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Stable sulphur and nitrogen isotopes of the moss *Haplocladium microphyllum* at urban, rural and forested sites

Hua-Yun Xiao*, Cong-Guo Tang, Hong-Wei Xiao, Xue-Yan Liu, Cong-Qiang Liu

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

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ABSTRACT

Elemental (S and N) and isotopic ($\delta^{34}S$ and $\delta^{15}N$) contents in the moss *Haplocladium microphyllum* at urban, rural and forested sites in acid rain area of South China have been analyzed for comparisons to show whether they are different and can be effectively used to identify S and N sources of atmospheric deposition. Average moss S content at rural sites (0.29 ± 0.06%) was found to be in between those at urban (0.35 ± 0.05%) and forested (0.25 ± 0.04%) sites, which are significantly different. Average N contents of urban (2.60 ± 0.56%) and rural mosses (2.84 ± 0.77%) are not significantly different, while both are significantly different to that of forested mosses at most areas, indicating that the atmosphere over rural sites has been polluted by N as seriously as that over urban sites. Nitrogen supply, relative to S supply, was in excess of the requirement for protein synthesis, especially at rural and forested sites. Moss stable isotope signatures have been proven to be effective tools for deciphering atmospheric S and N sources at these sites. Through moss $\delta^{34}S$ signatures, we found that atmospheric S at urban and forested sites was mainly from local coal combustion and domestic biomass burning, respectively, whereas northerly air masses contributed more S to forested sites. The relatively negative moss $\delta^{15}N$ values (−7.5 ± 3.0, −3.4 ± 2.1 and −0.8 ± 2.1‰) demonstrated that the main form in the N deposition was NH_x in these sites. More negative $\delta^{15}N$ signatures in urban mosses (−7.5 ± 3.0‰) indicated the contribution of NH_3 released from untreated city sewage and wastes, while relatively less negative $\delta^{15}N$ for rural and forested mosses (3.4 ± 2.1 and −0.8 ± 2.1‰) was largely derived from agricultural NH_3.

1. Introduction

Deposition of acid compounds and inorganic nitrogen (N) from the atmosphere has increased in some Chinese areas during recent decades (e.g. Lü and Tian, 2007), and there is increasing concern that deposition of these compounds is damaging the ecosystem. Combustion of sulphur containing fossil fuels and certain industrial processes involving sulphur compounds represent the main anthropogenic sources of primary SO_2 present in the atmosphere. Oxidation of H_2S derived mainly from natural processes (volcanic eruptions and forest fires) may produce secondary SO_2 (Saunders and Wood, 1973). Atmospheric NH_4^+ is derived from heterogeneous reactions involving ammonia (NH_3), and the major sources of NH_3 are animal excrement, soil emissions and fertilizer application (Dentener and Crutzen, 1994). The main anthropogenic sources for NO_x emissions are fossil fuel combustion during transport, industry, and energy production.

Sulphur and nitrogen isotope ratios ($\delta^{34}S$ and $\delta^{15}N$) in the atmosphere have been determined at many sites all over the world because they may hold source-specific information that can serve as a fingerprint to identify potential sources and, consequently, to assess the relative contribution and impacts of the different sources (Heaton, 1986; Ohizumi et al., 1997; Novák et al., 2001a; Xiao and Liu, 2002; Pruett et al., 2004; Liu et al., 2009). Moreover, isotopic signatures can give us a better understanding of mixing processes, transport pathways, deposition, and history of atmospheric pollutants in the environment (Krouse, 1977; Xiao and Liu, 2002; Pruett et al., 2004; Gislason and Torssander, 2006; Liu et al., 2008). The $\delta^{34}S$ values of anthropogenic emissions in industrial and consumer processes generally show a wide range depending on the nature of the source (coal, oil, natural gas): petroleum natural gas, −20 to +30‰; coal, −35 to +30‰ (Nielsen, 1978). The $\delta^{34}S$ values of Chinese coals at different localities also show wide variations, while specific individual coal deposits are relatively uniform in isotopic contents (Hong and Zhang, 1992). The $\delta^{15}N$ values of atmospheric N sources ranged from −15 to +10‰, with the oxidized N (NO_x) more positive and the reduced N (NH_x) more negative (Moore, 1977; Freyer, 1978; Heaton, 1987, 1990; Xiao and Liu, 2002).

