) on the filters collecting from rainwater or mosses were carefully rinsed with enough Milli-Q water to remove Cl⁻, and then transferred into crucibles with the filters and combusted at 800 °C for 40 min in the air. In order to determine the composition of white powder in the crucible, it was analyzed with X-ray diffractometry. The results showed >99% BaSO₄ in the powder. Thermal decomposition of BaSO₄ (Yanagisawa and Sakai, 1983) was conducted to prepare SO₂ for sulfur isotopic analysis in a Finnigan MAT-252 mass spectrometer. The standard deviation for the δ³⁴S analysis of NBS127 (barium sulfate) was better than ±0.2‰ (n=5).

Measurement of rainwater ion concentrations was conducted on ion chromatography (Dionex, ICS-90) with a detection limit of 0.01 mg/L. Tissue sulfur contents of mosses were determined by elemental analyzer (PE2400II, USA) with an analytical precision of 1%.

2.4. Statistical analysis

Statistical analysis was conducted by SPSS 11.5 statistical program, and graphs were mainly created with SigmaPlot 2000 software (both SPSS Science, Chicago, USA). Differences in sulfur contents and δ³⁴S values between sampling sites were tested for significance by using a one-way analysis of variance (ANOVA) procedure, and least significant differences (LSD) were used by a Tukey–HSD test to compare significant differences (at the 95% confidence level). Differences were considered significant at P<0.05.

3. Results

3.1. Sulfate concentrations and sulfur isotopic signatures in rainwater

Sulfate concentrations in rainwater at NNU ranged from 1.6 mg/L to 36.2 mg/L, with an average of 13.7 ± 11.1 mg/L. Relative to those at the urban site, as expected, rainwater sulfate concentrations at the rural site (QH) were significantly lower and had an average of 6.5 ± 5.1 mg/L (1.2–22.8 mg/L). This suggested that the atmosphere over the urban site was more seriously polluted by ambient SO₂ than that over the rural site.

The average rainwater δ³⁴S value at the rural site (QH) was about -0.2‰, significantly more negative (p<0.05) than that at the urban site (NNU: +1.6‰), possibly due to the difference in source contribution. As shown in Fig. 3, in rainwater having high sulfate concentrations, the δ³⁴S values were found between 0‰ and +3‰ at NNU and between -0.5‰ and +1‰ at QH.

3.2. Sulfur contents and sulfur isotopic signatures in mosses

Tissue sulfur contents of epilithic mosses in Nanchang region varied widely from 0.18% to 0.52%, with a mean of 0.29 ± 0.10%. The mean sulfur content of the urban mosses was 0.45 ± 0.06%, significantly higher (p<0.05) than that of the forested mosses (ML: 0.23 ± 0.03%) (Fig. 4a). And the mean sulfur content of the rural mosses sampled at QH (0.26 ± 0.01%) was significantly lower (p<0.05) than that of the urban mosses while slightly higher than that of the forested mosses (0.23 ± 0.03%).

Most of the epilithic mosses showed positive δ³⁴S signatures except for some sampled at QH (Fig. 4b). Compared to those at the

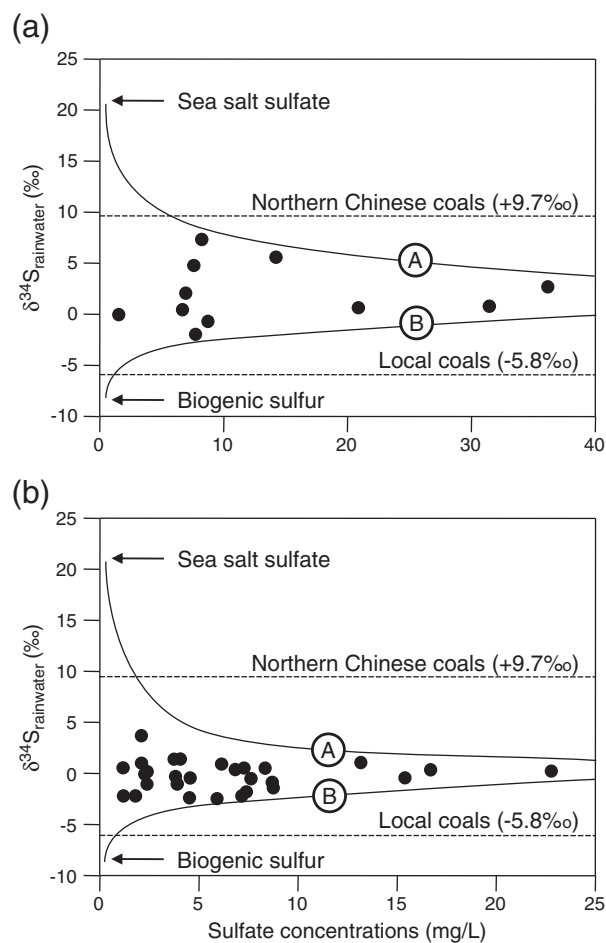


Fig. 3. The δ³⁴S values vs. sulfate concentrations in rainwater at NNU (a) and QH (b) compared to a ternary mixing model. Curve A: mixing between anthropogenic sulfur with a δ³⁴S value of about +3‰ (a) or +1‰ (b) and seawater sulfate with a δ³⁴S value of +21‰; Curve B: mixing between pollutant sulfate with a δ³⁴S value of about 0‰ (a) or -0.5‰ (b) and biogenic sulfur with a δ³⁴S value of -8‰.

forest site (ML: +5.8 ± 1.8‰), epilithic mosses sampled at the rural site (QH: +0.6 ± 0.1‰) and at the urban site (NNU: +1.7 ± 0.8‰) were significantly less ³⁴S enriched (p<0.05). Similar results were also reported by Xiao et al. (2008). But we did not find a significant difference (p<0.05) in the δ³⁴S values between the rural and urban sites in Nanchang region, reflecting the same sulfur sources at the two sites.

4. Discussion

4.1. Sulfur isotopic signatures in rainwater indicating atmospheric sulfur sources

The sulfur isotopic signatures of rainwater sulfate may be used to delineate anthropogenic sulfur in the atmosphere, provided the isotopic composition of pollutant sulfur is distinct from that of sulfur from natural sources (Xiao and Liu, 2002). In China, identification of atmospheric sulfur sources in rainwater has been conducted mainly in the acid rain regions through sulfur isotope analysis (Zhang et al., 1995; Xiao and Liu, 2002; Yao et al., 2003; Zhang et al., 2010). Usually the sulfur isotopic values of rainwater sulfate are altered by oxidation of SO₂ and different contribution of sulfur sources (e.g. coal burning, biogenic sulfur, etc.). These are discussed as follows:

After SO₂ is emitted into the atmosphere from coal combustion, sulfur isotope fractionation occurs during heterogeneous and homogeneous oxidation of SO₂ (e.g. Leung et al., 2001; Mukai et al., 2001;

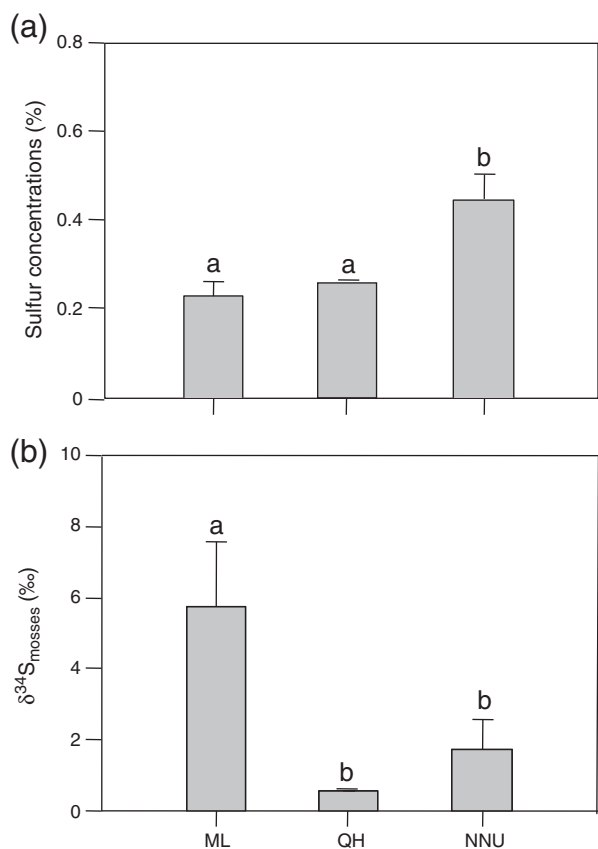


Fig. 4. Between-site comparisons of sulfur contents (a) and the $\delta^{34}\text{S}$ values (b) in mosses. ML—Meiling forest; QH—Qianhu campus of Nanchang University; NNU—north campus of Nanchang University. Different letters above the bars indicate a significant statistical difference between means at the level of $p < 0.05$.