* Corresponding author. Fax: +86 851 5891609.
E-mail address: xiaohuayun@vip.skleg.cn (H.-Y. Xiao).

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Mosses, being sensitive to both acid deposition and N fertilization, have been shown to be outstanding bioindicators in a wide range of air pollution studies (Hutchinson and Scott, 1988; Nygaard and Abrahamsen, 1991; Hicks et al., 2000; Pitcairn et al., 2001). This is due to physiological properties of the mosses: lacking a cuticle, a large absorbing surface and thus effectiveness in absorbing soluble and insoluble mineral nutrients from ambient air and precipitation with little subsequent loss (Gerdol et al., 2002; Liu et al., 2007).

Nriagu and Glooschenko (1992) found that terrestrial mosses acquire $\delta^{34}S$ values similar to those found for atmospheric SO_2. A research on some Chinese urban and forested mosses showed the conformity of moss isotopic ratios with rainwater isotopic ratios (Xiao et al., 2009). For example, at Emei Mountain moss S isotopic ratios averaged +4.63‰, comparable to the reported mean value of rainwater sulphate (+4.68‰) (Yanagisawa et al., 2003). In a study on mosses in forests, a $\delta^{34}S$ increase from the south to the north was found just like that for coal $\delta^{34}S$ (Xiao et al., 2008). All of these suggest that mosses preserve the average isotopic signals of atmospheric S and thus isotopic ratios in mosses can be used to discriminate atmospheric sulphur sources, possibly because little isotopic fractionation accompanies S assimilation (Mektiyeva et al., 1976; Trust and Fry, 1992). Compared with direct analysis of $\delta^{15}N$ in atmospheric N deposition, moss $\delta^{15}N$ was assumed as an integrator of the isotopic signatures of atmospheric N sources. In the light of the direct influx of N to living moss cells, isotopic fractionation during N uptake has been assumed to be absent or very low for mosses (Bragazza et al., 2005). Accordingly, the different $\delta^{15}N$ signatures of reactive N forms in the atmosphere (see, e.g., Heaton, 1986) would make isotopic composition of mosses a reliable monitor of N emission sources (Liu et al., 2008).

Some previous studies have reported moss $\delta^{34}S$ values at urban and forested sites (Xiao et al., 2008, 2009) and moss $\delta^{15}N$ values at urban sites (Liu et al., 2008), but much less work has been carried out on systematic investigation of moss S and N isotopes at urban, rural and forested sites of South China where acid rain and high atmospheric NH_x deposition were found (Galloway et al., 1996). In this study, we aim to assess the potential of using moss stable isotope signatures to identify sources of atmospheric S and N deposition at different kinds of sites. Specific questions addressed are to (1) show whether elemental and isotopic contents are different in urban, rural and forested mosses; (2) identify the main sources of atmospheric S deposition at the three different sites through moss $\delta^{34}S$ signatures; (3) differentiate the dominant N form and decipher their sources through moss $\delta^{15}N$ signatures.

2. Materials and methods

2.1. Sampling methods

The moss material *Haplocladium microphyllum* (Hedw.) was collected at urban, rural and forested sites of Nanchang, Changsha and Guiyang areas (South China) in 2006 (Fig. 1). These areas were chosen because they differ to some extent from each other as regards isotopic signatures of coals and are all within the range of the Southern Chinese acid rain area. Urban mosses were mainly collected around parks or hills. Sampling sites in the rural and forested 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 influence by throughfall N 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

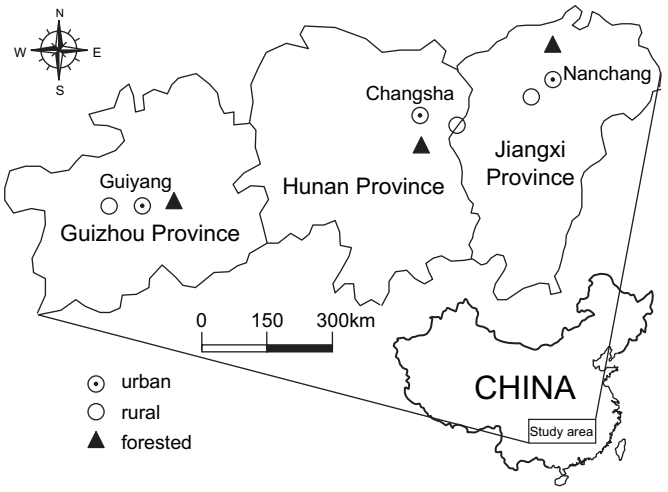

Fig. 1. Map showing the sampling sites in the 3 areas of South China.