Sinha et al., 2008). Homogeneous oxidation is accompanied only by a kinetic isotope effect, which leads to accumulation of isotopically lighter S in the resulting sulfate (^{32}S reacts faster than ^{34}S ; $\alpha = 0.991$ at 25 °C; Tanaka et al., 1994) whereas heterogeneous oxidation is accompanied by a large equilibrium fractionation, resulting in isotopically heavier S accumulating in the droplets (heavier S in the product; $\alpha = 1.0165$ at 25 °C; Eriksen, 1972). In South China, heterogeneous oxidation of SO_2 usually prevails in the atmosphere (e.g. Zhang et al., 2010). Therefore, preferential oxidation of the $^{34}\text{SO}_2$ will lead to a gradual depletion of the residual SO_2 and gradually the sulfate formed by the oxidation of the depleted SO_2 in the air mass during transport. However, because QH is located west to both the NNU and the power plant (NPP) and the predominant wind direction is southerly in summer and northerly in winter in Nanchang region (Fig. 1), the lower isotopic signature at QH than at NNU may not be explained by isotope fractionation during oxidation of SO_2 .

Some previous studies (e.g. Xiao and Liu, 2002; Zhang et al., 2010) have suggested that coal burning makes a significant contribution to rainwater sulfate in most Chinese cities. Isotopic fractionation may be expected in the processes of coal burning when the wet flue gas desulfurization techniques (using lime as a SO_2 adsorbent) are employed (Derda et al., 2007). Because no publications discussed the effect of alternate technology (e.g. the electrostatic precipitator) on the isotopic signature of the remaining flue gas, we cannot draw a conclusion that in these areas coals were combusted without employing flue gas desulfurization techniques. But it is true that many coals were used in daily use stoves for cooking and warming there. Furthermore, Mukai et al. (2001) reported that average sulfur isotope ratios for SO_2 and sulfate in the atmosphere in some Chinese cities were close to those of the coals used in each region. Similar

results were also observed by Kawamura et al. (2001) that the $\delta^{34}\text{S}$ values of the SO_2 collected at Fukuoka (Japan) were close to those of fossil fuels. Therefore, it is reasonable to compare the $\delta^{34}\text{S}$ values of rainwater sulfate with those of coals directly in China. In this study, rainwater $\delta^{34}\text{S}$ values in Nanchang region were observed between those of local coals and northern Chinese coals (Fig. 5), suggesting that both local and northern Chinese coals were combusted in the city. This was supported by the fact that part of coals consumed in Nanchang city was introduced from northern China. Accordingly, an explanation of the more positive rainwater $\delta^{34}\text{S}$ values at NNU than at QH was the higher contribution of northern Chinese coals ($\pm 9.7 \pm 5.2\text{‰}$).

Plots of $\delta^{34}\text{S}$ values vs. sulfate concentrations in rainwater could usually yield further insight into atmospheric sulfur sources (Panettiere et al., 2000). In this study, the plots at NNU and QH produced patterns such as those shown in Fig. 3, where the minor sources are only evident at lower concentrations. The minor sources are sea spray and biological activity as sea spray has a $\delta^{34}\text{S}$ value of about +21‰ (Rees et al., 1978) and the biogenic component shows a $\delta^{34}\text{S}$ value ranging from -10‰ to -2‰ (Liu et al., 1996; Panettiere et al., 2000; Zhang et al., 2010). Because more samples having low sulfate concentrations and low $\delta^{34}\text{S}$ values were found at QH than at NNU (Fig. 3), the significantly more negative rainwater $\delta^{34}\text{S}$ values (-0.2‰) at the rural site (QH) than at the urban site (NNU: $\pm 1.6\text{‰}$) may be also due to higher contribution of biogenic sulfur. The $\delta^{34}\text{S}$ values for rainwater and sea spray are sufficiently distinct to be able to conclude that seawater contributions are negligible. These observations also showed major anthropogenic origins of sulfate in the precipitation at QH and NNU. The dominant anthropogenic source of rainwater sulfate appears to have a nearly constant $\delta^{34}\text{S}$ value between 0‰ and +3‰ which is within the range of -5 to +10‰ observed in Chinese coals (Xiao et al., 2010).