5–10 subsamples at each site and combined them into one representative sample. In order the sampling to be representative for these sampling sites, more than 15 samples were collected in each of the three habitats (urban, rural and forested) in the three areas. Only green, healthy samples were taken, avoiding yellow or dark material.

2.2. Sample preparation and chemical analyses

Fresh mosses were stored in cleaned plastic bags enroute to the laboratory. Using the treatment method by Liu et al. (2007), samples were gently rinsed with 1.5 mol L^{-1} HCl solution, then sonicated and washed with deionized water for several times until no N (NH_4^+ and NO_3^-) was detected in the washed water (spectrophotometry, the limit of detection was <0.005 mg L^{-1}). The main purpose of this washing procedure was to remove adsorbed pollutants. 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 S and N contents were measured by an elemental analyzer (Model PE-2400 II, USA) with an analytical precision of 1%. Calibration of the instrument with cystine standard (N141-0324, provided by Perkin Elmer) was carried out. Accuracy and recovery of S and N were checked analysing a sample of this standard material after each set of eight moss analyses.

Moss samples were oxidized in a Parr bomb to convert all forms of sulphur present to sulphate. To assure complete conversion, hydrogen peroxide was added to all washings. Sulphate was recovered from moss or coal washings by precipitating as $BaSO_4$ with enough 2 mol L^{-1} $BaCl_2$ solution. After precipitated for 24 h, the mixture was filtered through a 0.22 μm acetate membrane filter. The precipitates ($BaSO_4$) on the filters 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 power in the crucible, it was analyzed with X-ray diffractometry. The results showed >99% $BaSO_4$ in the power. Thermal decomposition of $BaSO_4$ (Yanagisawa and Sakai, 1983) was conducted to prepare SO_2 for sulphur isotopic analysis in a Finnigan MAT-252 mass spectrometer. The standard deviation for the $\delta^{34}S$ analysis of NBS127 (barium sulphate) was better than ±0.2‰ ($n = 5$).

After combustion at 850 °C and high purification with liquid N, nitrogen isotope ratios were determined on a Finnigan MAT-252 mass spectrometer. Analysis of potassium nitrate standard

(MOR2386-01) provided by Shoko Co., Ltd., Tokyo, Japan (+1.9‰) gave a mean (±SD) $\delta^{15}N_{air}$ value of 1.9 ± 0.2‰ ($n = 5$). High purity N_2 reference gas was run with each analysis. Three to five replicate measurements per sample were carried out, and values were presented as the average of these measurements. The analytical precision (±SD, $n = 5$) for $\delta^{15}N$ was ±0.2‰.

2.3. 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). Correlation analysis was carried out by calculating the Pearson product–moment correlation coefficient (r). Differences in contents and isotopic values between areas and habitat types were tested for significance by using a two-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. Moss sulphur and nitrogen contents

Average S contents of urban, rural and forested mosses were 0.35 ± 0.05, 0.29 ± 0.06 and 0.25 ± 0.04%, respectively, and average N contents were 2.60 ± 0.56, 2.84 ± 0.77 and 2.21 ± 0.38%, respectively. In Nanchang and Guiyang areas, average S contents of urban mosses (0.36 ± 0.05% and 0.32 ± 0.03%) are significantly higher than those of forested mosses (0.22 ± 0.03% and 0.27 ± 0.03%), but the differences between urban and rural mosses and between rural and forested mosses are not significant (Fig. 2a). In Changsha area, a significant increase was found from forested, rural to urban mosses ($p < 0.05$). The differences in rural moss S contents are not significant for the three areas ($p > 0.05$). Average N contents of urban and rural mosses are not significantly different from each other in the three areas (Fig. 2b). In Nanchang and Changsha areas, urban and rural mosses have significantly higher N contents than forested mosses ($p < 0.05$).

There is a strong correlation between tissue S (y) and tissue N (x) for mosses in the three areas ($y = 0.091x + 0.073$, $R^2 = 0.47$, $p < 0.001$) (Fig. 3).

3.2. Sulphur and nitrogen isotopic signatures in mosses

The $\delta^{34}S$ values of urban, rural and forested mosses was on average −0.5 ± 3.8, +2.9 ± 1.9 and 3.9 ± 2.9‰, respectively, and the $\delta^{15}N$ values averaged −7.5 ± 3.0, −3.4 ± 2.1 and −0.8 ± 2.1‰, respectively.

Using a two-way analysis, we found that average $\delta^{34}S$ values of urban mosses were significantly lowest in Guiyang (−3.1 ± 1.7‰) areas, then in Nanchang (+0.3 ± 1.7‰), and the highest occurred in Changsha area (+5.2 ± 0.6‰) (Fig. 4a), which are assistant with isotopic values of their local coals (Xiao et al., 2010). All urban mosses in the three areas had lower ^{34}S contents than rural and forested mosses except in Changsha area where the lowest values occurred at rural site. Relative to forested mosses, rural mosses were more ^{34}S-depleted in Nanchang and Changsha areas.

Average $\delta^{15}N$ values increased from urban (−8.1 ± 2.4‰ and −8.7 ± 1.7‰), rural (−3.1 ± 2.2‰ and −4.7 ± 1.1‰) to forested (−1.7 ± 1.2‰ and −0.6 ± 1.5‰) mosses in Nanchang and Guiyang areas (Fig. 4b), while they are not significantly different in Changsha area ($p > 0.05$).

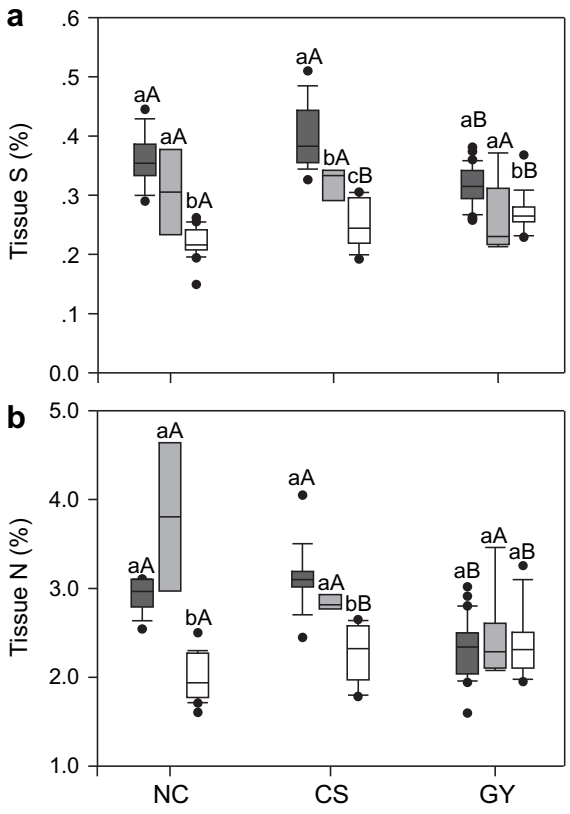

Fig. 2. Moss S contents (a) and moss N contents (b) at urban (dark grey box), rural (light grey box) and forested (white box) sites. The box encloses 50% of the data, the whiskers 90% of the data, the horizontal bar is the median, solid circles are outliers. NC-Nanchang, CS-Changsha, GY-Guiyang. The differences in means were statistically significant (two-way ANOVA, F-test, $p < 0.05$). Different uppercase letters denote means found to be statistically different by the Tukey-HSD test with LSD between regions and different lower case letters between habitat types.