4.2. Sulfur isotopic signatures in mosses indicating atmospheric sulfur sources

As a plant species sensitive to the atmospheric sulfur, mosses have been believed to hold source-specific information that can serve as a fingerprint to identify sulfur sources (Nriagu and Glooschenko, 1992). For instance, in our recently published paper (Xiao et al., 2010), we found that atmospheric sulfur at urban sites was mainly from coal combustion whereas northerly air masses contributed more sulfur to forested sites.

Compared with those at the urban site (NNU) and the rural site (QH), $\delta^{34}\text{S}$ values of mosses at the forested site (ML) were significantly higher (Fig. 5), reflecting an introduction of ^{34}S -enriched sulfur source. Several previous studies showed that natural DMS sources such as biogenic emissions in the form of dimethyl sulfide (DMS) and

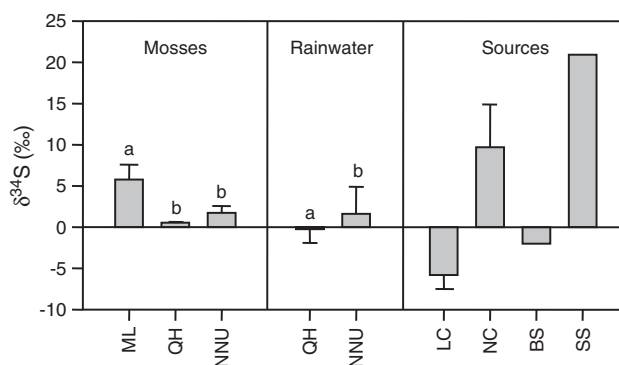


Fig. 5. Comparisons of the $\delta^{34}\text{S}$ values in rainwater, mosses and atmospheric sulfur sources. ML—Meiling forest; QH—Qianhu campus of Nanchang University; NNU—north campus of Nanchang University; LC—local coals; NC—northern Chinese coals; BS—Biogenic sulfur; SS—Sea salt sulfate. The $\delta^{34}\text{S}$ values in coals are cited from Xiao et al. (2010). Different letters above the bars indicate a significant statistical difference between means at the level of $p < 0.05$.

H₂S, volcanic SO₂, and sea salt sulfate are usually important sources of atmospheric sulfur in remote regions (Nriagu et al., 1987; Yang et al., 1996; Shooter, 1999). But these sources except sea salt sulfate could not give rise to the more positive moss δ³⁴S values at ML because among these sources only sea salt sulfate has a high ³⁴S content (+21%; Rees et al., 1978). And biogenic sources also tend to have δ³⁴S values <0‰ (Nriagu et al., 1987; Liu et al., 1996; Panettiera et al., 2000). Although sulfur isotope fractionation occurs during oxidation of SO₂ (e.g. Leung et al., 2001; Mukai et al., 2001; Sinha et al., 2008), it causes a gradual ³⁴S-depletion of the residual SO₂ and gradually the sulfate formed by the oxidation of the depleted SO₂ in the air mass during transport due to preferential oxidation of the ³⁴SO₂, and so it cannot be used to explain the higher δ³⁴S values of mosses at the forested site (ML). In a study on mosses in forests, Xiao et al. (2008) believed that sulfur in northerly air masses would contribute a lot to atmospheric sulfur in the southern Chinese mountains. As sulfur in northerly air masses is usually more ³⁴S enriched than that in southern China, the more positive moss δ³⁴S values at ML (Fig. 5) might be attributed to the contribution of sulfur in northerly air masses.