4. Discussion

4.1. Moss sulphur and nitrogen contents indicating atmospheric deposition

Moss S content was an important parameter to reflect the level of atmospheric S deposition (especially gaseous SO_2) because higher

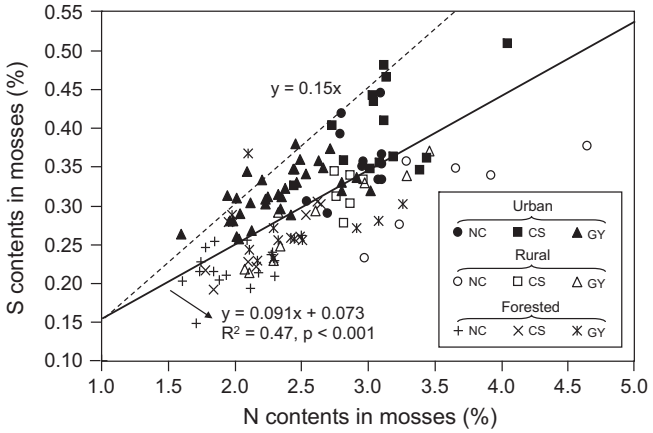

Fig. 3. S content (%) vs. N content (%) in mosses. The solid line $S = 0.091N + 0.073$ represents the over regression of S content (%) and N content (%). The dotted line $S = 0.15N$ is found in an unpolluted forest (Gongga Mountain, China; Xiao et al., 2010).

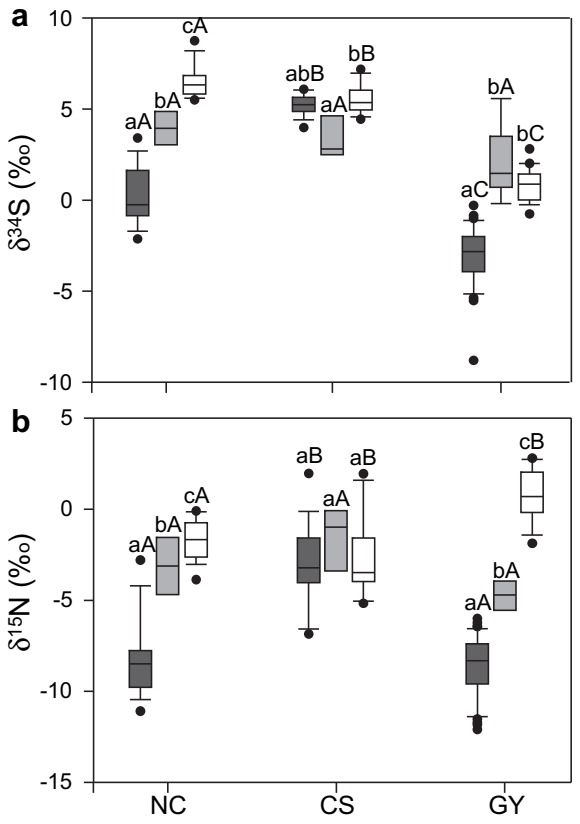

Fig. 4. Moss $\delta^{34}S$ values (a) and moss $\delta^{15}N$ values (b) at urban, rural and forested sites. The box encloses 50% of the data, the whiskers 90% of the data, the horizontal bar is the median, solid circles are outliers. The differences in means were statistically significant (two-way ANOVA, *F*-test, $p < 0.05$). Different uppercase letters denote means found to be statistically different by the Tukey-HSD test with LSD between regions and different lower case letters between habitat types.

atmospheric S directly caused higher tissue S in mosses (Novák et al., 2001b; Vingiani et al., 2004; Liu et al., 2009). An experiment of using moss bags to monitor atmospheric S pollution at 13 sites of Guiyang city showed a strong correlation between SO_2 concentration in air and moss S content (Qu et al., 1994). Accordingly, the relatively higher moss S contents at urban sites than at forested sites (Fig. 2a) indicated higher atmospheric S deposition in cities. Of the 3 cities, Guiyang showed the lowest atmospheric S deposition because of their lowest moss sulphur contents ($p < 0.05$). Although SO_2 concentrations at Guiyang reached 400–500 $\mu g\ m^{-3}$ in 1980s, S emission was limited to a small quantity since 1998 due to the control of coal burning. At rural sites, domestic biomass burning brought some S into the atmosphere, causing an intermediate S deposition. Similarly, moss N content has also been recognized as a sensitive and reliable tool to assess the level of atmospheric N deposition (e.g. Pitcairn et al., 1995; Skinner et al., 2006). Many studies have affirmed the positive correlation between atmospheric N deposition and moss N content (Liu et al., 2008). In areas with high N deposition, the N content of the bryophytes is usually increasing (Baddeley et al., 1994; Pitcairn et al., 1995). According to these and Fig. 2b, atmospheric N deposition at forested sites was the lowest, except in Guiyang area. Atmospheric N deposition at rural sites showed a high value, not significantly different to that at urban sites. This suggested that rural sites had been seriously polluted by agricultural N emissions in these areas.

Usually mosses are more exposed to the direct effects of N input and acid deposition than vascular plants are. The effect of S and N supply in excess of annual demand on mosses has been extensively studied (Xiao et al., 2010). When S supply is greater than that required for protein synthesis, sulphate accumulates in plant tissues, leading to an S/N ratio greater than healthy S/N ratio. On the contrary, if S is deficient in relation to the N supply, N will be accumulating, resulting in an S/N ratio smaller than the healthy ratio. In unpolluted areas, since most of the organic S in plants is used in protein synthesis a balance exists between it and organic N, and plants tend to maintain a relatively constant ratio of organic S to organic N (healthy S/N ratio), particularly in their vegetative tissues (Dijkshoorn and van Wijk, 1967). In this study, S/N = 0.15 obtained from remote forested mosses in Gongga Mountain (Xiao et al., 2010) was used as the healthy value. As shown in Fig. 3, almost all the points are below the line $S = 0.15N$, especially those at rural and forested sites, indicating that N supply, relative to S supply, is greater than that required for protein synthesis in the three areas. This means that limiting atmospheric N emission is needed in the 3 areas, especially at rural and forested sites.

4.2. The main sources of atmospheric S deposition

As a kind of sensitive plants 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; Xiao et al., 2009). In these study areas, the dominant atmospheric S sources include biogenic S, local coal combustion and northerly air masses as discussed below (Fig. 5).

The biogenic S (BS) was an important atmospheric S source in many Chinese areas (Zhang et al., 1995; Zhang, 2006; Xiao et al., 2009). BS released from soils and wetlands is characteristically depleted in ^{34}S (Wadleigh and Blake, 1999; Mast et al., 2001). The $\delta^{34}S$ values of BS reported in southern China have a narrow range of −3.0 to −2.0‰ (Zhang et al., 1995; Zhang, 2006). Based on this and Fig. 5, we concluded that BS was one of the main components of atmospheric S in these three areas. Sea spray is derived from the well-mixed reservoir of oceanic sulphate that currently has a constant $\delta^{34}S$ value of +21‰ (Rees et al., 1978). The $\delta^{34}S$ values for mosses and sea spray are sufficiently distinct to be able to conclude that seawater contributions are negligible.

Regional isotopic differences of atmospheric S in Chinese industrial cities are believed strongly associated with those in fossil fuels (mainly coals) used in the area (Mukai et al., 2001; Xiao et al., 2009). Among all the rainwater $\delta^{34}S$ data they obtained, the most ^{34}S-depleted rainwater occurred in Guiyang (−3.3 ± 2.8‰) and then in Nanchang (+0.5 ± 2.4‰). Similarly, the significantly lowest $\delta^{34}S$ values also occurred in urban mosses in Guiyang, then in Nanchang,

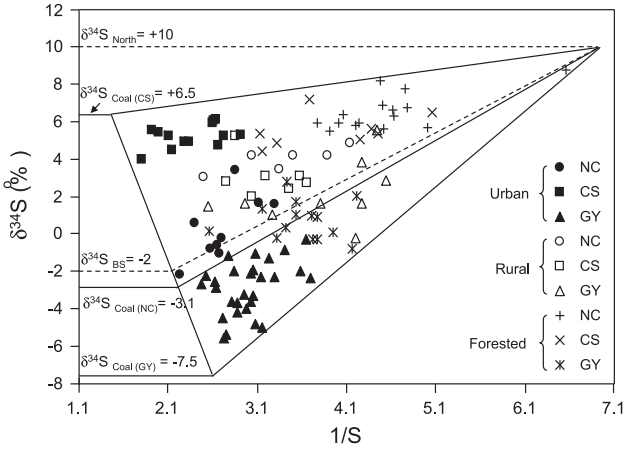

Fig. 5. $\delta^{34}S$ values vs. 1/S in mosses. The $\delta^{34}S$ values of biogenic S ($\delta^{34}S_{BS}$), local coal combustion ($\delta^{34}S_{coal}$) and northerly air masses ($\delta^{34}S_{North}$) are also included in the figure.