4.3. Sulfur content and isotopic comparisons between rainwater and mosses

Mosses might show multiple biological responses to changes of atmospheric sulfur, among which sulfur content was an important parameter to reflect the level of atmospheric sulfur deposition (especially gaseous SO₂) because higher atmospheric sulfur directly caused higher tissue sulfur in mosses (Novák et al., 2001a,b; Vingiani et al., 2004). In this study, the tissue sulfur contents of mosses were higher at NNU (0.45%) than at QH (0.26%), correspondent to that higher rainwater sulfate concentrations were observed at the urban site (13.7 mg/L) than at the rural site (6.5 mg/L). A study on epilithic mosses at Guiyang city (SW China) has also approved that it is reliable to use sulfur contents of epilithic mosses in open fields for assessing the level of atmospheric sulfur (Liu et al., 2009).

It has been demonstrated that little isotopic fractionation accompanies sulfur assimilation by mosses as they acquire sulfur from the atmosphere and their rhizines and rhizoids serve mainly for attachment, and they have no cuticles to block atmospheric inputs (Mekhtiyeva et al., 1976; Trust and Fry, 1992; Bragazza et al., 2005). An earlier comparison by Winner et al. (1981) showed that moss sulfur isotope (+24‰) around natural gas smelts closely reflected the influence of SO₂ from smelts (+25‰). A conclusion was also drawn by Nriagu and Glooschenko (1992) that *Sphagnum fuscum* on low hummocks in ombrotrophic bogs acquired δ³⁴S values similar to those found for atmospheric SO₂. It has further been shown by Krouse (1977) and his co-workers (Krouse and Case, 1981) that mosses acquire δ³⁴S values similar to those found for atmospheric SO₂.

As far as we know, no isotopic relationship was reported between mosses and rainwater sulfate in the literature. In this study, the δ³⁴S values of rainwater sulfate at QH and NNU were $-0.2 \pm 1.7\%$ and $1.6 \pm 3.3\%$, respectively, both similar to those of epilithic mosses ($0.6 \pm 0.1\%$ and $1.7 \pm 0.8\%$, respectively) (Fig. 5). At Guiyang city, the δ³⁴S values of epilithic mosses ($-4.2 \pm 0.9\%$) (Liu et al., 2009) were also found not only similar to the δ³⁴S values of SO₂ (-4.3%) reported by Mukai et al. (2001), but also much closer to the δ³⁴S values of rainwater sulfate ($-4.9 \pm 2.8\%$) collected in the same study area in 2001 (Xiao and Liu, 2002) and the average atmospheric δ³⁴S value ($-4.0 \pm 3.6\%$) (Mukai et al., 2001). Similar results were observed at Emei Mountain (SW China) where moss isotopic ratios averaged $+4.6\%$ (Xiao et al., 2009), much closer to the reported mean value of rainwater sulfate ($+4.7\%$) (Yanagisawa et al., 2003). These indicated that moss sulfur isotopic ratios were comparable to those of rainwater sulfate and thereby could reliably reflect rainwater sulfate.

5. Conclusions

This study has determined and compared the δ³⁴S values of rainwater sulfate and epilithic mosses in an acid rain region (Nanchang, China). Some principal conclusions drawn from this study were presented as follows:

- (1) The mean δ³⁴S values of rainwater ($-0.2 \pm 1.7\%$) and epilithic mosses ($+0.6 \pm 0.1\%$) at the rural site (QH) were significantly more negative than those at the urban site (NNU: $+1.6 \pm 3.3\%$ and $+1.7 \pm 0.8\%$, respectively). Similar δ³⁴S values were observed between rainwater sulfate and epilithic mosses at both the urban and rural sites (NNU and QH), suggesting that mosses acquire δ³⁴S values similar to those found for rainwater sulfate and thereby could reliably reflect rainwater sulfate. This has further demonstrated that moss δ³⁴S values hold valuable source-specific information as rainwater δ³⁴S values do.
- (2) The δ³⁴S signatures of both rainwater sulfate and epilithic mosses indicated that the predominant atmospheric sulfur source in Nanchang region was sulfur emissions from coal combustion and little contributions came from sea salt sulfate. Relatively higher contribution of local coals and biogenic sulfur gave rise to more negative δ³⁴S values in both rainwater and mosses at the rural site (QH) than at the urban site (NNU).

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