as shown in Fig. 4a. Chemical composition in cloud water and rainwater further confirmed the importance of the local coal combustion (Lei et al., 1997). In Fig. 5, urban mosses were high in tissue S contents (low 1/S) and had similar $\delta^{34}S$ values to that of their respective local coal, reflecting a local coal source. The significantly difference in moss $\delta^{34}S$ values between urban and rural sites was suggestive of their different S sources. At rural sites, biomass (+3.0‰; Xiao, unpublished data) is usually burned for cooking and becomes a main S source (not shown in Fig. 5). But at the rural site of Changsha area, coal from Jiangxi Province (Pingxiang coal deposition) was also burned domestically and thus rural mosses showed relatively low $\delta^{34}S$ values (Fig. 4a). Average S isotope ratios in southern Chinese mountainous mosses reported by Xiao et al. (2008) also corresponded well to the values of source coals in the characteristics of fuels as S sources: a similar changing trend between mountainous mosses and urban mosses, suggesting a considerable contribution of local coal combustion to atmospheric S at forested sites.

Sulphur in northerly air masses was believed to contribute much to many southern Chinese areas because $\delta^{34}S$ values of some mountainous mosses were found increasing from the south to the north (Xiao et al., 2008). According to previous reports (Hong and Zhang, 1992; Maruyama et al., 2000), northern Chinese coals (averaging +3.69‰) have been reported to have higher S isotope ratios than southern Chinese coals (averaging −0.32‰). Contribution from northerly air masses is relatively large at forested sites as shown in Fig. 5. Some atmospheric chemical data reported previously also confirmed this. Influenced by high S northerly air masses (e.g. ambient SO_2 levels averaged 425 μg m^{-3} at Taiyuan city, North China; Zhang, 2002), cloud water over some southern Chinese forested sites was found containing higher sulphate concentrations than rainwater (Wang, 1992; Wang et al., 1996).

4.3. The main sources of atmospheric N deposition

The $\delta^{15}N$ inventories of the main potential sources in these 3 study areas are shown in Fig. 6.

Moss $\delta^{15}N$ was assumed as an integrator of the isotopic signatures of atmospheric N sources over the lifetime of the moss so that measuring moss $\delta^{15}N$ and comparing these data to source $\delta^{15}N$ signatures could potentially determine the sources of atmospheric N deposition. Studies by Pearson et al. (2000) in the London area and Gerdol et al. (2002) in northern Italy have found that moss $\delta^{15}N$ values can effectively decipher atmospheric N sources from urban NO_x and from rural NH_3 because the former generally has a more positive $\delta^{15}N$ value than the latter in atmospheric deposition (Fig. 6). According to the $\delta^{15}N$ inventories of potential sources of atmospheric N (Fig. 6), the relatively negative moss $\delta^{15}N$ values in this study suggested that the main form in the N deposition was NH_x at these sites. In Guiyang area, the negative $\delta^{15}N$ signatures of urban mosses were rather closer to the $\delta^{15}NH_4^+$ value (−12.2 ± 6.7‰) than to the $\delta^{15}NO_3^-$ value (+2.0 ± 4.4‰) in rainwater (Xiao and Liu, 2002), consistent with that the concentration of the reduced form of N (NH_x–N) in the atmosphere was about 5 times higher than that of the oxidized N species (NO_x–N) (Xiao and Liu, 2002, 2004). This is in accordance with the reports by Galloway et al. (1996) that China is known as an area with high atmospheric NH_x deposition. In Changsha area, no significant difference was found among urban, rural and forested sites, possibly because the 3 sites in Changsha area all belong to high population regions. In the most populated regions of China, human activities, in particular livestock farming and fertilizer application, are believed important sources of atmospheric NH_3 (Schlesinger and Hartley, 1992; Zhao and Wang, 1994; Galloway et al., 1996).

Additionally, our recent studies in Guiyang area further showed that moss $\delta^{15}N$ value was a good indicator of sources of NH_3 in atmospheric deposition (Liu et al., 2008). As showed in Fig. 6, more

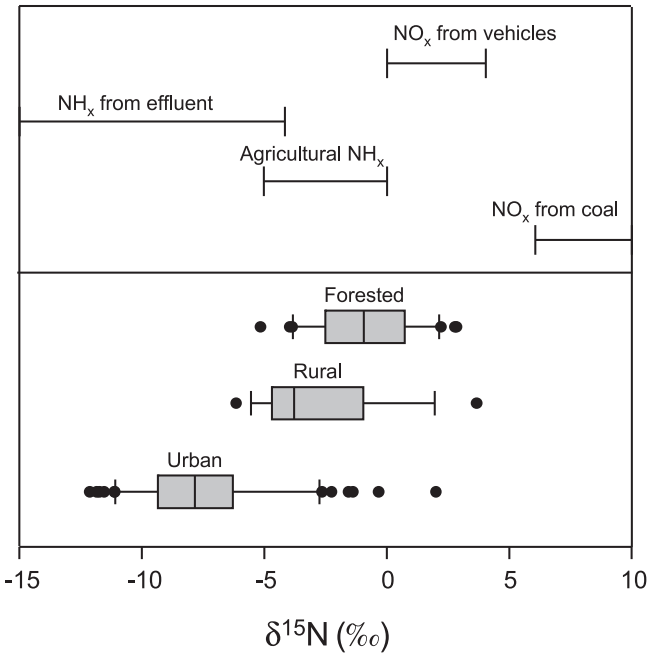

Fig. 6. The $\delta^{15}N$ signatures at urban, rural and forested mosses. The box encloses 50% of the data, the whiskers 90% of the data, the horizontal bar is the median, solid circles are outliers. The differences in means were statistically significant (two-way ANOVA, *F*-test, $p < 0.05$). Different letters denote means found to be statistically different by the Tukey-HSD test with LSD. The $\delta^{15}N$ ranges of the four main potential N sources are also included in the figure.

negative $\delta^{15}N$ signatures in urban mosses indicated the contribution of NH_3 released from untreated city sewage and wastes ($\delta^{15}NH_3 = -15$ to −5‰), while relatively less negative $\delta^{15}N$ for rural and forested mosses was largely derived from agricultural NH_3 ($\delta^{15}NH_3 = -5$ to 0‰). Because moss $\delta^{15}N$ values in the Guiyang area were mainly regulated by NH_x–N from urban sources (excretory wastes: −15 ~ −5‰) and suburban soil sources (−5.8 ~ −3.3‰), it was found by Liu et al. (2008) that variation of moss $\delta^{15}N$ values from the urban to the suburban area was controlled by the ratios of urban-derived NH_x to soil-derived NH_x in N deposition.

5. Conclusions

The relatively higher moss S contents are found at urban sites than at forested sites. Average N contents of urban and rural mosses are not significantly different. Nitrogen supply in excess of the requirement occurred in the three areas, suggesting that limiting atmospheric N emission is needed, especially at rural and forested sites. Additionally, it is found a strong correlation between tissue S and tissue N for mosses in the three areas.

The dominant atmospheric S sources, including biogenic S, local coal or biomass combustion and northerly air masses, have been determined through moss $\delta^{34}S$ data in this study. Atmospheric S at urban and rural sites was mainly from local coal combustion and biomass burning, respectively. Among the three sites, contribution of S from northerly air masses is the largest at forested sites.

Moss $\delta^{15}N$ values can effectively decipher atmospheric N sources of urban, rural forested sites. The relatively negative moss $\delta^{15}N$ values indicated that the main form in the N deposition was NH_x in all the study sites. More negative $\delta^{15}N$ signatures in urban mosses indicated the contribution of NH_3 released from untreated city sewage and wastes, while relatively less negative $\delta^{15}N$ for rural and forested mosses was largely derived from agricultural NH_3.

Acknowledgments

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